

Chapter 7

Sequestration of Organic Dyes from Wastewater Using Hydrogel Nanocomposites



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Abstract With the growth in civilization and industrialization, there is a rise in the release of organic dyes into water systems, which is causing serious public concern. Although adsorption using biopolymer-based hydrogels has proven to be an ideal technique for treating these dye contaminants from aqueous solutions, these hydrogels suffer from a lack of mechanical stability and recoverability compared to synthetic polymers. Herein, we review the low-cost synthesis of hybrid hydrogel nanocomposites to improve the mechanical stability and separation of the hydrogel in removing dyes from an aqueous solution. The literature reports hydrogels and their nanocomposites as noble adsorbents well-known for addressing water pollution issues. In adsorption technology, hydrogel nanocomposites act as adsorbents, prominent to improve the performance of removal efficiency. This current chapter pays particular attention to some recent breakthrough development in water remediation based on hydrogels as efficient adsorbents. In-depth discussions on adsorption and various methods for the synthesis of hydrogels have been devoted to applications of these nanocomposites and are compared in this contribution to the removal efficiency of organic dyes from wastewater.

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7.1 Introduction

Water is a vital resource for the survival of living things on earth [40]. Despite the need for this resource, water pollution continues to be a problem in most countries, including South Africa, where the mainstream water supplies are underground and surface water [72]. Water pollution may be defined as any water that is unsafe for drinking by humans and animals [72]. There are two classes of water contaminants, namely, point sources and non-point sources in which they are defined as a source of pollution at a fixed location (mines, industries, power stations, water treatment station, etc. and pollution from moving sources (cars, buses, and trains, respectively [79, 93]. In point source, water pollutants may be classified as either inorganic (fertilizers and toxic metals), organic (dyes), or microbial (viruses and bacteria) [12]. For example, dyes are organic complexes mostly used by textile industries to colour fabrics and contribute mainly to pollution [110]. Other applications may include medical, pharmaceutical, paper, rubber, plastics, leather, food, and cosmetics industries [56]. Dyes contain aromatic rings in their structure and can be either chromophores or auxochromes [23, 56]. Chromophores are responsible for the production of colour (OH, NH₂, NHR, NR₂, Cl, COOH), and auxochromes (NO₂, NO, and N = N) improve chromophores, make molecules soluble in water and improve their affinity to bind materials [23]. The discharging of dye effluents into either surface and/or groundwater sources leads to contamination, resulting in various health and environmental problems [23, 104]. Consumption of contaminated water by humans can lead to vomiting, mutation, cancer, breathing difficulties, diarrhoea, eyes burn, nausea, shock, cyanosis, jaundice, and tissue necrosis [23, 56, 61, 62, 104]. The environmental issues include the death of aquatic organisms, leading to the development of foul smell [5]. Hence, the need to eliminate dyes from waste effluents before discharging them into rivers and other water streams.

Due to the above-mentioned health and ecological problems, various techniques have been employed for eliminating dyes from wastewater [89]. However, because of the chemical stability and non-biodegradable nature of the dyes, most of these methods are less effective [56]. Additionally, each method has its major disadvantage, as shown in Table 7.1.

The adsorption technique is most favoured owing to its cheap synthesis and operation costs, easy design, and fast removal of dye [48, 66, 88]. Although the adsorption technique is effective for dye removal. Its efficiency is limited by the type of adsorbent used (Gómez et al. 20,107). Various materials have been used for organic dyes removal, which includes; activated carbon, fly ash, graphene, clay, carbon nanotubes, and hydrogels [35, 39, 52, 63, 71, 99, 100, 106, 116]. Among these adsorbents, hydrogels are reported as promising adsorbents for organic dyes removal from aqueous solutions owing to their cheap synthesis, tunable properties, and high removal capacity. This chapter summarises the recent advances and developments of hydrogel adsorbents for wastewater treatment. This is realized by doing a detailed review of various hydrogel adsorbents and their modified systems with great emphasis on the structure and properties of the hybrid hydrogels.

Table 7.1 Removal methods for organic dyes from wastewater

Adsorbent method	Disadvantage	References
Membrane filtration	Membrane fouling and production of concentrated sludge	[88]
Ion-exchange	Ineffective for all dye types	[2, 110]
Photochemical method	Production of by-products	[88]
Electrochemical destruction	Moderately high flow rates that decrease the amount of dye removed	[88]
Anaerobic bioremediation systems	Lead to the production of methane and hydrogen sulphide which are harmful	[2, 78]
Adsorbent using activated carbon	The adsorbent is expensive	[78]

7.2 Hydrogels

7.2.1 Background

Hydrogels are crosslinked gel structured polymers that swell in a liquid medium and can trap liquids for a long time without losing their structural integrity [39, 99]. Hydrogels' swelling capacity and hydrophilicity arise from the presence of hydroxyl, sulfonyl, amide, imide, and carboxylic groups in their 3D backbone [92]. Hydrogels are produced from non-toxic and highly hydrophilic natural polymers called Polysaccharides. Polysaccharides are made by connecting glycosidic bonds between the smaller saccharide units [39, 99, 116]. Polysaccharides provide energy storage and structural support in animals and plants [100]. Examples of these polysaccharides include, alginate, guar gum, locust bean gum, starch, chitosan, carboxymethyl cellulose, carrageenan, and starch [100, 116].

