



Hydrogel applications for adsorption of contaminants in water and wastewater treatment

Vinh Van Tran¹ · Duckshin Park² · Young-Chul Lee¹

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Abstract

During the last decade, hydrogels have been used as potential adsorbents for removal of contaminants from aqueous solution. To improve the adsorption efficiency, there are numerous different particles that can be chosen to encapsulate into hydrogels and each particle has their respective advantages. Depending on the type of pollutants and approaching method, the particles will be used to prepare hydrogels. The hydrogels commonly applied in water/wastewater treatment was mainly classified into three classes according to their shape included hydrogel beads, hydrogel films, and hydrogel nanocomposites. In review of many recently research papers, we take a closer look at hydrogels and their applications for removal of contaminants, such as heavy metal ion, dyes, and radionuclides from water/wastewater in order to elucidate the reactions between contaminants and particles and potential for recycling and regeneration of the post-treatment hydrogels.

Keywords Hydrogel · Heavy metal · Dye · Radioactive · Adsorption · Water/wastewater treatment

Introduction

Water is the most essential substance to humans and other living organisms. However, some harmful chemical compounds cause water pollution that exerts negative effects not

Highlights

- Unique particles entrapped in synthesis process of three types of hydrogels
- Adsorption kinetic models, adsorption isotherm models, and the mechanism of contaminants on hydrogels
- Impact factors on the adsorption capacity of hydrogels: pH, adsorbate concentration, swelling degree, and other ions
- Recycle and recovery methods of used hydrogels and effect of mechanical properties on the reusability of hydrogels
- Applications of hydrogels on removal of metal ion, dye, and radionuclides from water/wastewater

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✉ Young-Chul Lee
dreamdb@gachon.ac.kr

¹ Department of BioNano Technology, Gachon University, 1342 Seongnamdaero, Seongnam-si 13120, Gyeonggi-do, Republic of Korea

² Korea Railroad Research Institute (KRRRI), 176 Cheoldobakmulkwon-ro, Uiwang-si 16105, Gyeonggi-do, Republic of Korea

only on species living in water but also on the broader biological community (Guo et al. 2015).

Yearly, heavy metals are released into environments from various industrial production or auxiliary processes as well as other human activities (Chen et al. 2010; Patel et al. 2010). There are more than 40 elements of greater-than 5 g/cm³ mass, which are regarded as heavy metals (Srivastav et al. 1994; Zenk 1996). Heavy metal ions are among the main contaminants found in water. Due to their persistence and toxicity properties, such pollutants, heavy metals, have attracted considerable-attention within the scientific, governmental, and community-activist communities. Toxic metals are very dangerous to all biological organisms and the overall environment, especially when present above the given tolerance levels (Abachi et al. 2013; Ali et al. 2011) and even at low concentrations. Even so, nearly 1 million t of dyes is annually used in the chemical industry worldwide, more than 10% of which are discharged as effluents that seriously pollute the environment and affect humans as well as aquatic organisms (Sethuraman and Raymahashay 1975; Yagub et al. 2014). Generally, the dyes have complex and stable structures, and their degradation in nature is usually very difficult and slow; consequently, they will accumulate (Fu and Viraraghavan 2001; Kadirvelua et al. 2003; Zollinger 2003). Besides heavy metals and dyes,

radioactive waste, a waste product containing radioactive materials usually produced in a nuclear process such as nuclear fission, is also one of the common contaminants significantly affecting water resource. Although the radioactivity of such waste will decrease over time, it will do so only at a very slow rate; therefore, it can seriously affect human health and the environment over very long duration (Jing et al. 2013). In addition, in modern agriculture, pesticides have been widely used for protecting crops and livestock, which have also led to a lot of serious health implications. According to experts, these pesticides have been discharged through direct agricultural runoff, leaching, and improper disposal of empty containers (Dwivedi et al. 2014). Besides, the discharge of nitrogen components (nitrate) in the water source is currently harmful for both human and animal health. Nitrates may cause several serious problems when dispersed in water, since they cause the groundwater pollution and the eutrophication of rivers (Rossi et al. 2015). Therefore, the pesticides and nitrate remediation from aqueous solution has been a worldwide problem and challenge.

The investigation and application of various methods to remove these contaminants from water is absolutely essential for protection of the environment. Compared with chemical and physical methods commonly used to remove dyes, heavy metal ions, and others, currently, the adsorption methods stand out as one of the most effective and friendly methods for dye removal from aqueous solution (Azbar et al. 2004; Mohan et al. 1998). Hydrogel is a three-dimensional polymer that can be synthesized by the reaction between one or more monomers. Hydrogel's three-dimensional network and porous structure typically endows them with a hydrophilic property and corresponding capacity to adsorb large amounts of water or biological fluids (Ahmed 2015). Hydrogels' high water retention and low cost have attracted great attention as effective adsorbents. The hydrogels commonly applied in water/wastewater treatment were mainly classified into three classes including hydrogel beads, hydrogel films, and hydrogel nanocomposites according to their shape and physicochemical properties (Table 1).

In order to improve adsorption efficiency, there are many different and unique nanoparticles utilized for entrapment in hydrogel beads, hydrogel films, or hydrogel nanocomposite as hybrids (Jing et al. 2013). This study will provide an overview of the recent literature's results obtained in the treatment of wastewater utilizing hydrogels for the removal of heavy-metal ion, dyes, radionuclides, and other pollutants from aqueous solution as well as in the recovery and recycling of used hydrogels. It is evident from the literature survey that nanoparticles into hybrid hydrogels have shown good potential applicability for removal of various aquatic pollutants.

Application of hydrogel beads for adsorption of contaminants

Particles entrapped in hydrogel beads for heavy-metal ion removal

Cellulose is known as the most abundant renewable material in the world. However, its derivatives have usually received more interest in synthesizing hydrogels because they have a better solubility in water than cellulose. One of the most common derivatives is carboxymethyl cellulose (CMC), which is known as a water-soluble cellulose derivative that has been available on the market. A method commonly used to prepare CMC-based hydrogels is crosslinking method by using the crosslinking agents like polycarboxylic acids, epichlorohydrin (ECH), and *N,N'*-methylene-bisacrylamide (Fekete et al. 2017). In 2010, typical hydrogel beads were successfully prepared based on CMC by inverse suspension crosslinking using ECH as cross-linker (Fig. 1) (Yang et al. 2010). The adsorption capacity of these hydrogels was evaluated with model wastewater including heavy-metal ions, Pb^{2+} , Ni^{2+} , and Cu^{2+} . The results confirmed that a new bond, CAOAC, was formed by the reaction between ECH and CMC. Compared with pure CMC, the hydrogel beads had lower crystallinity. The hydrogel beads' adsorption of Pb^{2+} , Ni^{2+} , and Cu^{2+} were based on the formation of coordination bonds with the oxygen atoms in their carboxyl groups. The formed hydrogel beads thus exhibited a high adsorption capacity for heavy-metal ions.

Recently, a biopolymer based on chitosan (CS) has attracted great interest in various fields, especially environmental biotechnology, because of its very high adsorption capacity of heavy-metal ions and low cost (Jin and Bai 2002; Yoshida and Takemori 1997). Moreover, CS can be easily synthesized at the industrial level by a simple method based on chitin. CS hydrogel beads are regarded as a potential adsorbent for effective removal of heavy metals in industrial wastewater treatment (Chatterjee et al. 2005; Chatterjee et al. 2007; Ngah et al. 2002). CS has also shown a great material in the production process of hydrogel due to the combination ability with various materials. By blending CS with a high concentration of CMC solution, a novel CS-based hydrogel called CM(carboxymethylated)-cellulose/CS in the form of physical hydrogels was successfully synthesized by irradiation-based crosslinking (Zhao and Mitomo 2008). Due to adding CS, the hydrogel's adsorption capacity for divalent heavy-metal ions and crosslinking extent had been improved. Also, CS could combine with PVA to form a CS/poly(vinyl alcohol) (PVA) hydrogel bead for adsorption of lead ion from an aqueous solution (Jin and Bai 2002). The Pb^{2+} ion adsorption on these hydrogel beads showed a strong dependence on pH, and the mechanism of the adsorption process is based on complexation, ion exchange, and electrostatic interaction. For the electrostatic interaction, the hydrogels possessed a

Table 1 The physiochemical properties of three types of hydrogel

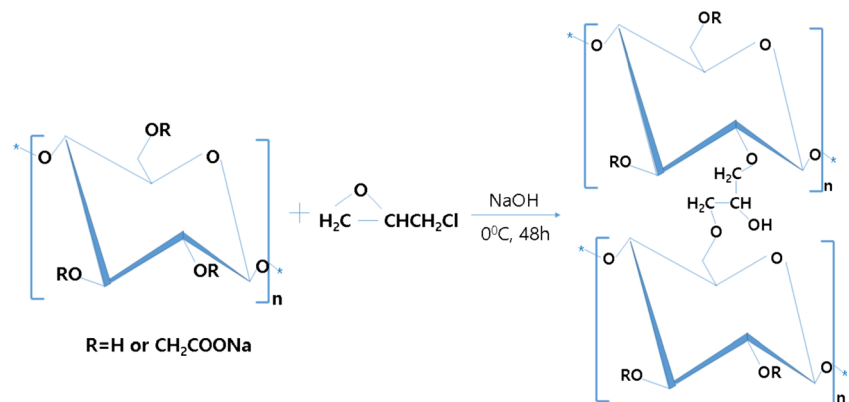
Physiochemical properties	Morphology	Swelling	Mechanical properties	Thermal stability	Reference
Hydrogel beads	<ul style="list-style-type: none"> - Spherical beads; rough surface. - Outer surface: quite rough, smooth or pores - Size: uniform, diameter: 20 nm–5 mm 	<ul style="list-style-type: none"> - High swelling ratio; - pH-dependence 	<ul style="list-style-type: none"> - Great mechanical strength - Quite tensile elasticity: Young’s modulus (0.93–2.14 MPa) 	<ul style="list-style-type: none"> - Stable up to 260 °C 	(Dwivedi et al. 2015; Ma et al. 2017; Mohammed et al. 2015; Pathak et al. 2016; Pour and Ghaemy 2015; Yu et al. 2015a; Zhuang et al. 2016)
Hydrogel films	<ul style="list-style-type: none"> - Thin film: thickness 10–300 μm - Homogenous texture 	<ul style="list-style-type: none"> Degree of swelling (245% - 2400%); - pH-dependence 	<ul style="list-style-type: none"> - High elongation at break - High tensile elasticity: Young’s modulus ~ 15 MPa 	–	(Al-Mubaddel et al. 2015; Baruah et al. 2016; Gogoi et al. 2015; Mirabedini et al. 2017; Nguyen and Liu 2014)
Hydrogel nanocomposite	<ul style="list-style-type: none"> - Soft, and elastic with a slippery surface; - Highly porous network structure 	<ul style="list-style-type: none"> - Degree of swelling (350–7300%) - Swelling ratio increases with time; - pH-dependence 	<ul style="list-style-type: none"> - Good mechanical properties: elongation near 1000% - Low tensile elasticity: Young’s modulus: ~453 kPa 	<ul style="list-style-type: none"> Stable up to 300 °C 	(Heydari and Sheibani 2015; Kasgoz and Durmus 2008; Pourjavadi et al. 2015; Zhao et al. 2015; Zhou et al. 2011)

ζ-potential. In the case of pH < 6.3, the ζ-potentials of the CS/PVA hydrogels were positive, and for pH > 6.3, negative. Therefore, the heavy metal ion adsorption occurs even though the interaction between the metal ions and the hydrogels is electrostatically repulsive at pH < 6.3. In an attempt to improve the efficiency of CS-hydrogel beads in metal ion removal applications, a glutamic-CS hydrogel beads (GCS) was synthesized by reactions between CS and different concentrations of glutamic acid (Abdelwahab et al. 2016). It is the presence of glutamic acid in the structure that affected the treatment efficiency of the hydrogels in removing Cu²⁺ and Ni²⁺ ion. It is found that when the concentration of glutamic acid increased, the adsorption of the hydrogels decreased. This phenomenon was explained that the increase of the crosslinking degree caused a decrease in the hydrogel pore size. Especially, it is notable that a combination of CS with ethylenediaminetetraacetic acid (EDTA), *N,N*-methylenebis(acrylamide) (MBA), and polyacrylamide (PAM) formed an exceptional type of hydrogel beads which its outstanding properties are a remarkable

mechanical strength and recyclability (Ma et al. 2017). The hydrogel preparation process was conducted with a two-step method by which EDTA is cross-linked with CS and MBA is cross-linked with PAM to form a double-network hydrogel (Fig. 2). The hydrogel showed a high adsorption capacity for Cd²⁺, Cu²⁺, and Pb²⁺ ion based on the mechanism of the ion exchange interactions between metal ions and carboxylate groups. This hydrogel was effectively demonstrated for treating practical wastewater with various kinds of heavy metal ions, with an adsorption efficiency of 98%.

In preparing a high-strength hydrogel for adsorption of metal ions from industrial lean solvents and reusability, a series of PAM hydrogel beads was successfully synthesized by using three components with different functions (Pal and Banat 2015). To fabricate these hydrogel beads, acrylamide as a monomer was polymerized with ammonium peroxodisulphate as initiator. The acrylamide monomer was then cross-linked to form PAM hydrogels using *N,N'*-methylenebisacrylamide as the cross-linker. The fabricated

Fig. 1 Preparation of CMC hydrogel particles with ECH as crosslinker



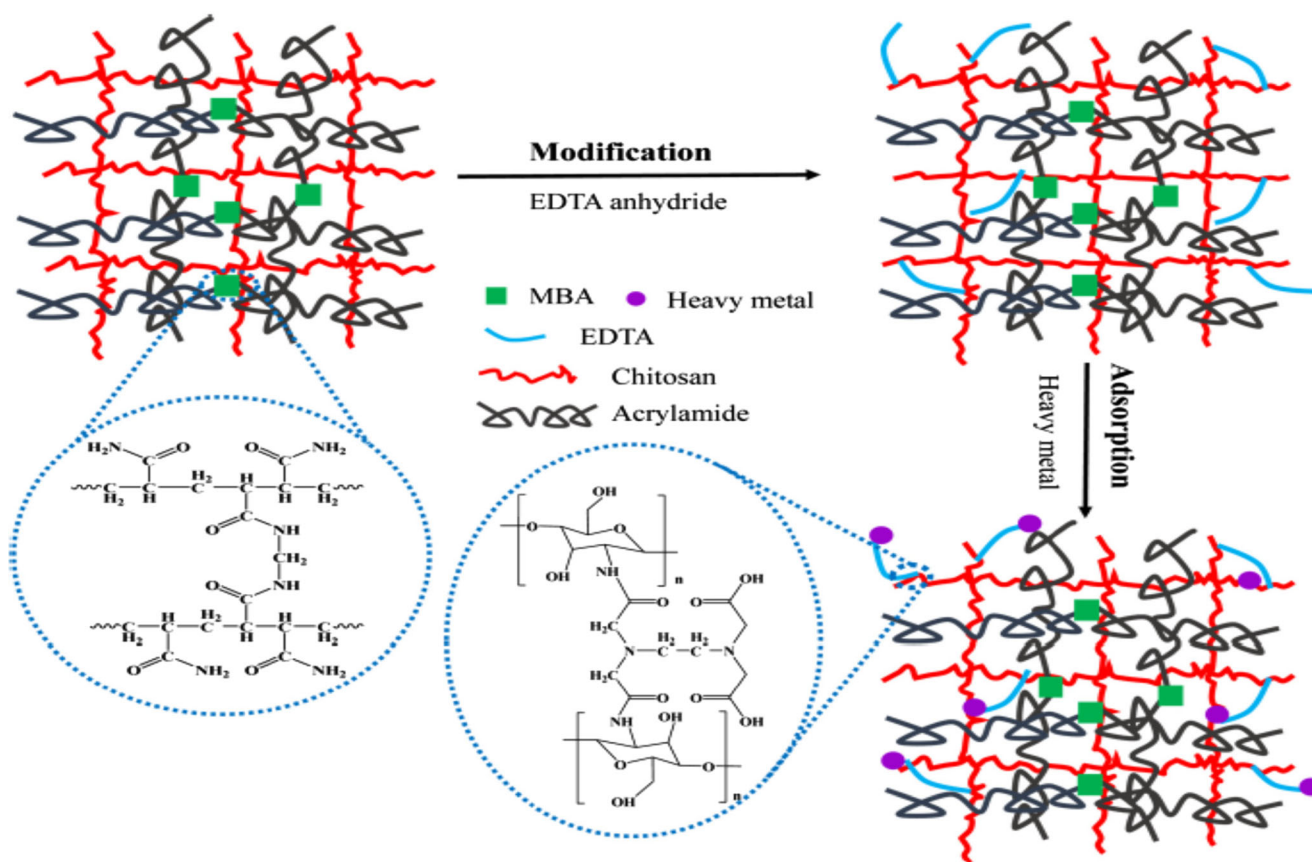


Fig. 2 Schematic representation of CTS/PAM gel synthesis (reprinted (adapted) with permission from Ma et al. 2017. Copyright (2017) American Chemical Society)

hydrogel beads with an entangled 3D network were effectively demonstrated for removal of metal ions. Moreover, the hydrogel beads also showed good reusability: the adsorption capacity had only slightly dropped even after 15 cycles of desorption and reuse. In addition, the hydrogel could easily be desorbed by sodium chloride and the hydrogel beads can be excellent adsorbents offering operation costs and good reusability.

The interaction between two oppositely charged polymers results in the formation of polyelectrolyte complexes (PECs) (Philipp et al. 1989). Recently, PECs have been widely applied as potential flocculent materials to precipitate metal ions in the wastewater treatment industry, owing to their relative cheapness and ease of use. Especially, after simply mixing with other oppositely charged polyelectrolytes according to each experiment condition, PECs will be formed as precipitates or thin films, or dispersed colloids in water, which makes them excellent materials for water treatment (Petzold and Schwarz 2014; Thünemann et al. 2004; Zhang and Sun 2009). Based on PECs' interaction between positively charged poly(allylamine hydrochloride) (PAH) and negatively charged poly(L-3,4-dihydroxyphenylalanine) (PDopa), new hydrogel beads, namely PDopa-PAH PEC hydrogel beads, were introduced for removal of ionic pollutants in aqueous

solution (Yu et al. 2015a). Due to PDopa-PAH PEC loaded inside the hydrogel matrix, this type of hydrogel beads can effectively and efficiently remove various ionic pollutants, both heavy metal ions and ionic organic dyes, from aqueous solution. Because the chemical structure of PDopa contains three types of functional group (catechol group, carboxyl group, and amino group), the formed PDopa-PAH PECs hydrogels possess a larger adsorption capacity of heavy metal ions compared to other adsorbents. Moreover, because both PDopa and PAH are pH-sensitive, the hydrogel beads can be easily recovered for reuse by adjusting the pH in the surrounding media. In addition, given the ease and appropriateness of synthesizing hydrogel beads for large-scale production with little raw material loss and byproduct generation, the synthesis can be extended to various polyelectrolytes.

Pectin (Pec) is a natural chemical compound with a heterogeneous structure that is basically formed by smooth and hairy regions having various unit of polymers, such as the poly(1 → 4) α -D-galacturonic acid (Pérez et al. 2000; Reis et al. 2009). Pec has been generally found in citric fruits, principally the lemon. This particular polysaccharide has been commonly used in feed compositions (Willats et al. 2006) and the pharmaceutical industry. Its structure includes large numbers of ionic groups, making it an excellent polymer matrix for

superabsorbent hydrogel synthesis. Recently, Pec also was applied in synthesis of materials for wastewater treatment through a novel Pec-based hydrogel that can be used to remove Cu^{2+} and Pb^{2+} ions (Guilherme et al. 2010). This hydrogel showed a high adsorption capacity and efficiency for removal of Cu^{2+} and Pb^{2+} from water: 120-mg Cu^{2+} and 130-mg Pb^{2+} per g hydrogel at pH 5.5 with 0.10-g mL^{-1} adsorbent concentration.

Fly ash (FA) is a waste product produced from thermal power plants, steel mills, and other facilities. Due to its low-cost and abundance, it has been utilized as an adsorbent in many fields (Wang & Wu 2006). With a new approach for preparation of hydrogels, a novel magnetic attapulgite/fly ash/poly(acrylic acid) (ATP/FA/PAA) ternary hydrogel beads was synthesized for removal of Pb^{2+} ion (Jiang and Liu 2014). In this method, magnetic FA particles were used as new cross-linkers (instead of the traditional cross-linkers) via an inverse suspension polymerization process. In this process, acrylic acid (AA) is attached onto an inorganic skeleton obtained by the functionalized ATP and FA to form ternary hydrogel beads. By using inorganic materials, FA, the production cost of the hydrogel beads is significantly lower and the mechanical strength, thermal stability, chemical resistance, and dimensional stability also are improved. These hydrogel beads showed effective treatment efficiency for removal of Pb^{2+} ion via a high adsorption capacity of 38 mg g^{-1} in 100-mg/L Pb^{2+} solution at pH 5. Besides, the Pb^{2+} ion adsorbed in the hydrogel beads could be completely desorbed in 0.10-mol/L HCl aqueous solution within 90 min.

Particles entrapped in hydrogel beads for dye removal

Crystal violet (CV) is a typical cationic dye commonly used in coloring paper, temporary hair colorant, dyeing cottons, and wools. When discharged into receiving environments, it can pollute the water source and cause some negative effects on human health such as accelerated pulse, vomiting, shock, cyanosis, jaundice, quadriplegia, and others (Kunz et al. 2002). Hence the removal of CV from industrial effluent has attracted the attentions of numerous scientists and researchers. Recently, a semi-IPN (interpenetrating polymer networks) hydrogel bead constituted of poly(acrylic acid-acrylamide methacrylate) and amylose was introduced for adsorption of CV with high adsorption efficiency (Li 2010). However, its adsorption capacity was found to be highly dependent on the amylose content and pH of the solution. As for adsorption mechanism, the results indicated that the CV dye adsorption of hydrogel occurs via swelling combined with electrostatic and hydrophobic interactions. And as for the morphology of the hydrogel, hydrophilic amylose was dispersed in continuous phases of poly(acrylic acid-acrylamide-methacrylate) hydrogel, and many open pores of 100- μm diameter were

formed in the hydrogel matrix, which may be favorable for CV adsorption.

In the past decade, graphene oxide (GO) sheets, given their outstanding structure, have become a target of numerous studies for dye removal from wastewater. Due to its two-dimensional structure, GO possesses a high adsorption capacity for different dye molecules through π - π stacking interactions (Singh et al. 2011). Moreover, GO also has negative charges due to the presence of various oxygen-rich functional groups, such as carboxyl, carbonyl, and hydroxyl groups, which enhance electrostatic interactions with dye cations. Therefore, GO has been used as a potential adsorbent in various applications, especially industrial wastewater treatment. By combining GO and polyethylenimine (PEI), a novel hydrogel bead as an efficient dye adsorbent was produced, which they named GO/PEI hydrogel (Guo et al. 2015). As for the preparation process, the hydrogel could be simply formed through a combination of amine-rich PEI and GO sheets achieved by hydrogen bonding and electrostatic interactions. Figure 3 shows that GO sheets possess numerous functional groups ($-\text{COOH}$ and $-\text{OH}$) that can form hydrogen bonds with amine molecules of PEI under appropriate conditions. For this type of hydrogel, PEI is added in solution to facilitate the gelation process of GO sheets, as GO sheets are regarded as the most important hydrogel ingredient for maintenance of dye adsorption capacity. Moreover, it is demonstrated that this hydrogel will be a new potential material for the organic dye removal with the high efficiency.

Halloysite is known as an aluminosilicate clay mineral produced by hydrothermal alteration and deposition (Joussein et al. 2005; Levis and Deasy 2002). As halloysite can effectively adsorb both cations and anions, it can be applied in various fields including ceramic raw materials, catalysis, and polymer nanofillers. In its structure, halloysite naturally appears as small cylinders (nanotubes) with a high aspect ratio, for which reason it usually is referred to as “Halloysite nanotubes (HNTs)” (Lvov et al. 2008). Compared with other tubular nanomaterials (such as carbon nanotubes) used in wastewater treatment, natural HNTs are more environmentally friendly and cheaper (Du et al. 2010; Zhixin et al. 2014). By combining the two cheap materials, CS and HNTs, Peng and co-workers fabricated novel hydrogel beads that can be applied for removal of MB and malachite green (MG) from wastewater (Peng et al. 2015). CS-HNTs hydrogel beads were obtained by the dropping and pH-precipitation method. It is found that CS and HNTs are compatible in the preparation of hydrogel adsorbents: (i) HNTs can be immobilized by CS hydrogel and completely incorporated into the hydrogel beads' structure and (ii) the thermal stability of the hydrogel beads is remarkably enhanced by HNTs. The appearance of hydrogel beads is shown in both wet and dry form (Fig. 4). The average diameter of the hydrogel beads is changed from 2.29 to 2.75 mm in the wet form. It is found that HNTs have an

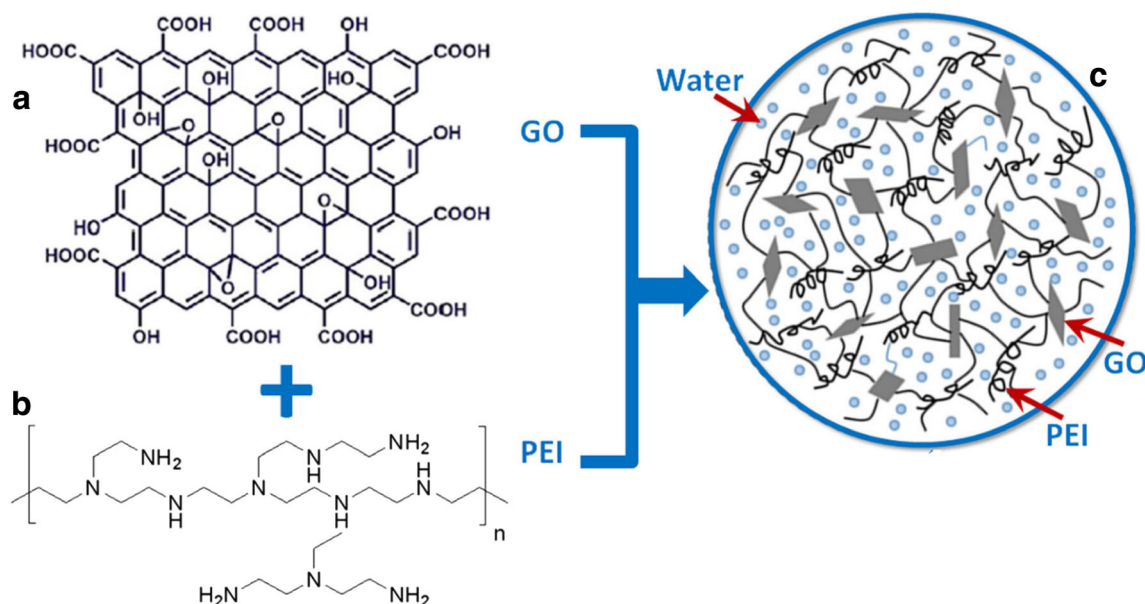


Fig. 3 Schematic depiction of formation of GO/PEI gels. **a** GO and **b** amine-rich PEI were combined to yield **c** GO/PEI hydrogels. (Reprinted (adapted) with permission from Guo et al. 2015. Copyright (2017) Springer Open)

influence on the appearance, diameter, and microstructures. Via the adsorption behavior of the hydrogel beads with MB and MG, it is found that HNTs affected the adsorption capacity of hydrogel beads. It is the presence of HNTs that can considerably increase the adsorption effect of hydrogel beads for both pollutants. Besides, these hydrogel beads can be regarded as an excellent adsorbent, as they can be simply recycled and reused by NaOH solution and acetone. Especially, the high removal ratio of dyes is maintained above 92.0% in all hydrogel beads at the second adsorption.

Congo red (CR) has been known as one of the dyes that causes an allergic reaction. It is metabolized to benzidine, a human carcinogen, and it is very difficult to biodegrade due to a complex aromatic structure that provides physico-chemical, thermal, and optical stability (Han et al. 2008). Recently, CS has been regarded as an excellent material for wastewater treatment due to the large number of active amine (—NH_2) groups in its structure. Accordingly, there have been many studies using CS to prepare hydrogel for anionic dyes and heavy metal removal. To enhance adsorption capacity of

CS-based hydrogels, certain modification methods, such as cross-linking (Vieira & Beppu 2006) and the addition of other functional groups (Suna et al. 2006), were conducted. By using cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, CTAB-impregnated CS hydrogel beads were prepared successfully for adsorption of CR (Chatterjee et al. 2009). The addition of CTAB to CS hydrogel beads significantly improved the adsorption capacity of the hydrogel. It is found that the increase of the CTAB concentration led to a significant increase of CR adsorption capacity of the hydrogel beads. Additionally, using cationic surfactant to impregnate CS can enhance the adsorption capacity of hydrogels for CR relative to other materials, and this approach will produce hydrogel adsorbents having a high adsorption efficiency for removal of anionic dyes.

Recently, the development of new adsorbents from feed-stock materials, such as starch, cellulose, and lignin, has been of interest to scientists due to the fact that the adsorbents produced from these materials have many unique advantages including low-cost, biodegradability, non-toxicity, and high efficiency (Li and Bai 2006). Lignin is a class of complex organic polymer that is synthesized by the chemical polymerization method from three type of alcohol (Ralph et al. 2004). Offering the outstanding advantages noted above, lignin is regarded as a potential material for preparation of excellent adsorbents. Recently, a type of lignin, lignosulfonate (LS), has been used in the synthesis process of a typical Lignosulfonate-g-acrylic acid (LS-g-AA) hydrogel bead with superabsorbent capacity (Yu et al. 2016). In this preparation method, AA molecules were grafted onto the backbone LS in the presence of *N,N'*-methylene-bis-acrylamide (MBA) as the cross-linker and laccase/t-BHP as the initiator (Fig. 5). It was found that

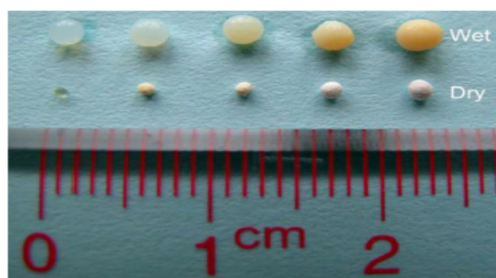


Fig. 4 Appearance of chitosan and chitosan–HNTs hydrogel beads in wet and dry state (reprinted (adapted) with permission from Peng et al. 2015. Copyright (2017) Elsevier)

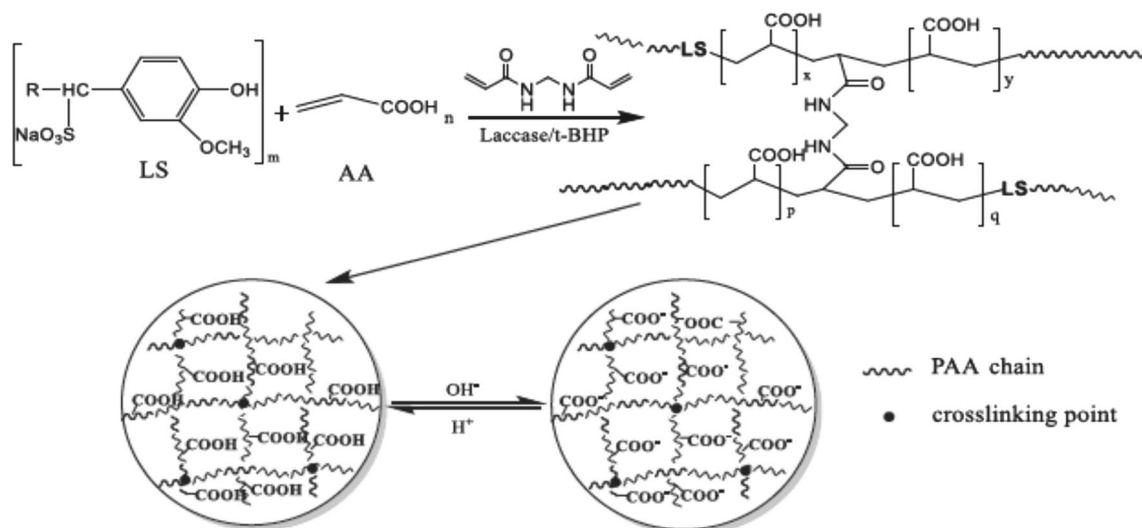


Fig. 5 Schematic of LS-g-AA hydrogel synthesis catalyzed by laccase in presence of hydrogen peroxide (reprinted (adapted) with permission from Yu et al. 2016. Copyright (2017) Elsevier)

the hydrogel shows a high adsorption efficiency for MB after 2 h and its adsorption capacity depends on the mass ratio of AA, the pH of solution, and the initial pollutant concentration. Moreover, the LS-g-AA hydrogel also showed that with its desorption and reuse capacities, it is an excellent adsorbent. The hydrogel could be desorbed by using a weak acid solution (pH of 4.0) and reused at least four times but still maintained high MB-adsorption levels. Employing a similar method, using another feedstock material (cellulose), a novel amphoteric hydrogels was introduced for removing three anionic dyes, namely acid red 9 (AR9), acid red 13 (AR13), and acid blue 92 (AB92) (Kono 2015). To prepare the hydrogel, a series of cellulose ampholytes (CAs) was produced by a cationization reaction between sodium carboxymethylcellulose and 2,3-epoxypropyltrimethylammonium chloride. Then, the hydrogels were formed by a crosslinking method according to which CAs is cross-linked by ethyleneglycoldiglycidylether (EGDE). The adsorption capacity of the fabricated hydrogel was revealed to be a function of two factors: the pH of the adsorption solution and the proportions of the cationic groups. The highest adsorption capacity of the anionic dyes could be reached at pH < 3 and with high proportions of cationic groups.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a water-soluble polymer that is quite friendly to the environment and to humans due to its non-toxic, biodegradable, and biocompatible properties. Owing to these advantages, PVP is totally suitable for synthesizing hydrogel materials. Hydrogels based on the interaction of PVP and other component for removing anionic dyes and metal ions (Lu et al. 2011; Senkal et al. 2006; Wang and Wang 2010) have been successfully prepared. Sodium alginate (NaAlg), a natural polysaccharide derived from brown seaweeds, also possesses the same friendly properties as PVP. Hydrogel beads can be fabricated from NaAlg by cross-linking the guluronic acid component of NaAlg with

other cations (Babu et al. 2007). When sodium alginate is dissolved in a neutral and alkaline solution, the carboxylate-functional group has a negative charge, which affects a greater affinity to cations (Rocher et al. 2008). Yet, it has been suggested that anionic hydrogels produced from polysaccharide like alginate have inadequate efficiency for adsorption of anionic dyes from aqueous solution (Blackburn 2004). However, by combining PVP with sodium alginate, that problem was overcome in preparing novel NaAlg/PVP-blend hydrogel beads (Inal and Erduran 2015). The hydrogel beads were fabricated by the gelation method in CaCl₂ solution. They have been effectively demonstrated for adsorption of different dyes such as reactive red-120 (RR), cibacron brilliant red 3B-A (CBR), and remazol brilliant blue R (RBB).

Titanium dioxide (TiO₂) is a flexible semiconductor that has attracted great interest in the wastewater treatment field. It has many advantages, such as strong oxidizing power, superhydrophilicity, chemical stability, long-term durability, non-toxicity, low cost, and transparency to visible light. Therefore, TiO₂ has seen many applications in water splitting, energy storage, dye-sensitized solar cells, and decomposition of various pollutants. Using TiO₂ as a photocatalyst is regarded one of the most promising applications in terms of the removal of hazardous organic substances, because it shows high photocatalytic activity under UV light irradiation (Nakata and Fujishima 2012; Schneider et al. 2014). According to this approach, a recyclable, recoverable, and reformable hydrogel-based photocatalyst was successfully synthesized (Mai et al. 2017). In the preparation process, the main observations were well-distributed TiO₂ nanoparticles in the agarose hydrogel matrix and the gelation of the agarose in hot water. The study used methyl blue (MB) to examine the photocatalytic activity of the hydrogel and the contents of TiO₂ and agarose in hydrogels as well as hydrogel size, shape,

and concentration of a hydrogel are main factors that significantly influenced the photodegradation efficiency. Furthermore, the additional excellent features of this type of hydrogel are its recyclability and the simplicity of the regeneration of pure TiO₂ NPs.

Particles entrapped in hydrogel beads for radioactive waste removal

With the rapid development of nuclear power application around the world, radioactive wastes containing enormous amounts of radionuclides have become a focus of concern, posing serious chemical and radiological toxicity threats to the environment. Among the common radioactive nuclides, ⁶⁰Co is one of the most harmful owing to its strong γ -emission and relatively long half-life of 5.3 years (Wang et al. 2013). The adsorption method is of great interest for removal of ⁶⁰Co, owing to advantages including high efficiency, low cost and operation convenience compared with the alternative methods (chemical precipitation, reverse osmosis, ion exchange, solvent extraction, coagulation, and membrane separation) (Thakura and Thakurb 2015). By using PVA and poly(acrylic acid-co-acrylic amide) P(AA-co-AM), novel PVA-P (AA-co-AM) semi-IPN hydrogels were successfully synthesized via free radical polymerization under the ultrasound-assisted condition for Co²⁺ ion removal (Wang et al. 2016). As for the adsorption capacity of the hydrogel for Co²⁺ ions, it showed an excellent capability, compared with other adsorbents. However, its adsorption efficiency was also influenced by various parameters, such as pH, temperature, adsorption time, and the initial concentration of pollutants. In addition, the hydrogel was also used as an adsorbent owing to the merits of low material cost and operational convenience.

Cesium (¹³⁷Cs) is known as an important radioactive contaminant that can cause serious radiological hazards that affect human health and the environment due to its long half-life and high mobility in aquatic environments (Howard et al. 1991). For the past many decades, development of efficient materials for removal of radioactive cesium from aqueous solutions has been the focus of great attention from researchers worldwide. Inorganic ion exchangers possess many special properties including selectivity, radiation, and thermal stabilities as well as good compatibility with various matrices. Currently, a popular and important inorganic ion exchanger is transition metal hexacyanoferrates, which can be applied in the nuclear industry for removal of cesium. Generally, inorganic ion exchangers can be used to remove cesium in two different ways: (i) coprecipitation of cesium ions and (ii) preparation of metal hexacyanoferrate slurry. In 2015, a new method for synthesis of spherical potassium nickel hexacyanoferrate hydrogel beads that binds the slurry of potassium nickel hexacyanoferrate (KNiHCF) particles in a alginate and polyvinyl alcohol (PVA) matrix was introduced by utilizing KNiHCF as an

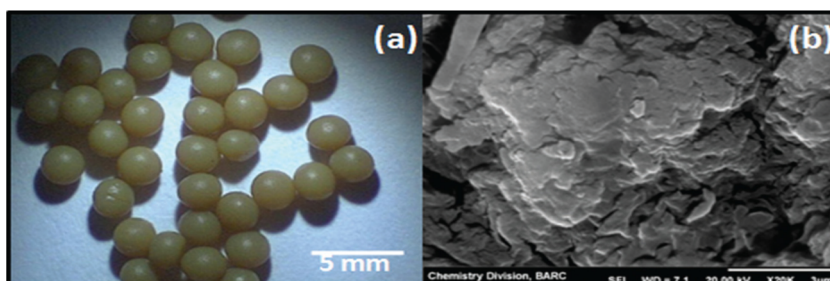
inorganic ion exchanger (Dwivedi et al. 2015). The hydrogel beads were found to have a high hydrophilicity and a high surface area. The optical microscope (OM) image of the swollen hydrogel beads shown in Fig. 6a reveals a round shape and a relatively uniform size of 2 mm. Figure 6b shows the SEM images of the outer surface of a dried hydrogel bead. As is apparent, it is quite rough and has some large pores. The adsorption of cesium ions onto the KNiHCF particles of the hydrogel beads happens by ion exchange between a potassium ion of KNiHCF and a cesium ion. Also, the hydrogel beads could be effectively applied to adsorb radioactive cesium ions within a wide range of pH (1–12), for a maximum capacity of about ~ 64 mg per g of dry beads. The KNiHCF hydrogel beads are an excellent material for use in cesium removal from low level radioactive waste.

Taking a similar approach but using another type of inorganic ion exchanger, new hydrogel beads for recovery or removal of cesium from low-level nuclear waste streams were fabricated by encapsulating an inorganic sorbent, potassium zinc hexacyanoferrate (KZnHCF) in hydrogel beads (Pathak et al. 2016). The preparation process of the hydrogel beads is shown in Fig. 7. The KZnHCF-gel beads were prepared using sodium alginate stabilizing PVA to form a binding matrix. The reaction of ZnSO₄ and KHCF will make KZnHCF sol in the presence of PVA. The size of the KZnHCF particles formed can be controlled by the PVA. An aqueous solution of 4% sodium alginate was added to stabilize the KZnHCF sol. Then, hydrogel beads can be formed by dropping this mixture into an aqueous bath containing 4-wt% CaCl₂. The adsorption process of the hydrogel beads was found to be quite efficient in the pH range from 3 to 10 and the adsorption capacity of the hydrogel beads for cesium can approximately reach 95%. Especially, the cesium adsorption efficiency of these hydrogel beads under the pH neutral condition was not affected significantly by the interfering ions (Na⁺, Ca²⁺, and Ba²⁺). This means that practical applications of such hydrogel beads for treatment of cesium in aqueous nuclear wastes is completely possible.

Particles entrapped in hydrogel beads for other contaminant removal

As has been noted, CS hydrogel beads are commonly used in contaminant removal applications due to their high adsorption capacity. In 2009, a CS hydrogel beads was introduced by Chatterjee and HanWoo 2009 for removal of nitrate. The nitrate adsorption capacity of the hydrogel beads was identified increasing along with decreasing the pH of the solution. Besides, the adsorption process also depends on the temperature: the optimum activity is achieved at 30 °C and the adsorption capacity will decrease with increases in temperature over 30 °C. The maximum adsorption capacity of this hydrogel could reach 92.1 mg g⁻¹ at 30 °C. It is found that the

Fig. 6 **a** OM image and **b** SEM images of outer surface (reprinted (adapted) with permission from Dwivedi et al. 2015. Copyright (2017) Royal Society of Chemistry)



adsorption process of nitrate is a spontaneous, exothermic process that has positive entropy, and that when increasing the pH of the solution to the alkaline condition, desorption of nitrate from hydrogel beads will be accomplished for a desorption ratio of 87% at around pH 12.0.

Methyl parathion (MP) is one of the many types of organophosphorus pesticides used on cotton, soybeans, vegetables, and other crops. When discharged into living systems, the toxic compounds from pesticides will prevent the action of acetyl cholinesterase, which can lead to great harm to living creatures, such as loss of muscle control, paralysis, convulsions, coma, and even death (Agrawal et al. 2010). Therefore, MP’s removal from the water is crucial. A novel hydrogel beads for removal of MP from waste water were introduced by developing a new method for one-pot synthesis of gold nanoparticle-loaded hydrogel beads by using a composite matrix of CS (Dwivedi et al. 2014). These hydrogel beads are a strongly hydrophilic material that can contain up to 96% water and remain stable up to 200 °C. Their high water capacity also enhances the interaction between the MP’s compounds and the active sites of the hydrogel, leading to a higher adsorption efficiency. The study also reveals that a loading of at least 0.5-

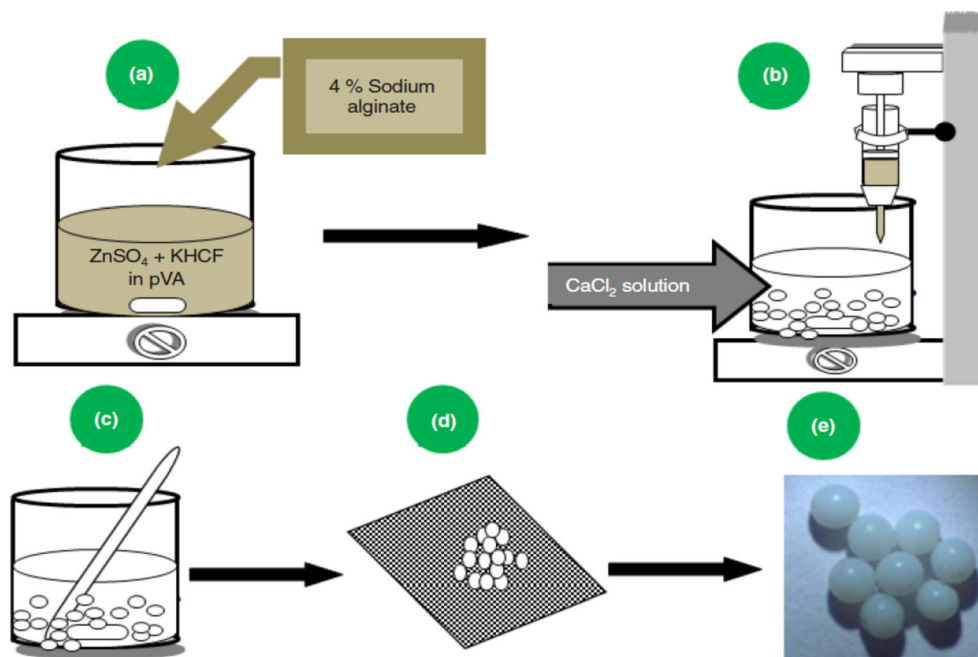
wt% gold nanoparticles on hydrogel beads is good enough to improve the adsorption capacity of the beads by more than twofold compared with pure beads.

Application of hydrogel films for adsorption of contaminants

Particles entrapped in hydrogel films for metal ion removal

The presence of Ca^{2+} and Mg^{2+} ions in liquid increases water hardness, which is one of the main problems in the water-treatment field. In 2016, a hybrid hydrogel film was successfully prepared by using conjugation of oxidized carbon dots (CDs) produced from 11-mercaptoundecanoic acid with CS (Baruah et al. 2016). Ca^{2+} and Mg^{2+} ions from the solution were removed by using the hydrogel film as a potential platform based on the principles of ion exchange. The removing efficiency of Ca^{2+} and Mg^{2+} ions from pond water by the hydrogel film was 68.01 and 56.35%, respectively. Figure 8 shows the method of synthesis of CS-MUA-SO₃Na-CDs

Fig. 7 Illustration of procedure for preparation of KZnHCF-gel beads (reprinted (adapted) with permission from Pathak et al. 2016. Copyright (2017) Asian Journal of Materials Chemistry). **a** Preparation of formulation of ZnSO₄ and KHCF in presence of PVA. **b** Drop wise addition of formulation to CaCl₂ aqueous solution. **c** Curing of beads for 4 h. **d** Separation and washing of prepared beads. **e** Optical microscopy (OM) image of the swollen beads



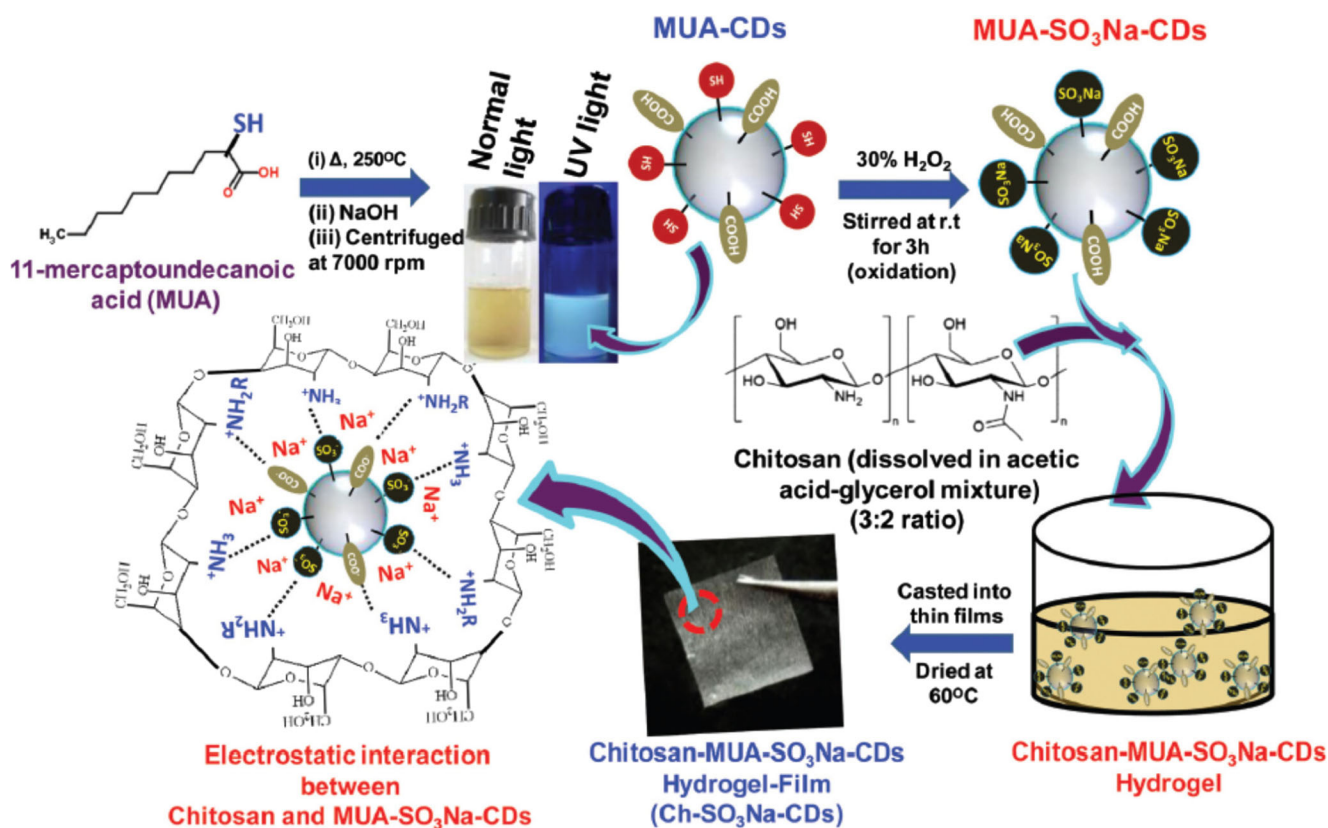


Fig. 8 Schema showing synthesis protocol of thiol functionalized carbon dots (CDs) from MUA followed by their oxidation to form sulfonated CDs and subsequent fabrication of polymeric nanocomposite films via

conjugation of sulfonated CDs with biopolymer chitosan (reprinted (adapted) with permission from Baruah et al. 2016. Copyright (2017) Royal Society of Chemistry)

hydrogel thin film. The presence of —SH functionalities on the CDs surface was superseded by SO_3Na after oxidizing. Then the hydrogel was formed by mixing the oxidized CDs and CS solution (dissolved in a 3:2 mixture of acetic acid and glycerol). This hydrogel was then spread onto glass slides and dried at 60°C for 2 h. Typically, the films were of a thickness of ~ 0.07 mm and the sulfonated CDs–CS hybrid hydrogel nanocomposite film can replace toxic conventional polystyrene crosslinked with divinylbenzene generally used for ion exchange because it is a green material for water-softening applications.

Agarose (Agr) is one of the most promising candidates for generation of thermal reversible hydrogels. It is a linear polymer that is a disaccharide of D-galactose and 3,6-anhydro-L-galactopyranose and is extracted from seaweeds (Golmohamadi et al. 2012). With combination of Agr, CS, and CDs, an Agr/CD hydrogel film as a solid sensing platform was introduced for detection and adsorption of heavy metal (Gogoi et al. 2015). The fabrication of the solid-sensing platform was illustrated in Fig. 9. The generation of the platform is mainly based on a simple electrostatic interaction between the OH^- groups present in agarose and the NH_3^+ group present in the CDs. This hydrogel can detect many different metal ions, specifically Cr^{6+} , Cu^{2+} , Fe^{3+} , Pb^{2+} , and Mn^{2+} . Besides, the

hydrogel film is also suitable for use as an efficient filtration membrane for removal of the above-noted heavy metal ions. Especially, the removal of the quintet of heavy-metal ions of the Agr/CD hydrogel was more effective than that of the only-Agr hydrogel. The removal percentage of the Agr/CD hydrogel for Cr^{6+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , and Pb^{2+} ion was found to be 27.75, 54.85, 38.48, 35.41, and 83.97%, respectively.

CS has many advantages for preparation of adsorbents for removal of pollutants from wastewater. However, pure CS materials have several drawbacks, such as low mechanical strength and difficult recovery (Wang and Wang 2008). Moreover, CS is dissolved in acidic solution, which a lot of metal ions are preferentially adsorbed. To improve the mechanical and chemical features of hydrogels synthesized from CS as well as to enhance its stability under acidic conditions, several cross-linking agents (ECH, glutaraldehyde, and others) are combined with CS in the hydrogel-preparation process. Using glyoxal (an organic compound with the chemical formula OCHCHO) as a crosslinked agent, Mirabedini and co-workers formulated a novel magnetic hydrogel via combination of CS and magnetic nanoparticles (Fe_3O_4) (Mirabedini et al. 2017). The outstanding properties of this hydrogel are its easy reusability and high Cr^{6+} ion removal rate (80–90%) in water solution with a maximum adsorption capacity of

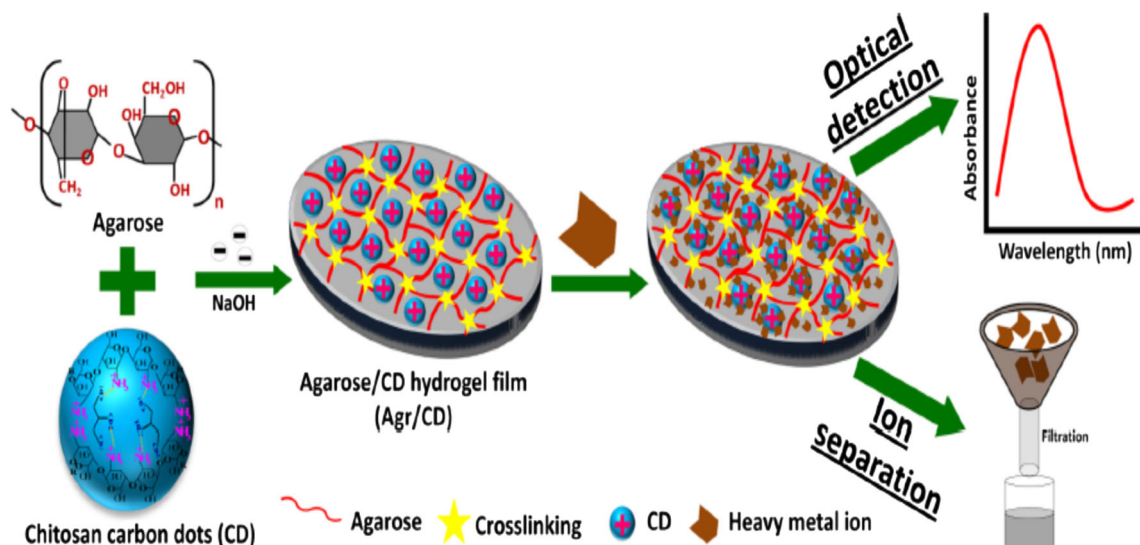


Fig. 9 Schematic illustration of preparation of Agarose/CD (Agr/CD) hydrogel film and its application for removal of heavy metal ions (reprinted (adapted) with permission from Gogoi et al. 2015. Copyright (2017) American Chemical Society)

27.25 mg g⁻¹. Moreover, it can be recycled for at least three adsorption cycles. But most especially, it can be easily desorbed by 0.1-M HCl solution without dissolving CS in the hydrogel. This means that the structure of CS can be significantly enhanced by strong cross-linking with glyoxal.

In recent decades, many studies have begun considering the effective and economic aspect of heavy-metal ion removal. The biosorption method, a common approach, uses the synthesis of raw materials, such as cellulose, starch, or CS for metal ion adsorption; they are abundant, low-cost, biodegradable, and environmentally friendly (Zhou et al. 2012).

Cellulose, abundant natural polymer with excellent biocompatibility properties, is one of the most commonly employed adsorption materials in wastewater treatment. However, it still has not reached its potential applications in many areas because it is difficult to process in common solutions (Zhou et al. 2004). Several efficient solvents have been studied and applied for the development of the production of cellulose-based adsorbents such as lithium chloride/*N,N*-dimethylacetamide (Zhou et al. 2004), *N*-methylmorpholine-*N*-oxide (Cai et al. 2004), and ionic liquid (Zhu et al. 2006). By using phosphoric acid as an efficient solvent for cellulose, several recent studies successfully developed a potential hydrogel, cellulose-graft-acrylic acid (C-g-AA) hydrogel, through the free-radical polymerization method (Zhou et al. 2011; Zhou et al. 2012). This type of hydrogel showed outstanding adsorption behavior for both dyes MB and metal ions (Cd²⁺, Pb²⁺, and Ni²⁺) in aqueous solutions. In case of adsorbing metal ions, the adsorption capacity of C-g-AA hydrogel depends on the pH of adsorbent solution, the most effective value being reached at pH 5.0.

By combining cellulose and GO, a simple and novel GO/cellulose hydrogel as a potential material was introduced for adsorption of metal ions (Chen et al. 2016). In this method, GO

nanosheets consisting of carboxyl and hydroxyl groups are linked into the surface of the cellulose hydrogel, while the gel structure and its nanoporous property are maintained. Due to the linking with GO, the GO/cellulose hydrogel films possess good compressive strength. Increasing the GO/cellulose ratio, furthermore, significantly improved the adsorption capacity for Cu²⁺ ions in aqueous solution. The GO/cellulose hydrogel showed a high adsorption capacity, compared with the pure cellulose hydrogels. The GO/cellulose hydrogel also showed other distinguishing features, such as high-efficiency regeneration and high adsorption capacities for other metal ions (Zn²⁺, Fe³⁺, and Pb²⁺).

Starch (St) is a raw material that is abundant, easy to produce, recoverable, and naturally biodegradable. Many published studies have used chemically modified starch via vinyl graft copolymerization to enhance the properties of starch, expand the range of its application (Khalil et al. 1993; Mostafa and El-Sanabary 2003), and provide for the biodegradability and biocompatibility of corresponding hydrogels. Combining starch with sodium humates in a polymer hydrogel made possible a series of starch-g-poly(acrylic acid)/sodium humate (St-g-PAA/SH) hydrogels that were tested for their Cu²⁺ ion adsorption capacity in aqueous solution (Zheng et al. 2010). This hydrogel displayed an excellent ability in adsorbing Cu²⁺ within a wide pH range in an acidic environment (2.7–5.0). Moreover, the most remarkable point respecting the hydrogel was that it could be regenerated by using NaOH solution as the regenerating agent, and it was found that the regeneration ability depends on the ratio of sodium humates to hydrogel.

Particles entrapped in hydrogel films for dye removal

For removal of dyes from aqueous solutions, various techniques have been investigated and developed, among which

adsorption is a widely used process within the field of advanced wastewater treatment. Particularly, nanoscale materials, such as hydrogel films, are typical adsorbents offering great utility in dye removal (Wang et al. 2015; Zhang et al. 2011; Zhang et al. 2012b). For hydrogel films, the properties of high flexibility and porosity along with the ability to interact with a number of different nanoscale adsorbents are particularly important in the purification field (Zhang et al. 2016).

Compared with synthetic polymers, microorganisms possess many more advantages, among which are maintainable, friendly and unvarying scaffolds with biomacromolecules (Moradi et al. 2016) (Zhou et al. 2016; Zhu et al. 2016). Filamentous fungus, a member of microorganism family, has a large aspect ratio and remarkable chemical characteristics, for example, high flexibility and ductility. These properties can make their efficient formation more stable in macroscopic monoliths (e.g., a porous membrane) (Chai et al. 2015; Wang et al. 2015; Zhu et al. 2016). Therefore, fungus hyphae have been trialed as great reinforcement agents with friendly, low-cost properties for improved mechanical stability of formed macroscopic structures by interaction with graphene. Based on interaction between the GO and fungus hyphae at a temperature of 130 °C, a porous and flexible hydrogel film was synthesized successfully and the primary mechanism for interaction between the fungus hyphae and GO is based on the reduction of GO by the biomacromolecules on the cell of the microorganism (Zhang et al. 2016). Notably, during this interaction process, nanoscale building blocks can be effectively loaded into the film by addition of a nanoparticle. The film-loading nanoparticles could be assembled in an adsorption setup to eliminate dyes from aqueous solution, which is useful for nanoparticles in water-purification applications. In addition, the hydrogel film is an excellent reusable and recycled material that could still maintain a high removal proportion after ten adsorption-desorption cycles.

Hydrogels based on PAM, polyacrylonitrile (PAN), methacrylic acid, CS, polyvinylpyrrolidone (PVP), and their derivatives have been shown to form complexes with dyes (Jeon et al. 2008; Reis et al. 2012). These types of hydrogels usually have been used as adsorbents in water treatment owing to advantages including high swelling and wettability, easy loading, creation of chelated complex, and a capacity for semi-continuous operation (Oladipo and Gazi 2015; Wang et al. 2012). With high swelling and wetting, adsorption of the target molecules or ions of the hydrogel can be enhanced due to the production of more precise surface area and contact with additional functional groups for adsorption (Wang et al. 2012). In order to develop these approaches, a number of studies have combined natural CS and synthetic PAN. When combined with CS, PAN has a role as an active component of an ion exchanger. Because of its possessing a nitrile group, PAN is able to form hydrogel bonds and complexes with other materials of positive charge. Besides, due to

its hydrophilicity, porosity, and mechanical strength, PAN is a potential material for hydrogel preparation in the water treatment field (Sebesta et al. 1995). For improved stability and swelling ratio, Fahad S. Al-Mubaddel's group fabricated a novel hydrogel in two steps for adsorption of rhodamine B in aqueous solution (Al-Mubaddel et al. 2015). Firstly, CS was interacted with PAN to form CS/PAN blend films. Then, the CS in these films was cross-linked with ECH to make the hydrogel films. PAN was found to significantly enhance the stability of the fabricated hydrogel film. For instance, with more than 50% PAN content, the stability reached a good degree, while it sharply decreased with less than 50% PAN content. As for the rhodamine B adsorption behavior, the hydrogel film's adsorption ratio rapidly increased during the initial time (~200 min), but in the equilibrium state, after ~240 min, the adsorption and desorption of the dyes attained a balance.

Particles entrapped hydrogel nanocomposites for adsorption of contaminants

Proteins are large biomolecules or macromolecules, and they are broadly distributed in nature. Proteins can be synthesized in nature from two main sources, animals and plants. For instance, proteins derived from animals are collagen, keratin, and gelatin and proteins derived from plants are soya. Basically, proteins are chain polymers of high molecular weight that are not soluble or only very slightly soluble in water. There are two ways to solubilize proteins in water: alkaline and enzymatic hydrolysis (Pourjavadi et al. 2006). Proteins have the ability to bind thoroughly with heavy-metal because they possess a number of electric arrays of chemical functionality such as $-\text{COOH}$, $-\text{NH}$, $-\text{SH}$, $-\text{OH}$, and imidazole groups. Therefore, it is expected that proteins will enhance the adsorption capacity of hydrogel (Hwang and Damodaran 1997). However, based on our search data, up to now there has been little research relating to the preparation of protein-based hydrogels for removal of heavy-metal ions. In 1997, soy protein, which is a sustainable, low cost, and abundant plant protein, was applied in preparing a soy-protein-based hydrogel by crosslinking an ethylenediaminetetraacetic acid dianhydride (EDTAD)-modified soy protein isolate for adsorption of divalent calcium, zinc, mercury, and lead ions from aqueous solution (Hwang and Damodaran 1997). The equilibrium adsorption capacities of the hydrogel for these metal ions were 0.70, 0.65, 0.95, and 0.70 mmol per gram of dry hydrogel, respectively. In 2017, soy protein was also introduced in new nanocomposite hydrogels synthesized by the crosslinking method using soy protein isolate as a matrix and polyethyleneimine (PEI) as a functional component to replace EDTAD (Liu et al. 2017).

These nanocomposite hydrogels were effectively demonstrated for adsorption of Cu^{2+} ions from aqueous solution, the results indicating a Cu^{2+} adsorption capacity that reached 136.2-mg Cu^{2+} /g hydrogel. In addition, the nanocomposite hydrogel showed an excellent selectivity for the removal of Cu^{2+} ions co-existing with competitive heavy-metal ions, including Zn^{2+} , Cd^{2+} , and Pb^{2+} . The two above-noted studies suggest that such a soy protein isolate-based hydrogel is a good candidate for selective adsorption and recycling of metal ions in the wastewater treatment industry. Other protein, cottonseed protein, was also used in synthesis process of a cottonseed protein-poly(-acrylic acid) hydrogel nanocomposite for removal of copper and lead ions in aqueous solution. The hydrogels showed high adsorption capacities that were influenced by various changes such as the content of cottonseed protein, the initial concentration of metal ions, and pH. Moreover, the hydrogel could be easily regenerated in HCl solution and reused while maintaining over 90 and 57% of its original adsorption capacity for Cu^{2+} and Pb^{2+} ions, respectively, after four cycles of reuse (Zhang et al. 2012a). Gelatin, another protein derived from collagen, is a natural protein present in the tendons, ligaments, and tissues of mammals. Gelatin has been applied to the preparation of many hydrogels for drug delivery through crosslinking reactions with monomers (Guo et al. 2015). In 2003, a gelatin hydrogel was introduced for removal of Cu^{2+} and Cr^{6+} ions from aqueous solution (Chauhan et al. 2003). The hydrogels were synthesized by crosslinking reaction of gelatin with three acrylamides monomers (Acrylamide (AAm), 2-acrylamido-2-methyl-1-propanesulfonic acid (AAmPSA), and *N*-iso-propylacrylamide (*N*-i-PAAm)) in the presence of a crosslinker (*N,N*-methylene bisacrylamide) at different temperatures. The structural aspects of the formed hydrogels depend on the nature of the amine group and the water uptake capacity. The hydrogels also effectively showed adsorption of metal ions (Fe^{2+} , Cu^{2+} , and Cr^{6+}) based on the mechanism of ion exchange.

GO is graphite oxide monolayer having a two-dimensional structure. GO is able to be dispersed in polar solvents such as water or organic solvents because of its possession of many functional hydroxyl, epoxy, and carboxyl groups (Haubner et al. 2010). Hyperbranched polymers are highly branched three-dimensional polymers. They have a globular and dendritic structure, which endows them with many interesting properties, such as abundant groups and numerous end groups, low viscosity, and high solubility. Owing to the end groups in their structure, hyperbranched polymers are used to synthesize, by the interaction of end groups and the hydrogel matrix, polymers or hydrogel materials with customizable structures (Carlmark et al. 2013). Through a novel cost-effective and environmentally friendly method, a poly(acrylic acid) (PAA) hydrogel nanocomposite was successfully synthesized by using hyperbranched polymers and GO (Yu et al. 2015b). The PAA hydrogel showed a high water-adsorption ability and a high, 209 mg g^{-1} (at pH = 5) adsorption capacity for Cu^{2+} ions in water solution. In addition, the

hydrogel nanocomposite was demonstrated to be suitable for use as a low-cost, environmentally friendly adsorbent for copper adsorption and recovery, because the Cu^{2+} ions adsorbed in the hydrogel can be eluted and the hydrogel nanocomposite recovered by using nitric acid solution. The adsorption capacity of the hydrogel, moreover, was maintained at over 90%.

Itaconic acid (IA) is a water-soluble monomer having two carboxylic acid groups. Due to their double functionality, IA-based polymers are regarded as functional polymers and potential materials for wastewater treatment. Besides, in recent years, researches using 2-hydroxyethyl acrylate (HEA) in the preparation of hydrogels have been reported and, indeed, HEA-based hydrogels have been shown to be promising adsorbents for removal of heavy-metal ions from aqueous solutions (Antić et al. 2015; Li et al. 2013; Wu and Li 2013). By combination of IA with 2-hydroxyethyl acrylate, pH-sensitive hydrogels were introduced for use as adsorbents to remove Pb^{2+} from aqueous solution (Antić et al. 2016). Because both HEA and IA are materials having a good adsorption capacity, HEA/IA hydrogels relative to corresponding homopolymers also have shown high adsorption capacities for Pb^{2+} ions. A comparison of the adsorption capacities between the reported adsorbents indicated that it is the combination between IA and HEA that significantly enhanced the adsorption capacity of the HEA/IA hydrogels relative to most of the previously investigated adsorbents. Moreover, the hydrogel nanocomposite could be easily regenerated, and desorption of the adsorbed Pb^{2+} ions could be conducted in HNO_3 , HCl, and CH_3COOH acid solutions. After three cycles, significantly, nearly 90% of the initial adsorption capacity had been maintained. IA also has been used in some other studies for synthesis of hydrogels, specifically in combination with alginate, a high-molecular-weight polysaccharide extracted from various species of brown algae. In 2012, sodium alginate/itaconic (NaAlg/IA) hydrogels were also successfully synthesized by a free-radical polymerization in which an aqueous solution of 20% IA was mixed with 10-wt% NaAlg at room temperature (Mahmoud and Mohamed 2012). This hydrogel was effectively demonstrated for removal of Pb^{2+} ions to a maximum capacity of 1.23 mmol/L. The same NaAlg/IA-type hydrogel was synthesized and introduced for removal of dyes, MB (Mahmoud et al. 2014). In MB adsorption process, parameters affecting the MB-adsorption capacity in wastewater including a concentration of NaAlg and temperature. The presence of NaAlg in the hydrogel changed the adsorption efficiency; in particular, when increasing the NaAlg percentage in the hydrogel, the adsorption capacity also increased. Especially, for reuse of the hydrogel after MB adsorption, acid fast red dye (AFR) was used to examine the adsorption capacity for the NaAlg/IA hydrogel-loaded MB in a second adsorption from aqueous solution. The results showed that after adsorbing MB, the surfaces of the NaAlg/IA hydrogel were covered with a layer of cationic dye and that in the second adsorption,

anionic AFR was adsorbed on the hydrogel-loaded MB through an electrostatic interaction. The AFR removal ratio of the hydrogel-loaded MB could reach 62 to 74%, depending on the amount of MB loaded onto the surface of the hydrogel.

Clay shows a strong affinity for both cationic and anionic dyes, whereas the adsorption capacity for basic dye is much higher than that for acidic dye due to the negative charge on the structure of the clay (Crini 2006). Clay minerals commonly have layered structures with a large surface area and high ionic exchange capacity. Besides, its current market price is cheaper than that of active carbon and some other materials (Babel and Kurniawan 2003). Numerous clays including kaolinite, laponite, montmorillonite, attapulgite, diatomite, vermiculite, alumina, mica, potassium humate, sodium humate, glass, smectite, vermiculite, sercite, rectorite, and sodium silicate have been added to the polymeric matrix to synthesize nanocomposite hydrogel materials (Kabiri et al. 2011; Magalhães et al. 2013). According to Zhao group's review (Zhao et al. 2015), clay mineral-loading nanocomposite hydrogels have possessed exceptional composition and properties. Consequently, it has attracted numerous interests in the synthesis of adsorbents over the last decades. Clay-mineral can be widely used to add into the hydrogel matrix to form novel superabsorbent nanocomposite hydrogels with high absorption capacities up to several hundred times for their dried weight. It was investigated that a successful combination between montmorillonite clay and cellulose in the design of superabsorbent cellulose/clay nanocomposite hydrogels is illustrated (Peng et al. 2016). In preparation method, these hydrogels were formed by crosslinking method, whose cellulose and CMC will make chemical crosslinking with ECH in the presence of clay nanosheets. The authors revealed that the hydrogels exhibit very high equilibrium swelling ratio in distilled water and the maximum ratio can reach 1443 g/g, which indicates their superabsorbent properties. Due to the superabsorbent properties, the hydrogels incorporated with intercalated clays exhibited superior MB removal capacity. Furthermore, the characteristic properties of hydrogels including the mechanical and thermal properties are able to be largely affected by the content of added clays (Haraguchi et al. 2003). These properties can be significantly enhanced when clay minerals are incorporated into the polymer matrix (Bitinis et al. 2011) because the increasing the clay amount will lead to an increase in the crosslink density. In some studies of Haraguchi's group, for instance, a modified clay was used as the cross-linker to synthesize poly (*N*-isopropylacrylamide)/clay (Haraguchi et al. 2002) and poly(*N,N*-dimethylacrylamide)/clay nanocomposite hydrogels (Haraguchi et al. 2003) with higher mechanical properties. They revealed that these hydrogels showed very high elongation at break, close to or greater than 1500% and their tensile properties strongly depended on the content of clay. The increase of modulus and strength values is proportional to the content of clay. In addition, clays can improve the higher toughness of hydrogels based on the formation of an intercalated architecture with more cross-linking points (Peng et al.

2016). For the enhancement of thermal properties, it was demonstrated that the use of bentonite clay can increase the thermal stability of a β -cyclodextrin/bentonite clay nanocomposite hydrogel (Heydari and Sheibani 2015). It was concluded that the clay plays a role in the prevention of the polymer thermal degradation. It is the presence of the clay nanolayer inside the polymer matrix that led to the improvement and the clays act as barriers to maximizing the heat insulation and minimizing the permeability of volatile degradation products to the hydrogels.

A novel hydrogel nanocomposite was achieved based on combining CS, AA, and organically modified nanosilica by 3-aminopropyl triethoxysilane (APTS) (Fig. 10) (Pourjavadi et al. 2015). The applicability of this hydrogel nanocomposite in water treatment was demonstrated for adsorption of metal ions (Co^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}) from aqueous solution. According to the result, the study concluded that the nanosilica played an important role in the properties and adsorption capacity of this hydrogel. The nanosilica might play the role of a physical cross-linker. It is certain, in any case, that the presence of modified nanosilica significantly contributed to the enhanced porosity of the hydrogel network. In addition, the nanosilica functionalized by APTS increased the porosity of the hydrogel and created extensive network domains capable of permeating water. The hydrogel showed a high adsorption capacity that was owed to the presence of amine groups on the nanosilica surface as well as the highly porous structure. Also, the effects of different parameters (Pb^{2+} concentration, adsorbent content, pH value, and contact time) on the adsorption capacity of the hydrogel were low. On the other hand, the electrostatic interaction between the hydrogel's carboxylate groups and the Co^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions lead to unselectivity for removal of these metal ions from aqueous solution (Pourjavadi et al. 2015). According to Table 2's comparison, the CS-based hydrogel crosslinked with AA exhibited a much higher Cu^{2+} uptake than most of the other adsorbents under the same condition.

Adsorption kinetics and mechanisms of adsorbates on hydrogel

Adsorption kinetics

To qualitatively evaluate adsorbents, determination of their kinetics is one of the most commonly used methods currently utilized and indeed, adsorption kinetics, are important characteristics in any evaluation of adsorption efficiency (Zhao and Mitomo 2008). The purpose of adsorption kinetics is to establish a period of time for adsorption of adsorbates on the hydrogels and to describe the adsorption process by means of a theoretical model. Generally, to express the adsorption kinetics of hydrogel, most studies have used three models, including the (1) pseudo-first order, (2) pseudo-second order, and (3) intra-particle diffusion models (Yagub et al. 2014).

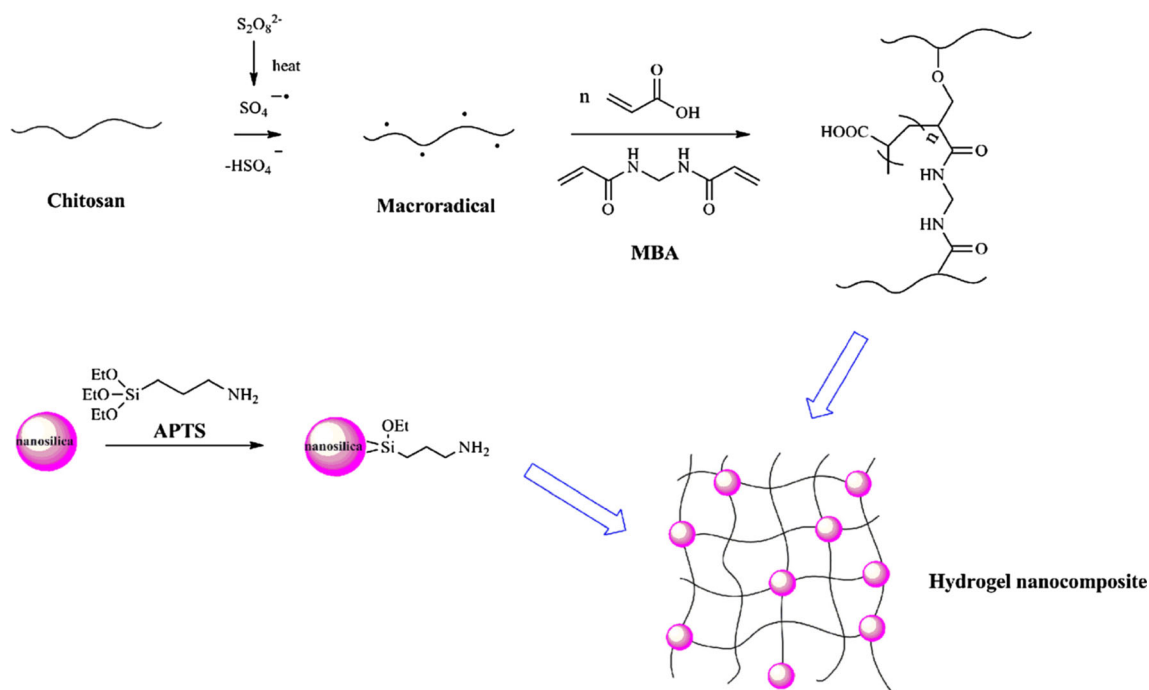


Fig. 10 Synthesis route of hydrogel nanocomposite based on chitosan, acrylic acid and modified nanosilica particles (reprinted (adapted) with permission from Pourjavadi et al. 2015. Copyright (2017) Springer)

Besides, some other models have been applied to describe the mechanism of the kinetics for the adsorption, such as Elovich model (Bhattacharyya and Ray 2013; Mittal et al. 2015) and Bangham model (Bhattacharyya and Ray 2013).

- (1) Pseudo-first-order model: This model describes the proportion of the adsorbate adsorption with time to the concentration of adsorbents (Table 3).

The pseudo-first-order model generally is represented by Formula (1) (Lagergren 1898)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the Formula (1) may be rewritten for linearized data plotting as the Formula (2):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{2}$$

where q_t and q_e are the amounts of pollutants adsorbed at time t and at equilibrium (mg g^{-1}) and t is the contact time (min) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t for different concentrations of pollutants and q_e being determined from the slope and intercept of the plot.

Table 2 Comparison of metal ion adsorption capacities of different hydrogels (reprinted (adapted) with permission from Pourjavadi et al. 2015. Copyright (2017) Springer)

Chitosan-based hydrogels	Adsorption capacity (mg g^{-1})	Metal ion	Ref.
CS-g-PAA ^a	161.8	Ni^{2+}	(Zheng et al. 2011)
CS/PAA-MCM ^b	174.0	Cu^{2+}	(Yan et al. 2012)
CS-MCM ^c	108.0	Cu^{2+}	(Yan et al. 2012)
CS/PAA-GLA ^d	120.0	Cu^{2+}	(Ngah et al. 2002)
CS-cross-linked ECH ^e	62.47	Cu^{2+}	(Ngah et al. 2002)
CS-AA nanocomposite ^f	795.4	Cu^{2+}	(Pourjavadi et al. 2015)

^a Chitosan grafted onto poly(acrylic acid)
^b Chitosan/poly(acrylic acid) magnetic composite microspheres
^c Chitosan-magnetic composite microsphere
^d Chitosan/poly(acrylic acid)-glutaraldehyde
^e Chitosan-cross-linked epichlorohydrin
^f Chitosan crosslinked acrylic acid

Table 3 Comparison of the maximum adsorption capacity q_{max} (mg/g) of hydrogels and other adsorbents

Adsorbents	Adsorbates	q_{max} (mg/g)	References
I. Dyes			
Modified montmorillonite	Methylene blue	322.6	(Wibulswas 2004)
Bentonite	Methylene blue	175	(Hong et al. 2009)
Clay	Methylene blue	58.2	(Gurses et al. 2006)
Kaolin	Congo red	1.98	(Vimonses et al. 2009)
Fly ash	Methylene blue	7.99	(Weng and Pan 2006)
Active carbon	Methylene blue	580	(Qada et al. 2006)
	Congo red	300	(Purkait et al. 2007)
Cellulose-clay hydrogel	Methylene blue	782.9	(Peng et al. 2016)
CTAB-chitosan hydrogel	Congo red	352.5	(Chatterjee et al. 2009)
Lignosulfonate-g-acrylic acid hydrogel	Methylene blue	2013	(Yu et al. 2016)
II. Heavy metal ion			
Modified montmorillonite	Cu ²⁺	2.76	(Akpomie and Dawodu 2016)
Bentonite	Ni ²⁺	200	(Akpomie and Dawodu 2015)
Active carbon	Cu ²⁺	43.47	(Demiral and Güngör 2016)
	Ni ²⁺	62.5	(Kadirvelu et al. 2001)
	Pb ²⁺	279.72	(Gerçel and Gerçel 2007)
CM cellulose/ chitosan hydrogel	Cu ²⁺	169.4	(Zhao and Mitomo 2008)
CS-AA-APTS hydrogel	Cu ²⁺	795	(Pourjavadi et al. 2015)
Cellulose-graft-acrylic acid hydrogel (C-g-AA)	Cd ²⁺	562	(Zhou et al. 2012)
	Pb ²⁺	825	
	Ni ²⁺	380.1	

(2) Pseudo-second-order model (Ho and McKay 1999).

According to Ho and McKay’s theory, the adsorption capacity of hydrogels depends on the number of active sites attached on the hydrogels. The pseudo-second-order model is expressed as Formula (3):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{4}$$

where k_2 (g/(mg min)) is the second-order rate constant of adsorption. The constants can be determined by the plot of t/q_t versus t .

(2) Intra-particle diffusion model:

According to Weber and Morris, the adsorption capacity of an adsorbent (q_t) will be proportional to $t^{0.5}$ in adsorption process and can be described as Formula (5) (Weber and Morris 1963):

$$q_t = K_{id} t^{0.5} + I \tag{5}$$

where q_t is the adsorption capacity at time t , $t^{0.5}$ is the half-life time in seconds, K_{id} (mg g⁻¹ min^{0.5}) is the rate constant of intra-

particle diffusion, and I is the intercept (mg/g). To determine the rate constants, q_t is plotted versus $t^{0.5}$ to yield a linear relationship, and K_{id} is calculated from the slope of the plot.

(4) Bangham kinetic model:

The linear form of this model is given by the following Formula (6) (Bhattacharyya and Ray 2013):

$$\ln q_t = \ln k_t + \frac{1}{m} \ln t \tag{6}$$

where $\frac{1}{m}$ measures the intensity of sorption and k_t is the rate constant for sorption. The values of rate constant k_t and m can be obtained by plot versus of $\ln q_t$ against $\ln t$.

(5) Elovich kinetic model:

The assumption of various activation energies and heterogeneous active sites of hydrogels for adsorption of organics can be represented by Elovich model as the following formula (Chien and Clayton 1980):

$$q_t = \frac{1}{\beta} \ln(\alpha \times \beta) + \frac{1}{\beta} \ln t \tag{7}$$

where α and β are the initial rate of adsorption (mg g⁻¹ min⁻¹) and desorption rate constant, respectively. The values of α and β are determined through plot versus of q_t against $\ln t$.

As suitable for the adsorption kinetics of an adsorbent, most of the literatures have based their models on the liner

regression correlation coefficient (R^2). A higher value of R^2 will indicate a better fitness of model. According to the summarized data provided in Table 4, the pseudo-first-order and pseudo-second-order model are the suitable models for describing the kinetic adsorption data. It is notable that, with intra-particle diffusion, Elovich, and Bangham kinetic models, only linear regression may carry out since non-linear regression will give the same statistical parameters, while with pseudo-first-order and pseudo-second-order models, both linear and nonlinear regression can carry out with experimental adsorption data (Bhattacharyya and Ray 2013).

Adsorption isotherm

The feasibility of the adsorption process and interaction between the adsorbents and adsorbates at a particular temperature might be evaluated and described using an adsorption isotherm. In addition, it is able to predict the distribution of adsorbate molecules between the liquid and solid phase at equilibrium (Mittal et al. 2015). There are several isotherm models that can be used to describe adsorption isotherm such as (i) two parameter isotherm including Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Flory–Huggins, and Hill isotherm models and (ii) three parameter isotherm like Redlich–Peterson, Sips, Toth, Koble, Khan, and Radke–Prausnitz isotherm models (Foo and Hameed 2010; Jana et al. 2017; Mittal et al. 2015).

Two parameter isotherm models

Langmuir and Freundlich models are the most two parameter isotherms widely used because they have usually shown the best fitness to the experimental data than the other isotherms.

(1) Langmuir adsorption isotherm model

The Langmuir isotherm model is built based on the assumptions of monolayer adsorption. According to the presumption of this model, the adsorbent surface is homogeneous and has only one type of binding site. The linear form of the Langmuir isotherm can be represented as formula (8) (Langmuir 1916):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{8}$$

where C_e (mg/L) and q_e (mg/g) are the adsorbate concentration and the amount of adsorbates adsorbed at the equilibrium, respectively. b is the Langmuir constant (L/mg) and q_m the maximum adsorption capacity of the adsorbent (mg/g) and the values of q_m and b can be obtained through the plot of C_e/q_e vs C_e .

The separation factor, R_L (also known as the equilibrium parameter) is a constant that can be calculated as Formula (9):

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

where C_0 is the initial concentration of adsorbates in solution (mg/L).

The value of R_L determines the shape and feasibility of isotherms and indicates if the Langmuir process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Bhattacharyya and Ray 2013).

(2) Freundlich adsorption isotherm

Contrary to Langmuir model, the Freundlich isotherm model can be applied to assume adsorption isotherm in case of heterogeneous surface as well as multilayer adsorption (Jana et al. 2017). The linear form of this isotherm is given by the following equation (Freundlich 1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{10}$$

where K_F is the Freundlich isotherm constants and n is the adsorption intensity.

Three parameter isotherm models

(1) Sips isotherm model

Sips isotherm is a combination of the Langmuir and Freundlich models deduced for predicting the heterogeneous adsorption systems, and it is expressed as (Sips 1948):

$$q_e = \frac{q_{\max} K_{eq} C_e^n}{1 + K_{eq} C_e^n} \tag{11}$$

where K_{eq} (L/mg) is the equilibrium constant of the Sips equation, and q_{\max} (mg/g) is the maximum adsorption capacity. The heterogeneity factor (n) of the Sips isotherm model represents the nature of the adsorption process. It is interesting that Sips will reduce to Freundlich isotherm at low adsorbate concentrations, while it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm at high concentrations (Foo and Hameed 2010).

(2) Redlich–Peterson isotherm model

The Redlich–Peterson isotherm (Redlich and Peterson 1959) is a hybrid isotherm featuring both Langmuir and Freundlich isotherms. This model assumes that monolayer formation and multi-site adsorption can occur simultaneously.

Table 4 Summary of hydrogel adsorption kinetics and mechanisms of pollutants for various pollutants

Hydrogel	Pollutant	Adsorption capacity (q_{max})	t_e	pH	Initial pollutant concentration	Isotherm model	Kinetic model	Adsorption mechanism	References
1. Hydrogel beads									
Carboxymethyl cellulose	Pb ²⁺ , Ni ²⁺	5.15 mmol/g 4.06 mmol/g	–	7.0	15 mmol/L	Langmuir isotherm	–	Coordination bonds of metal ions with oxygen atoms in carboxyl groups.	(Yang et al. 2010)
CM cellulose/CS	Cu ²⁺	6.49 mmol/g	2 h	5.0	100 ppm	Langmuir isotherm	Intra-particle diffusion model	Electrostatic interaction, chelation	(Zhao and Mitomo 2008)
PVA-CS	Pb ²⁺	2 mg g ⁻¹	1 h	2.0–7.6	30 mg/L	–	–	Ion exchange, electrostatic interaction	(Jin and Bai 2002)
Glutamic-chitosan (GCS)	Ni ²⁺	103.4 mg g ⁻¹	5 h	5.0	200 mg/L	Langmuir isotherm;	Pseudo-second order	electrostatic interaction	(Abdelwahab et al. 2016)
CS/PAM	Cu ²⁺	83.33 mg g ⁻¹	–	–	–	Freundlich isotherm	–	–	–
	Cd ²⁺	86 mg g ⁻¹	170 min	6.0	400 mg/L	Langmuir isotherm;	Pseudo-second order	Ion-exchange interaction	(Ma et al. 2017)
	Cu ²⁺	99.4 mg g ⁻¹	5.0	5.0	400 mg/L	Langmuir isotherm;	–	–	–
PAAM	Pb ²⁺	138.4 mg g ⁻¹	5 h	5.0	200 mg/L	Langmuir isotherm;	Pseudo-first-order model	Hydrogen bonding	(Pal and Banat 2015)
	Cr ⁶⁺	–	–	10.3	–	Freundlich isotherm	–	–	–
PDopa-PAH/PEC	Pb ²⁺	1625 mg g ⁻¹	30 min	6.0	20 mM	Langmuir isotherm;	Pseudo-second-order;	Metal ions chelated by catechol group and carboxyl and/or amino groups	(Yu et al. 2015a).
Pectin hydrogel	Cd ²⁺	657 mg g ⁻¹	30 min	–	–	–	Pseudo-first-order	–	–
	Cu ²⁺	388 mg g ⁻¹	90 min	–	–	–	–	–	–
ATP/FA/PAA	Cu ²⁺	120 mg g ⁻¹	8 h	5.5	–	–	–	Electrostatic interaction	(Guilherme et al. 2010)
	Pb ²⁺	130 mg g ⁻¹	–	–	–	–	–	–	–
PAA-AAAM/amylose	Pb ²⁺	38 mg g ⁻¹	24 h	5.0	100 mg/L	Langmuir isotherms	Pseudo-second-order Intra-particle diffusion;	- Chelating interaction of Pb ²⁺ ions and carboxyl group;	(Jiang and Liu 2014)
	Crystal Violet	28.60 mg g ⁻¹	3 days	7.4–8	50 mg/L	Langmuir isotherms	Pseudo-second-order;	- Electrostatic interaction and hydrophobic interaction	(Li 2010)
GO/PEI hydrogels	MB	334.4 mg g ⁻¹	200 min	–	10 mg/L	–	Pseudo-second-order	Electrostatic interactions;	(Guo et al. 2015)
	RhB	131.9 mg g ⁻¹	–	–	4 mg/L	–	–	hydrogen bonding	–
HNTs/CS	MB	75.37 mg g ⁻¹	40 min	–	160 mg/L	Langmuir isotherm;	Pseudo-second-order	External diffusion and pore diffusion	(Peng et al. 2015)
	MG	276.9 mg g ⁻¹	7 days	–	750 mg/L	Freundlich isotherms	Intra-particle diffusion	Electrostatic interaction	(Chatterjee et al. 2009)
CTAB-CS	Congo red	352.5 mg g ⁻¹	3.5 h	4.0–9.0	500 mg/L	Langmuir and Sips isotherm	Pseudo-second-order;	–	–
LS-g-AA	MB	2013 mg g ⁻¹	200 min	3.0–8.0	2400 mg/L	Freundlich isotherm;	Intra-particle diffusion	Electrostatic interaction	(Yu et al. 2016)
	AR9	866 mg g ⁻¹	800 min	<3	2000 mg/L	Langmuir isotherm;	Pseudo-second-order;	Electrostatic interaction	(Kono 2015)
Amphoteric hydrogels	AR13	911 mg g ⁻¹	–	–	–	–	–	–	–
	AB92	816 mg g ⁻¹	–	–	–	–	–	–	–
NaAl/PVP blend	RR	116.8 mg g ⁻¹	600 min	1.2–5.0	300 mg/L	Langmuir isotherm;	Pseudo-second-order;	Electrostatic interaction	(Inal and Erduran 2015).
	CBR	73.3 mg g ⁻¹	–	–	250 mg/L	–	–	–	–
PVA-P (AA-co-AM)	RBB	55.3 mg g ⁻¹	–	–	250 mg/L	–	–	–	–
	⁶⁰ Co	184 mg g ⁻¹	3 h	4.0–6.0	250 mg/L	Freundlich isotherms	Pseudo-second-order	Multi-molecular layer chemisorption	(Wang et al. 2016)
		332 mg g ⁻¹	–	–	400 mg/L	–	–	–	–

Table 4 (continued)

Hydrogel	Pollutant	Adsorption capacity (q_{max})	t_e	pH	Initial pollutant concentration	Isotherm model	Kinetic model	Adsorption mechanism	References
KNIHCF	^{137}Cs	64 mg g^{-1}	60 min	1–12	50 mg/L	Langmuir isotherms; Freundlich isotherm	Pseudo-second-order	Ion exchange	(Dwivedi et al. 2015)
	^{137}Cs	–	2 h	3–10	5–20 mg/L	–	–	Ion exchange Fixing of Cs ion into porous framework of hydrogel.	(Pathak et al. 2016)
2. Hydrogel film									
CS-MUA- $\text{SO}_3\text{Na-CD}$	Ca^{2+}	150 mg g^{-1}	–	–	5×10^{-4} M	–	–	Ion exchange	(Baruah et al. 2016)
	Mg^{2+}	218 mg g^{-1}	–	–	–	–	–	–	–
Agr/CD	Cu^{2+} , Cu^{2+} , Fe^{3+} , Pb^{2+} , Mn^{2+}	–	12 h	–	10 mg/L	–	–	Chitosan in hydrogel films forms chelates with heavy metals	(Gogoi et al. 2015)
	Cu^{2+}	27.5 mg g^{-1}	110 min	4.0	30 mg/L	Langmuir isotherm	Pseudo-first-order	Ion exchange and electrostatic interactions	(Mirabedini et al. 2017)
Cellulose-C-g-AA	Cd^{2+} , Pb^{2+}	562 mg g^{-1} 825 mg g^{-1}	6 h	5.0	2000 mg/L	Langmuir isotherm	Pseudo-second-order	Ion exchange and chelation	(Zhou et al. 2012),
	Ni^{2+}	380.1 mg g^{-1}	–	–	–	–	–	–	–
GO/cellulose	Cu^{2+}	94.34 mg g^{-1}	150 min	1.0–7.5	200 mg/L	Langmuir isotherm	Pseudo-second-order;	Ion exchange between COO^- group and Cu^{2+} ion	(Chen et al. 2016)
St-g-PAA/SH	Cu^{2+}	2.83 mmol/g	60 min	2.7–5.0	0.02 mol/L	Langmuir isotherm	Pseudo-second-order;	Ion-exchange and chelation between Cu^{2+} ion and COO^- group of hydrogel	(Zheng et al. 2010)
GO/fungus hyphae	Orange G	387 mg g^{-1}	–	2.0	500 mg/L	–	–	Chelation and, electrostatic interaction	(Zhang et al. 2016)
CS/PAN	RB	21.90 mg g^{-1}	240 min	7.0	100 mg/L	Langmuir isotherm	Pseudo-second-order;	Hydrogen bonding	(Al-Mubaddel et al. 2015)
Soy protein/ EDTAD	Zn^{2+}	0.65 mmol/g	48 h	4.0–6.0	0.3 mM	–	–	Electrostatic interactions	(Hwang and Damodaran 1997)
	Pb^{2+}	0.70 mmol/g	–	–	0.2 mM	–	–	–	–
	Hg^{2+}	0.95 mmol/g	–	–	0.2 mM	–	–	–	–
3. Hydrogel nanocomposites									
Soy protein/PEI	Cu^{2+}	136.2 mg g^{-1}	24 h	4.0–5.5	250 ppm	Langmuir isotherm; Freundlich model	Pseudo-second-order; Pseudo-first order kinetic	Ion exchange and electrostatic interactions	(Liu et al. 2017)
Cottonseed protein-PAA PAA/GO	Cu^{2+}	1.45 mmol/g	180 min	4.0–5.5	2.0 mmol/L	Langmuir isotherm	Pseudo-second-order;	Electrostatic interactions	(Zhang et al. 2012a)
	Pb^{2+}	1.44 mmol/g	–	–	–	Freundlich model	–	–	–
	Cu^{2+}	209 mg g^{-1}	24 h	5.0	100 mg/L	–	–	Electrostatic interaction; ion exchange; forming of complexation interaction	(Yu et al. 2015b)
P(HEA/2IA)	Pb^{2+}	392.2 mg g^{-1}	48 h	3.0–6.0	520 mg/L	Langmuir; Freundlich;	Pseudo-second-order;	Electrostatic interaction	(Antić et al. 2016)
P(HEA/10IA)	–	409.8 mg g^{-1}	–	–	–	Redlich–Peterson.	–	–	–
NaAlg/IA	Pb^{2+}	6.9 mmol/g	24 h	5.0	1.2 mmol/L	Freundlich model	–	–	–

Table 4 (continued)

Hydrogel	Pollutant	Adsorption capacity (q_{max})	t_e	pH	Initial pollutant concentration	Isotherm model	Kinetic model	Adsorption mechanism	References
	MB	9.16 mg g ⁻¹	5 h	8.0	80 mg/L		Pseudo-second-order; Pseudo-first-order; Intra-particle diffusion	Ion exchange; Pb ²⁺ ions reacted with functional groups of hydrogel;	(Mahmoud and Mohamed 2012; Mahmoud et al. 2014)
Cellulose-clay	MB	782.9 mg g ⁻¹	40 h	1–11	200 mg/L	Langmuir isotherm	Pseudo-second-order	Hydrophobic interaction; electrostatic interaction	(Peng et al. 2016)
CS-AA-APTS	Cu ²⁺	795 mg g ⁻¹	120 min	3.5–5.5	400 ppm	Langmuir isotherm	Pseudo-second-order	Electrostatic interactions	(Pourjavadi et al. 2015)

The non-linear and linear forms of the Redlich–Peterson isotherm are described as Formulas (12) and (13), respectively (Paulino et al. 2011).

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (12)$$

$$\ln\left(\frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln B \quad (13)$$

where A , g , and B are the Redlich–Peterson constants, C_e (mg/L) is the adsorbate concentration remaining in the solution, and q_e (mg/g) is the adsorption capacity of the hydrogels at equilibrium.

This model can be applied both homogeneous or heterogeneous systems due to its versatility. In the limitation, it only approaches Freundlich isotherm model at high concentration and Langmuir isotherm model at low concentration (Foo and Hameed 2010).

The applicability of isotherm models to the removal of contaminants by hydrogels was evaluated in terms of regression coefficient (R^2) and non-linear x^2 . In the good fitness, R^2 will be close to unity; x^2 will be very low (Bhattacharyya and Ray 2013).

Adsorption mechanism

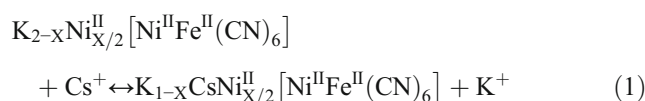
One of the biggest challenges to the development of new adsorbents for adsorption of pollutants in wastewater is to clearly define and identify the adsorption mechanism. Especially, it is really important to represent the interaction between adsorbates and adsorbents at the interface. To determine the adsorption mechanism, most studies have used two isotherm models, namely the Langmuir and Freundlich models, which are expressed the above section (Jiang and Liu 2014). Moreover, in order to better understand the mechanism of pollutant sorption on hydrogels, a number of studies have used FTIR, XPS scans, and X-ray diffraction to examine the functional groups and structure of the adsorbent before and after adsorption of pollutants. XPS is a commonly used technique to realize the mechanism of heavy-metal adsorption on hydrogels, as it can indicate the change of the distribution of the electrons around the corresponding atoms caused by the interaction between metal ion and functional groups (Deng et al. 2003).

According to Table 4's summarized data, electrostatic interactions have been regarded the main mechanisms in the adsorption of pollutants by hydrogels. The functional groups in unique particles or monomers of hydrogels, such as the —COOH group in AA (Jiang and Liu 2014; Li 2010; Pourjavadi et al. 2015; Yu et al. 2015b), GO (Guo et al. 2015), IA (Antić et al. 2016), cellulose (Peng et al. 2016) and cellulose ampholytes (Kono 2015), the amine group in CS (Jin and Bai 2002, Mirabedini et al. 2017), the imine group

in poly(m-phenylenediamine) (Zhang et al. 2016), the tertiary amine group in PVP (Inal and Erduran 2015), and PEI (Guo et al. 2015), will interact with pollutants because of their charge oppositeness. In the adsorption mechanism by electrostatic interaction, the functional groups on the surface of hydrogels will protonate to form anions attracting cationic pollutants (metal ions, cationic dyes) or deprotonate to form cations interacting with anionic pollutants. For cationic pollutants, such as metal ions and cationic dyes, most studies in the literature have used the —COOH group as a functional group for adsorption of pollutants through electrostatic interactions. The —COOH group deprotonate as negatively charged —COO[−] groups under the optimum condition of pH and the negatively charged functional groups attract the positively charged ions. In order to increase the adsorption efficiency and prevent the hydrolysis of cationic pollutants, the selection of the optimum pH, where hydrogels will reach the highest adsorption capacity, is very important (Jiang and Liu 2014). Generally, the pH value commonly selected for adsorption of metal ions and cationic dyes will be higher than the pKa of unique particles or monomers containing —COOH groups (Chatterjee et al. 2009, Li 2010) and that value commonly is neutral or basic. On the other hand, in the case of anionic pollutants, such as anionic dyes (Congo red (CR), AR9, AR13, and AB92), adsorption usually occurs under the acidic condition. For example, the tertiary amine groups of PVP molecules in the hydrogel protonates and possesses a positive charge in acidic pH, to which charge dye anions of negative charge are attracted (Inal and Erduran 2015). Especially, in acidic solution, a metal cation, Cr⁺⁶, also can be adsorbed on the surface of hydrogel, because it exists as HCrO₄[−] with a pH < 4. The electrostatic interactions in the adsorption of HCrO₄[−] by Fe₃O₄ NPs/CS/glyoxal hydrogel film are illustrated in Fig. 11. Under acidic condition, the amino groups (—NH₂) of CS protonated to form the —NH₃⁺ group and the surface of the hydrogel were loaded with a positive charge. The adsorption of Cr⁺⁶ ion was accomplished through the electrostatic interaction between HCrO₄[−] ions (negative charge) and the —NH₃⁺ group (positive charge) (Mirabedini et al. 2017).

Beside electrostatic interaction, ion exchange is also an important mechanism in the adsorption of pollutants from aqueous solution. Several studies have indicated that some metal ions can be effectively removed from solution by the ion exchange mechanism. Charu Dwivedi et al. (2015) and Pathak et al. (2016) used potassium nickel hexacyanoferrate (KNiHCF) and potassium zinc hexacyanoferrate (KZnHCF) loaded onto hydrogel beads to remove cesium ions according to the principle of ion exchange. The adsorption of cesium ions onto KNiHCF or KZnHCF particles takes place by the exchange between a potassium ion of KNiHCF or KZnHCF and a cesium ion (Dwivedi et al. 2015; Pathak et al. 2016). According to the hypothesis of L. Vrtoch and co-workers, this ion exchange mechanism

can be achieved by a cation-exchange Reaction (1) (Vrtoch et al. 2011).



Baruah's group specifically explained, as in Fig. 12, the ion exchange mechanism in the adsorption process of Ca²⁺ and Mg²⁺ from solution on CS-MUA-SO₃Na-CDs hydrogel film (Baruah et al. 2016). The scheme indicates that the electrostatic interaction between the positively charged amine groups of CS and the negatively charged sulphonate groups on the surface of the CDs is maintained under acidic condition. In the left-hand scheme, when hydrogel films are dipped in sodium hydroxide solution, the sulphonate groups of the CDs interact with Na⁺ ions to form ion-pairs (Na⁺ SO₃[−]) and thereby, the Na⁺ ions adhere to the CDs embedded in the hydrogel film. In the right-hand scheme, because of the presence of M²⁺ (Ca²⁺/Mg²⁺) metal ions in the aqueous solution, the M²⁺ ions are able to replace Na⁺ ions in the hydrogel film through ion exchange interactions. In this way, Na⁺ ions from the hydrogel film are released into the solution and M²⁺ ions in the solution are adsorbed into the hydrogel film.

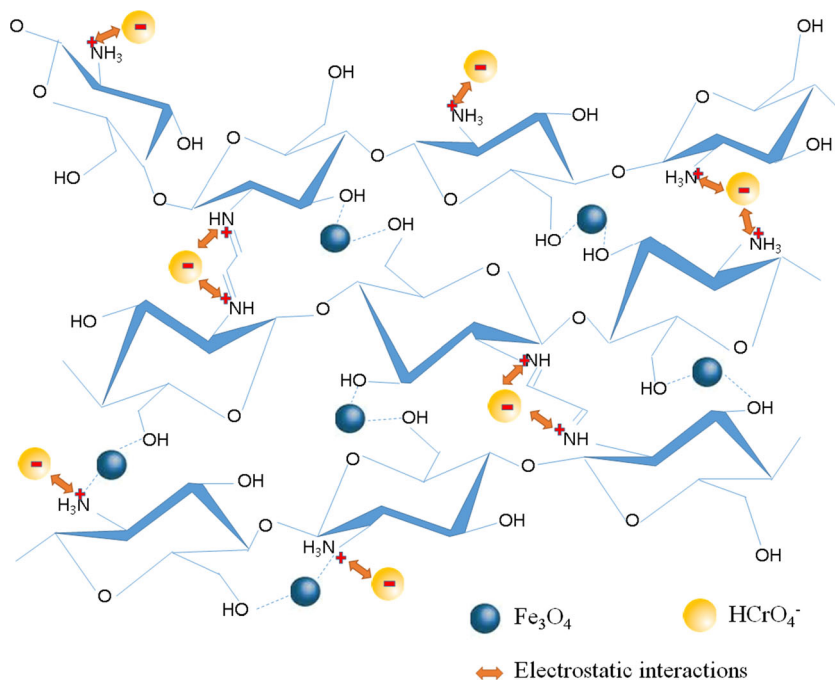
Other studies have demonstrated that the adsorption of pollutants by hydrogels also can take place by several other mechanisms: hydrogen bonding (Al-Mubaddel et al. 2015; Pal and Banat 2015), coordination bonds (Yang et al. 2010), chelating interaction (Gogoi et al. 2015; Yu et al. 2015a), or a combination of interactions, such as ion exchange/electrostatic interaction (Jin and Bai 2002; Liu et al. 2017; Mirabedini et al. 2017; Yu et al. 2015b), chelating/electrostatic interaction (Zhang et al. 2016), ion-exchange/chelating interaction (Zheng et al. 2010; Zhou et al. 2012), electrostatic interaction/chelation (Jiang and Liu 2014; Zhang et al. 2016; Zhao and Mitomo 2008), or electrostatic/hydrophobic interaction (Li 2010; Peng et al. 2016).

Adsorption capacity and affecting factors

Adsorption capacity

The adsorption process of hydrogels can be divided into two stages: first stage (or rapid stage) at initial time of adsorption and second stage (or slow stage) at later time of adsorption (Kasgoz et al. 2003; Tu et al. 2017). During the first stage, adsorption process will be so fast due to the high concentration of ions and also the high number of free adsorptive sites, while at second stage, adsorption process will slow down and then reach an equilibrium state because of a concentration reduction and exhaustion of the free adsorptive sites (Pour and Ghaemy 2015). Adsorption capacity of a hydrogel may be determined as an equilibrium adsorption capacity through mentioned adsorption isotherm models. It will be determined when the contact time between adsorbents and adsorbates is

Fig. 11 Adsorption of Cr^{6+} ion on Fe_3O_4 NPs/CS/glyoxal hydrogel film by electrostatic interactions under optimum condition (pH 4)



sufficient, and the adsorption rates and the desorption rates are equal (Foo and Hameed 2010). There are many factors affecting adsorption capacity, such as contact time, pH of medium, initial adsorbate concentration, mechanical properties, and competition, and some of the factors are discussed in the next section. Optimization of such conditions will define the maximum adsorption capacity of hydrogels.

Compared with other conventional adsorbents, it is notable that hydrogels possess a remarkable adsorption capacity. It

presents a comparison of the maximum adsorption capacity q_{max} (mg/g) between hydrogel materials and other adsorbents for dyes and metal ion from aqueous solution (Table 3). Among the adsorbents, hydrogels loaded unique particles show a highest q_{max} value for both dyes and metal ions. Especially, in case of lignosulfonate-g-acrylic acid hydrogels and cellulose-graft-acrylic acid hydrogels (C-g-AA), these hydrogels have a three-fold greater q_{max} value to active carbon, a popular material for pollutant adsorption in water and wastewater. This

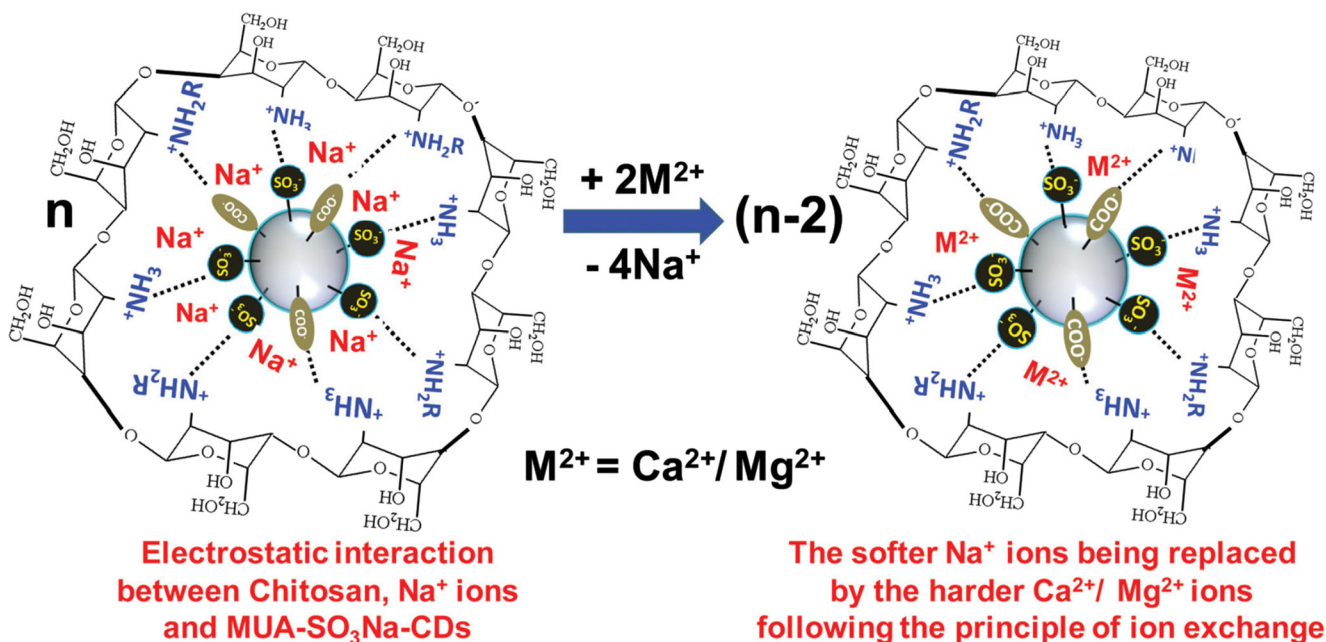


Fig. 12 Scheme illustration of adsorption mechanism of Ca^{2+} , Mg^{2+} on $\text{Ch-SO}_3\text{Na-CD}$ hydrogel nanocomposite based on principle of ion exchange (reprinted (adapted) with permission from Baruah et al. 2016. Copyright (2017) Royal Society of Chemistry)

demonstrates that hydrogels are one of the most potential material for water/wastewater treatment in the present and future.

pH of solution

The pH of the adsorption media is one of the most important external parameters that can affect the adsorption capacity of hydrogel (Kono 2015). Generally, the pH of a solution can cause the protonation or deprotonation of functional groups, such as carboxylic (Yang et al. 2010) or amine (Abdelwahab et al. 2016; Zhao and Mitomo 2008) groups and the precipitation of metal ions in hydrogels. In most of kinetic studies in adsorption of heavy metals, the adsorption capacity of hydrogels for metal ions will increase towards the basic pH of the solution; in fact, there is a range of optimal pH values wherein the highest adsorption capacity can be reached. Some of the literature has explained this phenomenon in terms of the fact that at low pH (acidic solution), the concentration of H^+ is high and the functional groups in hydrogels are easily protonated to form an electrostatic repulsion of cationic metal ions; therefore, there is a competition between H^+ and cationic metal ions, which causes a decrease of adsorption capacity. When increasing the pH of solution, the H^+ concentration declines, and consequently, deprotonation of functional groups occurs and electrostatic repulsion decreases. As a result, the adsorption capacity of metal ions increases (Abdelwahab et al. 2016; Jiang and Liu 2014; Yang et al. 2010; Zhao and Mitomo 2008). However, a further increase in pH leads to the precipitation of metal hydroxide, thereby inhibiting the adsorption process. At $pH > 7.0$, precipitation will occur, and then a pH of 5.0–6.0 usually is chosen as the optimal value for the adsorption process of metal ions (Chen et al. 2016; Liu et al. 2017; Yu et al. 2015b; Zhao and Mitomo 2008; Zheng et al. 2010; Zhou et al. 2012). For Cr^{6+} ions, because they exist predominantly as anions ($HCrO_4^-$) in solution, so the maximum capacity of Cr^{6+} adsorption is attained at the pH of 4.0 (Mirabedini et al. 2017). In the case of the adsorption of cesium, Pathak et al. and Charu Dwivedi et al. introduced the types of hydrogel that can be effectively adsorb cesium with a wide range of pH (3–10) because transition metal hexacyanoferrates are able to effectively bind cesium under both acidic- and alkaline-pH conditions (Dwivedi et al. 2015; Pathak et al. 2016).

In the dye-adsorption process, the adsorption efficiency also is strongly pH-dependent, because pH can change the chemical structure of dye molecules and functional groups on the surface of hydrogels (Inal and Erduran 2015). In the case of cationic dyes MB or CV, the adsorption capacity will increase with increasing pH, which is the same phenomenon as is operative in the adsorption process of metal ions (Li 2010; Peng et al. 2016). Peng and co-workers explained this phenomenon based on the electrostatic interaction of positively charged MB with negatively charged hydrogels, which interaction is increased at high pH values and decreased at low

pH values (Peng et al. 2016). Besides electrostatic interaction, an electro-osmotic expanding network-like ultrastructure in the hydrogels can be produced by electrostatic repulsive forces among adjacent ionized groups in the hydrogel matrix, which forces are generated by the increased levels of ionized groups at high pH values, which further results in greater uptake of MB (Yu et al. 2016). By contrast, for adsorption of anionic dyes (congo red, AR9) into hydrogels, the process is inversely proportional to the change of the solution pH: when the pH of the adsorption solution is increased, the adsorption capacity of hydrogels usually decreases. This mechanism is indicated by the change in the electrostatic interaction between the dye anions and the hydrogel cations under different conditions of pH (Chatterjee et al. 2009; Inal and Erduran 2015; Kono 2015).

Initial concentration of pollutant and adsorbent dosage

The initial concentration of pollutants and the adsorbent dosage are parameters that play important roles in the adsorption efficiency of hydrogels. The effects of the initial adsorbate concentration and the adsorbent weight mainly depend on the direct relation between the concentration of adsorbates and the available sites on an adsorbent surface (Peng et al. 2015). Several studies have indicated that the increase of adsorbate concentration leads to enhancement in the adsorption capacity represented by the value of q_e (adsorption amount per unit adsorbent weight), but decreases the adsorbate removal efficiency (Abdelwahab et al. 2016; Pourjavadi et al. 2015; Yang et al. 2010; Zhou et al. 2012). However, the increase of adsorbent weight showed opposite results which gradually increase the removal ratio of pollutants and decrease the adsorption capacity (Antić et al. 2016; Chatterjee et al. 2009; Chen et al. 2016; Dwivedi et al. 2015; Kono 2015; Mirabedini et al. 2017; Peng et al. 2015). These phenomena are explained in the following way: at low adsorbate concentrations, the ratio of the initial number of moles of adsorbate ions to the available surface area of hydrogel is large, whereas at higher concentrations, the available sites of adsorption become fewer, and the percentage removal of pollutants decreases in turn (Abdelwahab et al. 2016). In the case of an increasing amount of hydrogel, there are two explanations of those phenomena. First, the higher adsorbent dosage offers a larger number of active sites and a larger surface area for adsorption (Dwivedi et al. 2015); second, a decrease in the total surface area of the adsorbent and the correspondingly high adsorbent concentration results in particle interactions, such as aggregation (Chen et al. 2016).

Existence of other ions and the selectivity of hydrogel

The existence of multiple ionic species in aqueous solution can influence the adsorption efficiency of hydrogel for each

ion species (Antić et al. 2016). Some of the pollutants in the effluent might decrease the adsorption of others through competition or enhance the adsorption together through cosorption (Zheng et al. 2010). Moreover, there are always several co-existing ions in wastewater in real applications (Liu et al. 2017); thus, it is necessary to examine the adsorption selectivity performance of hydrogel under typical multi-component conditions. According to Ma and co-workers, the presence of interference ions (K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) in solution can cause competition around the same active sites of the adsorbent between these ions and the target ions (Cd^{2+} , Cu^{2+} , and Pb^{2+}), which decreases the removal efficiency of heavy-metal ions. In addition, the inhibitory effect of these co-ions on the removal of Cd^{2+} , Cu^{2+} , and Pb^{2+} ions follow the order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ (Ma et al. 2017). The reason for the adsorption decrease through competition in the vicinity of chelation sites on hydrogels or the sharing of the same binding sites was also explained (Antić et al. 2016; Hwang and Damodaran 1997; Zheng et al. 2010).

Besides, the functional groups of unique particles entrapped in hydrogel, such as carboxyl and amine groups have shown adsorption selectivity to specific ions based on ion properties including radius, electronegativity, and ionization potential. For instance, the carboxyl group in ATP/FA/PAA nanocomposite hydrogel beads has a higher adsorption selectivity to Pb^{2+} ions than to Cu^{2+} , Cd^{2+} , Ni^{2+} , or Zn^{2+} ions, owing to their different properties (Jiang and Liu 2014). If ions have a larger ionic radius, they will possess a higher affinity with hydrogels than with other ions. In other words, the larger the ionic radius, the better the binding capacity (Antić et al. 2016; Hwang and Damodaran 1997; Zhou et al. 2012). Therefore, the selectivity of hydrogels for these ions also is better than for other ions. Besides ionic radius, the selectivity of hydrogels for ions can be affected by ion hydration radius as well. Dwivedi's group demonstrated that the removal percentage and adsorption capacity of KNiHCF-gel hydrogel beads for cesium ions had no significant change in the presence of interfering cations (Na^+ , Ca^{2+} , and Ba^{2+}), because the cesium ion has a smaller hydration radius than that of the other interfering ions (Dwivedi et al. 2015).

The selectivity of an adsorbent for a target adsorbate can be altered by changing the types and structures of the polymeric matrix. However, it is found that the functional groups play a more critical role in changing the selectivity because the functional groups are where the adsorbates are adsorbed (Fritz 2005). It was demonstrated that the metal ion adsorption selectivity of a series of PAM hydrogels prepared by Mannich reaction using different amine compounds, such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and sulfomethylation reaction, largely depends on the functional groups (Kasgoz et al. 2003). These hydrogel's selectivity is displayed in (Fig. 13). The M8 hydrogel, a Mannich product which was prepared

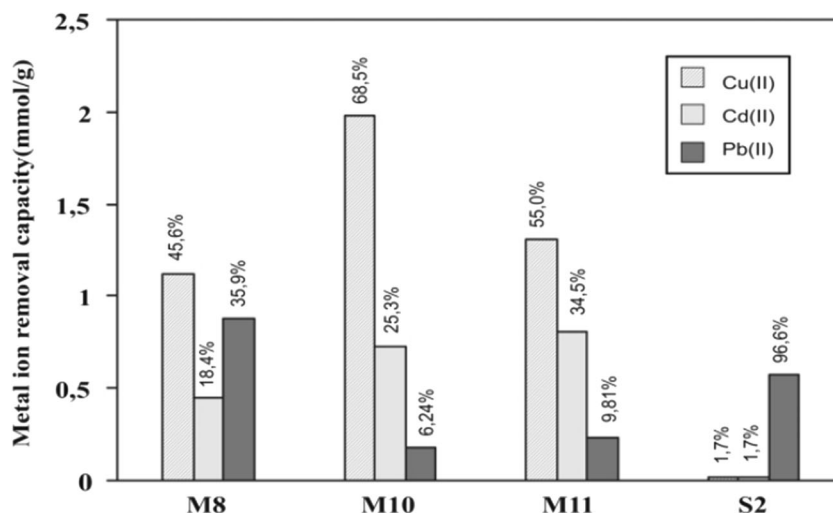
with EDA, was not significantly selective to any metal ion, while the other Mannich product prepared with DETA (M10) possesses a distinct selective towards Cu^{2+} ions. This difference is mainly due to the presence of the secondary amine groups in the hydrogel matrix. Compared to M10, however, M11 hydrogels prepared with TETA have the lower selectivity towards Cu^{2+} , although TETA has higher amount of secondary amine groups than that of DETA. This is because of the result of lower amine value and a decrease in swelling degree due to crosslinking during the Mannich reaction. Contrary to amine group, the presence of carboxylate group in hydrogel matrix (S2) showed a very distinct selectivity towards Pb^{2+} .

The swelling degree of hydrogel

Swelling behavior is one of the most important characteristics of the hydrogel as well as adsorbents and the formation of porous structure may lead to the high swelling ratio of hydrogel. According to Flory's theory, swelling degree of a gel depends on the ionic osmotic pressure, crosslinking density and affinity of the gel for water (Flory 1953). Many studies indicated that the pH value in solution has a significant impact on the swelling degree of the hydrogel in term of increase in swelling ratio along with increasing the pH of medium (Mahmoud et al. 2014; Souda and Sreejith 2014; Zhou et al. 2011). At $pH < pK_a$ of functional groups (carboxylic and amine groups), these functional groups are protonated ($-COOH$), which result in a decrease of swelling ratios due to the reduction of the electrostatic repulsion between the molecular chains of the hydrogel (Mahmoud et al. 2014). At $pH > pK_a$, these functional groups are deprotonated ($-COO^-$) and this increases amount of ionized group, which causes electrostatic repulsion forces among the adjacent ionized groups of polymer matrix. This produces an expansion network-like ultrastructure of the hydrogels, which will improve the swelling ratio (Zhou et al. 2011). In the relation between the swelling ratio and the adsorption capacity of hydrogels, it is found that the higher swelling capacities means the higher number of ionic groups in hydrogels (Flory 1953), which will enhance the adsorption capacity of hydrogels. Therefore, the adsorption capacity of hydrogels will be proportional to the swelling degree. It was found that because the high swelling capacity of the hydrogel networks is likely to give high specific surface area and more functional groups exposed are readily approachable for adsorption, the high swelling ratio can facilitate the adsorption of metal ions (Trakulsujaritchok et al. 2011).

Also, the swelling ability can largely depend on the content of nanoparticle entrapped on the hydrogels. It was found that when amount of added clays can be uniformly dispersed into hydrogel networks, the hydrogel's swelling ratio will be enhanced due to their surface containing negative charges (Peng et al. 2016). However, the swelling ratio will decrease as the

Fig. 13 The metal ion selectivity properties of various hydrogels at pH = 4.5. M8—hydrogel which was prepared by Mannich reaction with EDA. M10—hydrogel which was prepared Mannich reaction with DETA. M11—hydrogel which was prepared Mannich reaction with TETA. S2—hydrogel which was prepared by sulfomethylation reaction (reprinted (adapted) with permission from Kasgoz et al. 2003. Copyright (2018) Elsevier)



clay contents is so high. This phenomenon can be explained that a stable structure will be formed to inhibit traversing of water molecules based on hydrogen bonds formed between polymers and the crosslinking agent when increasing the content of crosslinking agents (Tu et al. 2017).

Recycling and recovery of used hydrogel

To economically and usefully evaluate the effect of an adsorbent, one of the most important factors is the recyclable and recoverable ability. This means that effective hydrogels must be easily reused for more than a few cycles without incurring any significant change in its adsorption capacity. The regeneration and reuse ability is also an essential factor for broad, practical assessment of the applicability of a material. A novel hydrogel based on polydopamine (PDA)-functionalized graphene (PDA-GH) was successfully synthesized, and this hydrogel effectively demonstrated its adsorption capacity for different contaminants, such as heavy-metal ions (Pb^{2+} and Cd^{2+}) and organic pollutants (rhodamine B and ρ -nitrophenol) (Gao et al. 2013). Notably, the hydrogel could be easily regenerated by a simple process using low-cost reagents, and it maintained a high adsorption capacity even after multiple adsorption-desorption cycles. According to the authors, to recover the ions (Pb^{2+} , Cd^{2+}) from the adsorbents of PDA-GH, they used HCl solution (0.1 M) as the desorption agent. The reduced stability of the PDA covering in a strong acid possibly can cause the decline of the adsorption capacity of PDA-GH. Nevertheless, the regenerated PDA-GH still maintained a high adsorption capacity (more than 80%) after ten adsorption and desorption cycles. Hence, PDA-GH has been highly regarded as a potential adsorbent, owing especially to its easy recyclability and reusability in the process of heavy-metal ion removal. However, to regenerate the hydrogel in the case of the adsorption of organic pollutants, they used ethanol as a

desorption agent instead of HCl, as a consequence of which, the high adsorption capacities for removal of organic pollutants (rhodamine B and ρ -nitrophenol) were not significantly decreased.

In another study, a chelator-mimetic multi-functionalized hydrogel possessing a high adsorption capacity for metal ions (Cd, Pb, and As) and excellent reusability was introduced (Mohammadi et al. 2017). By using a low concentration of HCl acid, the hydrogel can be regenerated in its functionality, and also, the ions adsorbed by the hydrogel can be eluted. This particular hydrogel could maintain a better-than 60% removal ratio after five consecutive sorption-wash-reuse cycles. Employing a similar method, Pourjavadi and co-workers performed recycling experiments for a novel hybrid hydrogel based on CS, AA, and amine-functionalized nanosilica (Pourjavadi et al. 2015). HCl (1 M) solution was used as a solvent to recover the Pb^{2+} -loaded CS-g-acrylic hydrogel. Then, the adsorbent was regenerated by filtering and washing with distilled water and reused in the next cycle of the adsorption process. Significantly, the desired capacity of the regenerated adsorbent remained at 685–715 (mg g^{-1}) after three cycles. Thus, due to its good recycling efficiency, the hydrogel nanocomposite was judged to be suitable for practical applications.

Vivek and Prasad described the regeneration and reusability process of a self-healing hydrogel prepared by a novel method using in situ polymerization of AA and acrylamide (Vivek and Prasad 2015). The hydrogel performed with remarkable efficiency (90–98%) in adsorbing organic dyes (MB and methyl orange) and metal ions (Cd^{2+} , Pb^{2+} , and Hg^{2+}). The hydrogel was recovered by using methyl orange as the adsorbent. The methyl orange adsorbed from the hydrogel was extracted by ethanol solution, and the hydrogel was separated when reaching the equilibrium condition. According to the result of that study, it took approximately 20 min to conduct the desorption process, and the dye-recovery efficiency

was rather high, about 97%. Besides, the authors indicated that with five cycles of regeneration process, the hydrogel still performed at an excellent adsorption capacity, maintaining an adsorption rate of 90–98%.

Magnetic hydrogels represent one of the most effective techniques widely used for removal of metal ions from flowing streams (Yavuz et al. 2009). Recently, a novel magnetic hydrogel possessing advantages in fast Cr(IV) removal and a high adsorption capacity of about 200 mg g^{-1} was developed (Tang et al. 2010). Another advantage of this hydrogel is that it shows an easy recoverability by regeneration in sodium chloride solution (Tang et al. 2014). The application utility of any magnetic hydrogel in wastewater depends on two factors: a reduced amount of recovery solution and an increased metal-ion concentration in that solution. Tang's group's method, schematized in Fig. 14, satisfies these requirements. Briefly, treated wastewater is collected in a magnetic separation unit that separates the hydrogel; sodium chloride at various concentrations is added for the regeneration process; the recovery solution is collected by separating the magnetic hydrogel. Tang et al. conducted a set of regeneration tests with stepwise additions of NaCl solution. They collected the recovery solution, followed by another addition of NaCl solution. Their results suggested that the Cr(VI) removal and recovery performance of the magnetic hydrogel were likely to be maintained for 20 cycles for a 97–98% Cr(VI)-removal efficiency. According to their data, the Cr concentration in the recovery solution reached 500–600 mg/L with the stepwise adsorption and regeneration process, representing a 40:1 wastewater- to-recovery-volume ratio.

Easy separation and recycling without additional costs are important factors impacting on the practical applicability of hydrogel-based photocatalysts. In 2017, a hydrogel-based smart photocatalyst, $\text{TiO}_2/\text{agarose}$ hydrogel, which has an excellent recyclability was introduced (Mai et al. 2017). Because

the prepared hydrogel is much larger than TiO_2 NPs, separation is very convenient. The recyclability of this hydrogel was evaluated using MB and some other dyes. The results indicated that the degradation of MB can be maintained until the fifth cycle with high photodegradation efficiency, and that it gradually decreases beginning with the sixth cycle. In addition, the recyclability of the hydrogel for various dyes was demonstrated using acidic dyes (MB, MO) and an alkaline dye (RhB). There were two different trends that were noted with respect to the photocatalytic efficiency. The photodegradation ability with the MB and MO dyes increased until the second cycle and then decreased slightly in the third cycle, whereas that with RhB decreased progressively after the third cycle. The reason for the difference was that various dye parameters, such as pH and molecular structure, effected different diffusion mechanisms and adsorption behaviors. More importantly, with this type of hydrogel, pure TiO_2 NPs can be recovered by the simple process shown in Fig. 15. In this process, after recycling, the hydrogel is re-melted at high temperature into a diluted $\text{TiO}_2/\text{agarose}$ aqueous solution (Fig. 15a, b). Then, centrifugation is conducted to separate TiO_2 NPs, the result being that higher-purity TiO_2 NPs can be obtained (Fig. 15c, d). For further-increased purity, the purification process is repeated several times.

Reusability is one of the most essential properties for most applications for hydrogels; however, it is a huge challenge for conventional hydrogels because they are commonly poor strength and unrecyclable due to the lost mechanical toughness after swelling in water (Kamata et al. 2014). Therefore, enhancing the strength mechanical plays a key role in maintaining the adsorption capacity of pollutant-adsorbed hydrogels. If hydrogels possess strength mechanical properties, their reusability in practical applications is available to be greatly enhanced (Gong et al. 2016). Hydrogels with desirable mechanical properties is available to maintain their service life

Fig. 14 Schematic illustration of wastewater treatment prototype with magnetic separation unit (reprinted (adapted) with permission from Tang et al. 2014. Copyright (2017) American Chemical Society)

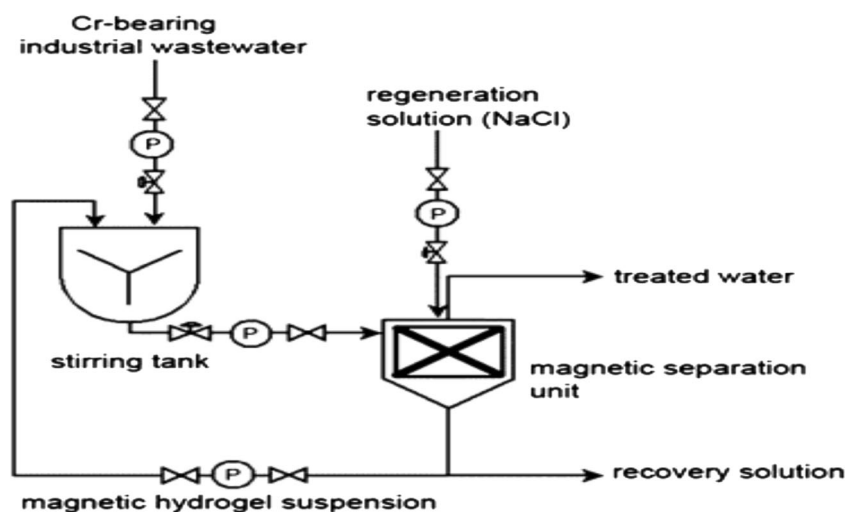
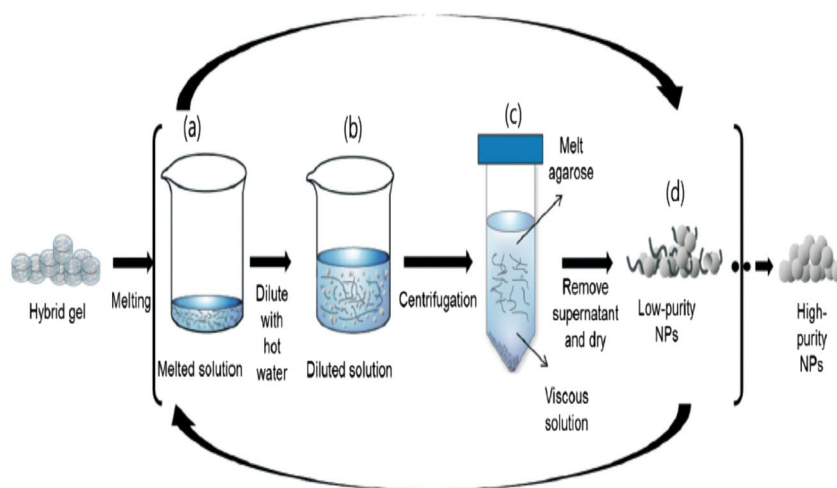


Fig. 15 Recovery of pure TiO₂ NPs from a TiO₂/agarose. **a** Melting, **b** dilution, **c** centrifugation, and **d** separation (reprinted (adapted) with permission from Mai et al. 2017. Copyright (2017) Royal Society of Chemistry)



due to their self-healing ability when they suffer the swollen state. Cui's group also supported these when they introduced a graphene oxide (GO)/hydrophobically associated PAM nanocomposite hydrogels (GHA gels) as a reusable adsorbent for the removal of dye pollutants by incorporating GO with hydrophobically associated PAM (Cui et al. 2015). This hydrogel has superior mechanical strength and high toughness due to strong hydrogen bonds between GO sheets and polymer chains. They also indicated that incorporation of GO highly increases the wall thickness of GHA gels and the higher GO concentration lead to thicker pore walls. Therefore, GHA gels can go through the swollen state in water over a long period of time without breakdown. It is the preservation of desired mechanical properties of GHA gels after swelling that significantly enhances their reusability and makes it promising to use them as recyclable adsorbents in pollutant removal. Also, Gong's group has the same point of view. They prepared double network hydrogels exhibiting high mechanical strength compared with single physical network and physically chemically hybrid network hydrogels (Gong et al. 2016). These hydrogels combine PVA and PAM-co-PAA to form a dual physically cross-linked network. The hydrogels have excellent mechanical properties, which improved the self-healing ability and reusability of hydrogels.

Conclusion

In this review, we have summarized the recent research into the development of hydrogels for water-treatment applications, and we have also emphasized the unique particles that have been encapsulated into those hydrogels. Three classes of hydrogel are commonly employed for removal of pollutants in aqueous solutions: hydrogel bead, hydrogel film, and hydrogel nanocomposite. The particles encapsulated into hydrogel are very diverse, each particle having its unique characteristics

and advantages. According to the hydrogel-synthesis method and the contaminant type, particles are chosen for improved adsorption efficiency and enhancement of hydrogel properties including mechanical strength, swelling ratio, pH sensitivity, recyclability, and regeneration. Many hydrogels have already been effectively synthesized and successfully applied for removal of pollutants from water, with more, no doubt, to come in the near future.

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References

- Abachi MQA, Awady NSA, Al-Anbakey AM (2013) Evaluation of poly acrylic acid(PAA) hydrogel beads as adsorbent for the removal of lead(II) ion from water. *J Al-Nahrain Univ* 16:30–39
- Abdelwahab HE, Hassan SY, Mostafa MA, Sadek MME (2016) Synthesis and characterization of glutamic-chitosan hydrogel for copper and nickel removal from wastewater. *Molecules* 21:14
- Agrawal A, Pandey RS, Sharma B (2010) Water pollution with special reference to pesticide contamination in India. *J Water Resource Prot* 2:432–448
- Ahmed EM (2015) Hydrogel: preparation, characterization, and applications. a review *J Adv Res* 6:105–121
- Akponmie KG, Dawodu FA (2015) Potential of a low-cost bentonite for heavy metal abstraction from binary component system. *Beni-Suef Uni J Appl Sci* 4:1–13
- Akponmie KG, Dawodu FA (2016) Acid-modified montmorillonite for sorption of heavy metals from automobile effluent. *Beni-Seuf Uni J Appl Sci* 5:1–12
- Al-Mubaddel FS, Aijaz MO, Haider S, Haider A, Almasry WA, Al-Fatesh AS (2015) Synthesis of chitosan based semi-IPN hydrogels using epichlorohydrine as crosslinker to study the adsorption kinetics of rhodamine B. *Desalin Water Treat* 57:17523–17536

- Ali ZA, Venkatesan J, Kim SK, Sudha PN (2011) Beneficial effect of chitosan-g-polyacrylamide copolymer in removal of heavy metals from industrial dye effluents. *Inter J Environ Sci* 1:820–833
- Antić KM, Babić MM, Vuković JJJ, Vasiljević-Radović DG, Onjia AE, Filipović JM, Tomić SL (2015) Preparation and characterization of novel P(HEA/IA) hydrogels for Cd²⁺ ion removal from aqueous solution. *Appl Surf Sci* 338:178–189
- Antić KM, Babić MM, Vuković JS, Onjia AE, Filipović JM, Tomić SL (2016) Removal of Pb²⁺ from aqueous solution by P(HEA/IA) hydrogels. *Hem Ind* 70:695–705
- Azbar N, Yonar T, Kestioglu K (2004) Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere* 55:35–43
- Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J Hazard Mater* 97:219–243
- Babu VR, Sairam M, Hosamani KM, Aminabhavi TM (2007) Preparation of sodium alginate–methylcellulose blend microspheres for controlled release of nifedipine. *Carbohydr Polym* 69:241–250
- Baruah U, Konwar A, Chowdhury D (2016) A sulfonated carbon dot–chitosan hybrid hydrogel nanocomposite as an efficient ion-exchange film for Ca²⁺ and Mg²⁺ removal. *Nanoscale* 8:8542–8546
- Bhattacharyya R, Ray SK (2013) Kinetic and equilibrium modeling for adsorption of textile dyes in aqueous solutions by carboxymethyl cellulose/poly(acrylamide-co-hydroxyethyl methacrylate) semi-interpenetrating network hydrogel. *Polym Eng Sci* 2013:2439–2453
- Bitinis N, Hernandez M, Verdejo R, Kenny JM, Lopez-Manchado MA (2011) Recent advances in clay/polymer nanocomposites. *Adv Mater* 23:5229–5236
- Blackburn RS (2004) Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment. *Environ Sci Technol* 38:4905–4909
- Cai J, Zhang L, Zhou J, Li H, Chen H, Jin H (2004) Novel fibers prepared from cellulose in NaOH/urea aqueous solution. *Macromol Rapid Commun* 25:1558–1562
- Carlmark A, Malmström E, Malkoch M (2013) Dendritic architectures based on bis-MPA: functional polymeric scaffolds for application-driven research. *Chem Soc Rev* 42:5858–5879
- Chai L, Wang J, Wang H, Zhang L, Yud W, Mai L (2015) Porous carbonized graphene-embedded fungus film as an interlayer for superior Li–S batteries. *Nano Energy* 17:224–232
- Chatterjee S, Chatterjee S, Chatterjee BP, Das AR, Guha AK (2005) Removal of eosin Y from aqueous solution by chitosan hydro beads. *J Colloid Interface Sci* 288:30–35
- Chatterjee S, Chatterjee S, Chatterjee BP, Guha AK (2007) Adsorptive removal of Congo red, a carcinogenic textile dye by chitosan hydrobeads: binding mechanism, equilibrium and kinetics. *Colloids Surf A Physicochem Eng Asp* 299:146–152
- Chatterjee S, HanWoo S (2009) The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *J Hazard Mater* 164:1012–1018
- Chatterjee S, Lee DS, Lee MW, Woo SH (2009) Enhanced adsorption of Congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide. *Bioresour Technol* 100:2803–2809
- Chauhan GS, Kumar S, Kumari A, Sharma R (2003) Study on the synthesis, characterization, and sorption of some metal ions on gelatin and acrylamide-based hydrogels. *J Appl Polym Sci* 90:3856–3871
- Chen S, Yue Q, Gao B, Xu X (2010) Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue. *J Colloid Interface Sci* 349:256–264
- Chen X, Zhou S, Zhang L, You T, Xu F (2016) Adsorption of heavy metals by graphene oxide/cellulose hydrogel prepared from NaOH/urea aqueous solution. *Materials* 9:582–596
- Chien SH, Clayton WR (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci Soc Am J* 44:265–168
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour Technol* 97:1061–1085
- Cui W, Ji J, Cai Y-F, Li H, Ran R (2015) Robust, anti-fatigue, and self-healing graphene oxide/hydrophobically associated composite hydrogels and their use as recyclable adsorbents for dye wastewater treatment. *J Mater Chem A* 3:17445–17458
- Demiral H, Güngör C (2016) Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse. *J Clean Prod* 124:103–113
- Deng S, Bai R, Chen JP (2003) Aminated polyacrylonitrile fibers for lead and copper removal. *Langmuir* 19:5058–5064
- Du M, Guo B, Jia D (2010) Newly emerging applications of halloysite nanotubes: a review. *Polym Int* 59:574–582
- Dwivedi C, Gupta A, Chaudhary A, Nandi CK (2014) Gold nanoparticle chitosan composite hydrogel beads show efficient removal of methyl parathion from waste water. *RSC Adv* 4:39830–39838
- Dwivedi C, Pathak SK, Kumar M, Tripathi SC, Bajaja PN (2015) Preparation and characterization of potassium nickel hexacyanoferrate-loaded hydrogel beads for the removal of cesium ions. *Environ Sci: Water Res Technol* 1:153–160
- Fekete T, Borsa J, Takács E, Wojnárovits L (2017) Synthesis of carboxymethylcellulose/starch superabsorbent hydrogels by gamma-irradiation. *Chem Cent J* 11:1–10
- Flory PJ (1953). *Principles of polymer chemistry*. Cornell University: Ithaca, New York 1953
- Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chem Engin J* 156:2–10
- Freundlich HMF (1906) Over the adsorption in solution. *J Phys Chem* 57: 385–471
- Fritz JS (2005) Factors affecting selectivity in ion chromatography. *J Chromatogr A* 1085:8–17
- Fu Y, Viraraghavan T (2001) Fungal decolorization of dye waste waters: a review. *Bioresour Technol* 79:251–262
- Gao H, Sun Y, Zhou J, Xu R, Duan H (2013) Mussel-inspired synthesis of polydopamine-functionalized graphene hydrogel as reusable adsorbents for water purification. *ACS Appl Mater Interfaces* 5:425–432
- Gercel O, Gercel HF (2007) Adsorption of lead(II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*. *Chem. Engin. J.* 132:289–297
- Gogoi N, Barooah M, Majumdar G, Chowdhury D (2015) Carbon dots rooted agarose hydrogel hybrid platform for optical detection and separation of heavy metal ions. *ACS Appl Mater Interfaces* 7:3058–3067
- Golmohamadi M, Davis TA, Wilkinson KJ (2012) Diffusion and partitioning of cations in an agarose hydrogel. *J Phys Chem A* 116:6506–6510
- Gong Z, Zhang G, Zeng X, Li J, Li G, Huang W, Sun R, Wong C (2016) High-strength, tough, fatigue resistant, and self-healing hydrogel based on dual physically cross-linked network. *ACS Appl Mater Interfaces* 8:24030–24037
- Guilherme MR, Reis AV, Paulino AT, Moia TA, Mattoso LHC, Tambourgi EB (2010) Pectin-based polymer hydrogel as a carrier for release of agricultural nutrients and removal of heavy metals from wastewater. *J Appl Polym Sci* 117:3146–3154
- Guo H, Jiao T, Zhang Q, Guo W, Peng Q, Yan X (2015) Preparation of graphene oxide-based hydrogels as efficient dye adsorbents for wastewater treatment. *Nanoscale Res Lett* 10:272
- Gurses A, Dogar C, Yalcin M, Acikyildiz M, Bayrak R, Karaca S (2006) The adsorption kinetics of the cationic dye, methylene blue, onto clay. *J Hazard Mater B* 131:217–228
- Han R, Ding D, Xu Y, Zou W, Wang Y, Li Y, Zou L (2008) Use of rice husk for the adsorption of Congo red from aqueous solution in column mode. *Bioresour Technol* 99:2938–2946

- Haraguchi K, Takehisa T, Fan S (2002) Effects of clay content on the properties of nanocomposite hydrogels composed of poly(*n*-isopropylacrylamide) and clay. *Macromolecules* 35:10162–10171
- Haraguchi K, Farnworth R, Ohbayashi A, Takehisa T (2003) Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(*n,n*-dimethylacrylamide) and clay. *Macromolecules* 36:5732–5741
- Haubner K, Murawski J, Olk P, Eng LM, Ziegler C, Adolphi B, Jaehne E (2010) The route to functional graphene oxide. *ChemPhysChem* 11: 2131–2139
- Heydari A, Shebani H (2015) Fabrication of poly(*b*-cyclodextrin-co-citric acid)/bentonite clay nanocomposite hydrogel: thermal and adsorption properties. *RSC Adv* 5:2438–82449
- Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. *Process Biochem* 34:451–465
- Hong S, Wen C, He J, Gan F, Ho Y-S (2009) Adsorption thermodynamics of methylene blue onto bentonite. *J Hazard Mater* 167:630–633
- Howard BJ, Beresford NA, Hove K (1991) Transfer of radiocesium to ruminants in natural and semi-natural ecosystems and appropriate countermeasures. *Health Phys* 61:715–725
- Hwang D-C, Damodaran S (1997) Metal-chelating properties and biodegradability of an ethylenediaminetetraacetic acid dianhydride modified soy protein hydrogel. *J Appl Polym Sci* 64:891–901
- Inal M, Erduran N (2015) Removal of various anionic dyes using sodium alginate/poly(*N*-vinyl-2-pyrrolidone) blend hydrogel beads. *Polym Bull* 72:1735–1752
- Jana S, Pradhan SS, Tripathy T (2017) Poly(*N,N*-dimethylacrylamide-co-acrylamide) grafted hydroxyethyl cellulose hydrogel: a useful Congo red dye remover. *J Polym Environ* 2017:1–18
- Jeon YS, Lei J, Kim J-H (2008) Dye adsorption characteristics of alginate/polyaspartate hydrogels. *J Ind Eng Chem* 14:726–731
- Jiang L, Liu P (2014) Design of magnetic attapulgite/fly ash/poly(acrylic acid) ternary nanocomposite hydrogels and performance evaluation as selective adsorbent for Pb²⁺ ion. *ACS Sustain Chem Eng* 2:1785–1794
- Jin L, Bai R (2002) Mechanisms of lead adsorption on chitosan/pva hydrogel beads. *Langmuir* 18:9765–9770
- Jing G, Wang L, Yu H, Amer WA, Zhang L (2013) Recent progress on study of hybrid hydrogels for water treatment. *Colloids Surf A Physicochem Eng Asp* 416:86–94
- Joussein E, Petit S, Churchman J, Theng B, Righi D, Delvaux B (2005) Halloysite clay minerals a review. *Clay Miner* 40:383–426
- Kabiri K, Omidian H, Zohuriaan-Mehr MJ, Doroudiani S (2011) Superabsorbent hydrogel composites and nanocomposites: a review. *Polym Compos* 2011:277–289
- Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coir pith. *Sep Purif Technol* 24:497–505
- Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour Technol* 87:129–132
- Kamata H, Akagi Y, Kayasuga-Kariya Y, Chung U-i, Sakai T (2014) Nonswellable hydrogel without mechanical hysteresis. *Science* 343:873–875
- Kasgoz H, Ozgumus S, Orbay M (2003) Modified polyacrylamide hydrogels and their application in removal of heavy metal ions. *Polymer* 44:1785–1793
- Kasgoz H, Durmus A (2008) Dye removal by a novel hydrogel-clay nanocomposite with enhanced swelling properties. *Polym Adv Technol* 19:838–845
- Khalil MI, Mostafa KM, Hebeish A (1993) Graft polymerization of acrylamide onto maize starch using potassium persulfate as initiator. *Angew Makromol Chem* 213:43–54
- Kono H (2015) Preparation and characterization of amphoteric cellulose hydrogels as adsorbents for the anionic dyes in aqueous solutions. *Gels* 1:94–116
- Kunz A, Mansilla H, Durán N (2002) A degradation and toxicity study of three textile reactive dyes by ozone. *Environ Technol* 23:911–918
- Lagergren S (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsademiens. Handlingar* 24:1–39
- Langmuir I (1916) The constitution and fundamental properties of solids and liquids. *J Am Chem Soc* 38:2221–2295
- Levis SR, Deasy PB (2002) Characterisation of halloysite for use as a microtubular drug delivery system. *Int J Pharm* 243:125–134
- Li N, Bai R (2006) Highly enhanced adsorption of lead ions on chitosan granules functionalized with poly(acrylic acid). *Ind Eng Chem Res* 45:7897–7904
- Li S (2010) Removal of crystal violet from aqueous solution by sorption into semi-interpenetrated networks hydrogels constituted of poly(acrylic acid-acrylamide-methacrylate) and amylose. *Bioresour Technol* 101:2197–2202
- Li Z, Wang Y, Wu N, Chen Q, Wu K (2013) Removal of heavy metal ions from wastewater by a novel HEA/AMPS copolymer hydrogel: preparation, characterization, and mechanism. *Environ Sci Pollut Res* 20:1511–1525
- Liu J, Su D, Yao J, Huang Y, Shao Z, Chen X (2017) Soy protein-based polyethylenimine hydrogel and its high selectivity for copper ion removal in wastewater treatment. *J Mater Chem A* 5:4163–4171
- Lu Q, Yu J, Gao J, Yang W, Li Y (2011) Glow-discharge electrolysis plasma induced synthesis of polyvinylpyrrolidone/acrylic acid hydrogel and its adsorption properties for heavy-metal ions. *Plasma Process Polym* 8:803–814
- Lvov YM, Shchukin DG, Mohwald H, Price RR (2008) Halloysite clay nanotubes for controlled release of protective agents. *ACS Nano* 2: 814–820
- Ma J, Zhou G, Chu L, Liu Y, Liu C, Luo S, Wei Y (2017) Efficient removal of heavy metal ions with an EDTA functionalized chitosan/polyacrylamide double network hydrogel. *ACS Sustain Chem Eng* 5:843–851
- Magalhães ASG, Neto MPA, Bezerrac MN, Feitosa JPA (2013) Superabsorbent hydrogel composite with minerals aimed at water sustainability. *J Braz Chem Soc* 24:304–313
- Mahmoud GA, Mohamed SF (2012) Removal of lead ions from aqueous solution using (sodium alginate/itaconic acid) hydrogel prepared by gamma radiation. *Aust. J. Basic Appl Sci* 6:262–273
- Mahmoud GA, Mohamed SF, Hassan HM (2014) Removal of methylene blue dye using biodegradable hydrogel and reusing in a secondary adsorption process. *J Desalin Water Treat* 54:1–12
- Mai NXD, Bae J, Kim T, Park SH, Lee G-W, Kim JH, Lee D, Son HB, Lee Y-C, Hur J (2017) A recyclable, recoverable, and reformable hydrogel-based smart photocatalyst. *Environ Sci: Nano* 4:955–966
- Mirabedini M, Kassae MZ, Poorsadeghi S (2017) Novel magnetic chitosan hydrogel film, cross-linked with glyoxal as an efficient adsorbent for removal of toxic Cr(VI) from water. *Arab J Sci Eng* 42:115–124
- Mittal H, Maity A, Ray SS (2015) The adsorption of Pb²⁺ and Cu²⁺ onto gum ghatti-grafted poly(acrylamide-co-acrylonitrile) biodegradable hydrogel: isotherms and kinetic models. *J Phys Chem B* 119:2026–2039
- Mohammadi Z, Shangbin S, Berklund C, J-t L (2017) Chelator-mimetic multi-functionalized hydrogel: highly efficient and reusable sorbent for Cd, Pb, and As removal from waste water. *Chem Eng J* 307:496–502
- Mohammed N, Grishkewich N, Berry RM, Tam KC (2015) Cellulose nanocrystal–alginate hydrogel beads as novel adsorbents for organic dyes in aqueous solutions. *Cellulose* 22:3725–3738
- Mohan SV, Sailaja P, Srimurali M, Karthikeyan J (1998) Color removal of monoazo acid dye from aqueous solution by adsorption and chemical coagulation. *Environ Eng Policy* 1:149–154

- Moradi M, Kim JC, Qi J, Xu K, Li X, Ceder G, Belcher AM (2016) Bio-facilitated synthetic route for nano-structured complex electrode materials. *Green Chem* 18:2619–2624
- Mostafa KM, El-Sanabary AA (2003) Graft polymerization of different monomers onto carbamated starches derived from native and hydrolyzed starches. *J Appl Polym Sci* 88:959–965
- Nakata K, Fujishima A (2012) TiO₂ photocatalysis. Design and applications. *J Photochem Photobiol C* 13:169–189
- Ngah WSW, Endud CS, Mayanar R (2002) Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *React Funct Polym* 50:181–190
- Nguyen N-T, Liu J-H (2014) A green method for in situ synthesis of poly(vinyl alcohol)/chitosan hydrogel thin films with entrapped silver nanoparticles. *J Taiwan Inst Chem Eng* 45:2827–2833
- Oladipo AA, Gazi M (2015) Microwaves initiated synthesis of activated carbon-based composite hydrogel for simultaneous removal of copper(II) ions and direct red 80 dye: a multi-component adsorption system. *J Taiwan Inst Chem Eng* 47:125–136
- Pal P, Banat F (2015) Removal of contaminants from industrial lean amine solvent using polyacrylamide hydrogels optimized by response surface methodology. *Adsorpt Sci Technol* 33:9–24
- Patel AM, Patel RG, Patel MP (2010) Nickel and copper removal study from aqueous solution using new cationic poly[acrylamide/N,N-DAMB/N,N-DAPB] super absorbent hydrogel. *J Appl Polym Sci* 119:2485–2493
- Pathak SK, Dwivedi C, Banerjee C, Singh KK, Tripathi SC, Kumar M, Gandhi PM (2016) Potassium zinc hexacyanoferrate encapsulated hydro-gel beads for removal of radio-caesium. *Asian J Mater Chem* 1:14–20
- Paulino AT, Belfiore LA, Kubota LT, Muniz EC, Almeida VC, Tambourgi EB (2011) Effect of magnetite on the adsorption behavior of Pb(II), Cd(II), and Cu(II) in chitosan-based hydrogels. *Desalination* 275:187–196
- Peng N, Hu D, Zeng J, Li Y, Liang L, Chang C (2016) Superabsorbent cellulose–clay nanocomposite hydrogels for highly efficient removal of dye in water. *ACS Sustain Chem Eng* 4:7217–7224
- Peng Q, Liu M, Zheng J, Zhou C (2015) Adsorption of dyes in aqueous solutions by chitosan–halloysite nanotubes composite hydrogel beads. *Microporous Mesoporous Mater* 201:190–201
- Pérez S, Mazeau K, CHD P (2000) The three-dimensional structures of the pectic polysaccharides. *Plant Physiol Biochem* 38:37–55
- Petzold G, Schwarz S (2014) Polyelectrolyte complexes in flocculation applications. *Adv Polym Sci* 256:25–66
- Philipp B, Dautzenberg H, K-j L, Kotz J, Dawydoff W (1989) Polyelectrolyte complexes—recent developments and open problems. *Prog Polym Sci* 14:91–172
- Pour ZS, Ghaemy M (2015) Removal of dyes and heavy metal ions from water by magnetic hydrogel beads based on poly(vinyl alcohol)/carboxymethyl starch-g-poly(vinyl imidazole). *RSC Adv* 5: 64106–64118
- Pourjavadi A, Salimi H, Amini-Fazl MS, Kurdtabar M, Amini-Fazl AR (2006) Optimization of synthetic conditions of a novel collagen-based superabsorbent hydrogel by taguchi method and investigation of its metal ions adsorption. *J Appl Polym Sci* 102:4878–4885
- Pourjavadi A, Tehrani ZM, Salimi H, Banazadeh A, Abedini N (2015) Hydrogel nanocomposite based on chitosan-g-acrylic acid and modified nanosilica with high adsorption capacity for heavy metal ion removal. *Iran Polym J* 24:725–734
- Purkait MK, Maiti A, DasGupta S, De S (2007) Removal of Congo red using activated carbon and its regeneration. *J Hazard Mater* 145: 287–295
- Qada ENE, Allen SJ, Walker GM (2006) Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm. *Chem Eng J* 124: 103–110
- Ralph J, Lundquist K, Brunow G (2004) Lignins: natural polymers from oxidative coupling of 4-hydroxyphenyl-propanoids. *Phytochem Rev* 3:29–60
- Redlich O, Peterson DL (1959) A useful adsorption isotherm. *J Phys Chem* 63:1024
- Reis AV, Guilherme MR, Paulino AT, Muniz EC, Mattoso LHC, Tambourgi EB (2009) Synthesis of hollow-structured nano- and microspheres from pectin in a nanodroplet emulsion. *Langmuir* 25:2473–2478
- Reis LA, Chiu LLY, Liang Y, Hyunh K, Momen A, Radisic M (2012) A peptide-modified chitosan–collagen hydrogel for cardiac cell culture and delivery. *Acta Biomater* 8:1022–1036
- Rocher V, Siaugue J-M, Cabuil V, Bee A (2008) Removal of organic dyes by magnetic alginate beads. *Water Res* 42:1290–1298
- Rossi F, Motta O, Matrella S, Proto A, Vigliotta G (2015) Nitrate removal from wastewater through biological denitrification with OGA 24 in a batch reactor. *Water* 7:51–62
- Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M, Bahnemann DW (2014) Understanding TiO₂ photocatalysis. Mechanisms and materials. *Chem Rev* 114:9919–9986
- Sebesta F, John J, Motl A, Stamberg K (1995) Evaluation of polyacrylonitrile (PAN) as a binding polymer for absorbers used to treat liquid radioactive wastes. Technical Report in Sandia National Labs. SciTech Connect, Albuquerque, pp 1–46
- Senkal BF, Erkal D, Yavuz E (2006) Removal of dyes from water by poly(vinyl pyrrolidone) hydrogel. *Polym Adv Technol* 17:924–927
- Sethuraman VV, Raymahashay BC (1975) Color removal by clays. Kinetic study of adsorption of cationic and anionic dyes. *Environ. Sci. Technol.* 9:1139–1140
- Singh V, Joung D, Zhai L, Das S, Khondaker SI, Seal S (2011) Graphene based materials: past, present and future. *Prog Mater Sci* 56:1178–1271
- Sips R (1948) Combined form of Langmuir and Freundlich equations. *J Chem Phys* 16:490–495
- Souda P, Sreejith L (2014) Environmental sensitive hydrogel for purification of waste water: part 1: synthesis and characterization. *Polym Bull* 71:839–854
- Srivastav RK, Gupta SK, Nigam KDP, Vasudevan P (1994) Treatment of chromium and nickel in wastewater by using aquatic plants. *Water Res* 28:1631–1638
- Suna S, Wanga L, Wang A (2006) Adsorption properties of crosslinked carboxymethyl-chitosan resin with Pb(II) as template ions. *J Hazard Mater* 136:930–937
- Tang SCN, Wang P, Yin K, Lo IMC (2010) Synthesis and application of magnetic hydrogel for Cr(VI) removal from contaminated water. *Environ Eng Sci* 27:947–954
- Tang SCN, Yan DYS, Lo IMC (2014) Sustainable wastewater treatment using microsized magnetic hydrogel with magnetic separation technology. *Ind Eng Chem Res* 53:15718–15724
- Thakura VK, Thakurb MK (2015) Recent advances in green hydrogels from lignin: a review. *Int J Biol Macromol* 72:834–847
- Thünnemann AF, Müller M, Dautzenberg H, Joanny J, Löwen H (2004) Polyelectrolyte complexes. *Adv Polym Sci* 166:113–171
- Trakulsujaritthok T, Noiphom N, Tangtreamjitmun N, Saeeng R (2011) Adsorptive features of poly(glycidyl methacrylate-co-hydroxyethyl methacrylate): effect of porogen formulation on heavy metal ion adsorption. *J Mater Sci* 46:5350–5362
- Tu H, Yu Y, Chen J, Shi X, Zhou J, Deng H, Du Y (2017) Highly cost-effective and high-strength hydrogels as dye adsorbents from natural polymers: chitosan and cellulose. *Polym Chem* 8:2913–2921
- Vieira RS, Beppu MM (2006) Dynamic and static adsorption and desorption of Hg(II) ions on chitosan membranes and spheres. *Water Res* 40:1726–1734
- Vimonses V, Lei S, Jin B, Chow CWK, Saint C (2009) Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials. *Chem Eng J* 148:354–364

- Vivek B, Prasad E (2015) Reusable self-healing hydrogels realized via in situ polymerization. *J Phys Chem B* 119:4881–4887
- Vrtoch L, Pipiska M, Hornik M, Augustin J, Lesny J (2011) Sorption of cesium from water solutions on potassium nickel hexacyanoferrate-modified *Agaricus bisporus* mushroom biomass. *J Radioanal Nucl Chem* 287:853–862
- Wang H, Li X, Chai L, Zhang L (2015) Nano-functionalized filamentous fungus hyphae with fast reversible macroscopic assembly & disassembly features. *Chem. Comm.* 51:8524–8527
- Wang L, Wang A (2008) Adsorption properties of Congo red from aqueous solution onto N,O-carboxymethyl-chitosan. *Bioresour Technol* 99:1403–1408
- Wang N, Han Y, Liu Y, Bai T, Gao H, Zhang P, Wang W, Liu W (2012) High-strength hydrogel as a reusable adsorbent of copper ions. *J Hazard Mater* 213–214:258–264
- Wang S, Wu H (2006) Environmental-benign utilisation of fly ash as low-cost adsorbents. *J Hazard Mater* 136:482–501
- Wang W, Wang A (2010) Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone. *Carbohydr Polym* 80:1028–1036
- Wang X, Hou H, Li Y, Wang Y, Hao C, Ge C (2016) A novel semi-IPN hydrogel: preparation, swelling properties and adsorption studies of Co (II). *J Ind Eng Chem* 41:82–90
- Wang Y, Wang W, Shi X, Wang A (2013) A superabsorbent nanocomposite based on sodium alginate and illite/smectite mixed-layer clay. *J Appl Polym Sci* 130:161–167
- Weber W, Morris J (1963) Kinetics of adsorption on carbon from solution. *J Sanit Eng Div* 89:31–60
- Weng C-H, Pan Y-F (2006) Adsorption characteristics of methylene blue from aqueous solution by sludge ash. *Colloids Surf A Physicochem Eng Asp* 274:154–162
- Wibulswas R (2004) Batch and fixed bed sorption of methylene blue on precursor and QACs modified montmorillonite. *Sep Purif Technol* 39:3–12
- Willats WGT, Knox JP, Mikkelsen JD (2006) Pectin: new insights into an old polymer are starting to gel. *Trends Food Sci Technol* 17:97–104
- Wu N, Li Z (2013) Synthesis and characterization of poly(HEA/MALA) hydrogel and its application in removal of heavy metal ions from water. *Chem Eng J* 215–216:894–902
- Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. *Adv Colloid Interf Sci* 209:172–184
- Yan H, Yang L, Yang Z, Yang H, Li A, Cheng R (2012) Preparation of chitosan/poly(acrylic acid) magnetic composite microspheres and applications in the removal of copper(II) ions from aqueous solutions. *J Hazard Mater* 229–230:371–380
- Yang S, Fu S, Liu H, Zhou Y, Li X (2010) Hydrogel beads based on carboxymethyl cellulose for removal heavy metal ions. *J Appl Polym Sci* 119:1204–1210
- Yavuz CT, Prakash A, Mayoia JT, Colvin VL (2009) Magnetic separations: from steel plants to biotechnology. *Chem Eng Sci* 64:2510–2521
- Yoshida H, Takemori T (1997) Adsorption of direct dye on cross-linked chitosan fiber: breakthrough curve. *Water Sci Technol* 35:29–37
- Yu C, Wang F, Zhang C, Fu S, Lucia LA (2016) The synthesis and absorption dynamics of a lignin-based hydrogel for remediation of cationic dye-contaminated effluent. *React Funct Polym* 106:137–142
- Yu L, Liu X, Yuan W, Brown LJ, Wang D (2015a) Confined flocculation of ionic pollutants by poly(l-dopa)-based polyelectrolyte complexes in hydrogel beads for three-dimensional, quantitative, efficient water decontamination. *Langmuir* 31:6351–6366
- Yu Y, Andrade LCXD, Fang L, Ma J, Zhang W, Tang Y (2015b) Graphene oxide and hyperbranched polymer-toughened hydrogels with improved absorption properties and durability. *J Mater Sci* 50:3457–3466
- Zenk MH (1996) Heavy metal detoxification in higher plants—a review. *Gene* 179:21–30
- Zhang B, Cui Y, Yin G, Li X (2012a) Adsorption of copper (II) and lead (II) ions onto cottonseed protein-paa hydrogel composite. *Polym Plast Technol Eng* 51:612–619
- Zhang L, Chai L, Liu J, Wang H, Yu W, Sang P (2011) pH manipulation: a facile method for lowering oxidation state and keeping good yield of poly(m-phenylenediamine) and its powerful Ag⁺ adsorption ability. *Langmuir* 27:13729–13738
- Zhang L, Wang H, Yu W, Su Z, Chai L, Lia J, Shia Y (2012b) Facile and large-scale synthesis of functional poly(m-phenylenediamine) nanoparticles by Cu²⁺-assisted method with superior ability for dye adsorption. *J Mater Chem* 22:18244–18251
- Zhang L, Li X, Wang M, He Y, Chai L, Huang J, Wang H, Wu X, Lai Y (2016) Highly flexible and porous nanoparticle-loaded films for dye removal by graphene oxide-fungus interaction. *ACS Appl Mater Interfaces* 8:34638–34647
- Zhang L, Sun J (2009) Layer-by-layer deposition of polyelectrolyte complexes for the fabrication of foam coatings with high loading capacity. *Chem Comm* 3091–390. <https://doi.org/10.1039/b907691c>
- Zhao L, Mitomo H (2008) Adsorption of heavy metal ions from aqueous solution onto chitosan entrapped CM-cellulosehydrogels synthesized by irradiation. *J Appl Polym Sci* 110:1388–1395
- Zhao LZ, Zhou CH, Wang J, Tong DS, Yua WH, Wang H (2015) Recent advances in clay mineral-containing nanocomposite hydrogels. *Soft Matter* 11:9229–9246
- Zheng Y, Hua S, Wang A (2010) Adsorption behavior of Cu²⁺ from aqueous solutions onto starch-g-pol (acrylic acid)/sodium humate hydrogels. *Desalination* 263:170–175
- Zheng Y, Huang D, Wang A (2011) Chitosan-g-poly(acrylic acid) hydrogel with crosslinked polymeric networks for Ni²⁺ recovery. *Anal Chim Acta* 687:193–200
- Zhixin J, Baochun G, Demin J (2014) Advances in rubber/halloysite nanotubes nanocomposites. *J Nanosci Nanotechnol* 14:1758–1771
- Zhou J, Zhang L, Deng Q, Wu X (2004) Synthesis and characterization of cellulose derivatives prepared in NaOH/urea aqueous solutions. *J Polym Sci A Polym Chem* 42:5911–5920
- Zhou W, Xiong T, Shi C, Zhou J, Zhou K, Zhu N, Li L, Tang Z, Chen S (2016) Bioreduction of precious metals by microorganism: efficient gold@n-doped carbon electrocatalysts for the hydrogen evolution reaction. *Angew Chem Int Ed* 55:8416–8420
- Zhou Y, Fu S, Liu H, Yang S, Zhan H (2011) Removal of methylene blue dyes from wastewater using cellulose-based superadsorbent hydrogels. *Polym Eng Sci* 51:2417–2424
- Zhou Y, Zhang L, Fu S, Zheng L, Zhan H (2012) Adsorption behavior of Cd²⁺, Pb²⁺, and Ni²⁺ from aqueous solutions on cellulose-based hydrogels. *Bioresources* 7:2752–2765
- Zhu S, Wu Y, Chen Q, Yu Z, Wang C, Jin S, Ding Y, Wuc G (2006) Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chem* 8:325–327
- Zhu W-K, Cong H-P, Guan Q-F, Yao W-T, Liang H-W, Wang W, Yu S-H (2016) Coupling microbial growth with nanoparticles: a universal strategy to produce functional fungal hyphae microspheres. *ACS Appl Mater Interfaces* 8:12693–12701
- Zhuang Y, Yu F, Chen H, Zheng J, Ma J, Chen J (2016) Alginate/graphene double-network nanocomposite hydrogel beads with low-swelling, enhanced mechanical properties, and enhanced adsorption capacity. *J Mater Chem A* 4:10885–10892
- Zollinger H (2003). *Color chemistry: synthesis, properties, and applications of organic dyes and pigments*, 3rd revised edition. VCH-Verlag Helvetica Chimica Acta and Wiley-VCH, 637 pp