7.2.1.1 Classification of Hydrogels

Hydrogels may well be categorized depending on various characteristics depending on their nature. Hydrogels are classified based on whether they are natural (produced from biological monomers), synthetic (made from artificial monomers), or a combination of natural and synthetic monomers forming a hybrid gel [62] (Table 7.2). The method used for the synthesis of a polymeric composite can also be used to classify hydrogels [62]. These include but are not limited to;

- i. Homopolymeric hydrogels: they are hydrogels comprising of a similar kind of monomer.
- ii. Copolymeric hydrogels: the polymeric gels contain two or more distinct varieties of monomers resulting in a hydrogel with at least one hydrophilic part.

Table 7.2 Classification of physical and chemical stimuli

Physical	Chemical
Light	Composition of solvent
Magnetic field	pH
Temperature	Molecular species
Sound	Ionic strength
Electric field	
Pressure	

- iii. Multipolymer Interpenetrating polymeric hydrogel (IPN): the polymer chain contains two independently cross-linked synthetic and/or natural polymer portions.

Classifications of hydrogels could also be categorized based on the following properties [33],

- i. Amorphous,
- ii. Crystalline or,
- iii. Semicrystallinity: displaying characteristics of both amorphous and crystalline phases.

Moreover, hydrogels can be classified based on whether they are chemically or physically crosslinked. Briefly;

- i. The crosslinking of the hydrogel can be achieved physically (1) between oppositely charged groups, (2) by establishing a hydrogen bond, (3) by subjecting gels to freeze and thaw procedure during crystallization using PVA/PVP solution at controlled conditions. Lastly, (4) through hydrophobic connections between polymer chains, the hydrogel strength is improved, and the dissipation energy prevents breakage of bonds. [23].
- ii. The crosslinking of hydrogels can be realized chemically through (1) aldehydes, namely; glutaraldehyde, formaldehyde, and acetaldehyde, (2) radiation through ultraviolet rays, gamma rays, an electron beam, or at ambient temperatures to form free radicals where monomers can be added to form or grow the hydrogel chain. Lastly, (3) using MBA crosslinker for free radical polymerization. In this method, an initiator (e.g., potassium persulfate) generates free radicals to interact with monomers in the presence of MBA crosslinks to form the hydrogel [16, 39].

Additionally, the classification of hydrogels could be established according to the charge of the hydrogel polymer chain [21, 55]. Whether the charge is,

- i. Non-ionic (neutral).
- ii. Ionic (anionic/ cationic)
- iii. Zwitterionic (each recurring structural unit has cationic and anionic parts). The overall charge of the polymer chain is zero.
- iv. Amphoteric (contains both acidic and basic groups).

Lastly, hydrogels can be categorized depending on whether a chemical or physical stimulus (Table 7.2) encourages their reaction. These hydrogels are sometimes called smart hydrogels [16, 62]. Sometimes environmental conditions can affect the swelling or de-swelling of hydrogels and therefore result in a volume collapse (phase change).

7.2.2 *Synthesis of Hydrogels*

For application in water remediation processes, the low stability and solubility of hydrogels are improved by developing hybrid hydrogel systems that consist of nanofillers and/or synthetic polymers [21]. Most researches have reported that crosslinking, grafting, and free radical polymerization. Therefore, the type of method used to prepare the hydrogel affects its structural makeup or physical properties. Below are brief descriptions of the methods as mentioned above.

7.2.2.1 **Grafting**

Grafting uses artificial polymers, namely; methacrylamide, acrylic acid, vinyl alcohol, and acrylamide, to improve the hydrogel backbone [55]. An initiator generates free radical sites to which monomer units are attached [94]. Grafting can initiate through either radiation or chemical stimulus. Chemical grafting makes use of chemicals such as potassium persulfate (KPS), ammonium persulfate (APS) as initiators [68]. Radiation grafting initiates free radicals through microwave or UV visible energy [20].

It was reported in the literature that using a microwave radiation method for synthesizing hydrogels produces sterilized hydrogels [20]. Naturally, polysaccharides have poor mechanical and chemical stability [21]. Grafting solves these problems and improves the biopolymers efficiency by establishing new functional groups from grafted monomers.

7.2.2.2 **Crosslinking**

Crosslinking process can occur through chemical or physical interaction. During chemical crosslinking, complementary groups within the polymer chain react to form irreversible covalent bonds [91]. In contrast, physical crosslinking occurs through reversible van der Waals forces, hydrogen bonding, and electrostatic reactions [14, 44]. Hydrogels that are crosslinked chemically are mainly applied in the medical field during tissue engineering, wound dressing, wastewater treatment, and drug delivery [57, 105]. Several chemical crosslinkers exist that may be used for hydrogel synthesis. For example, in a study by Mittal et al. hydrogels was produced using a mixture of ascorbic acid and KPS as a redox initiator and MBA as a cross linking

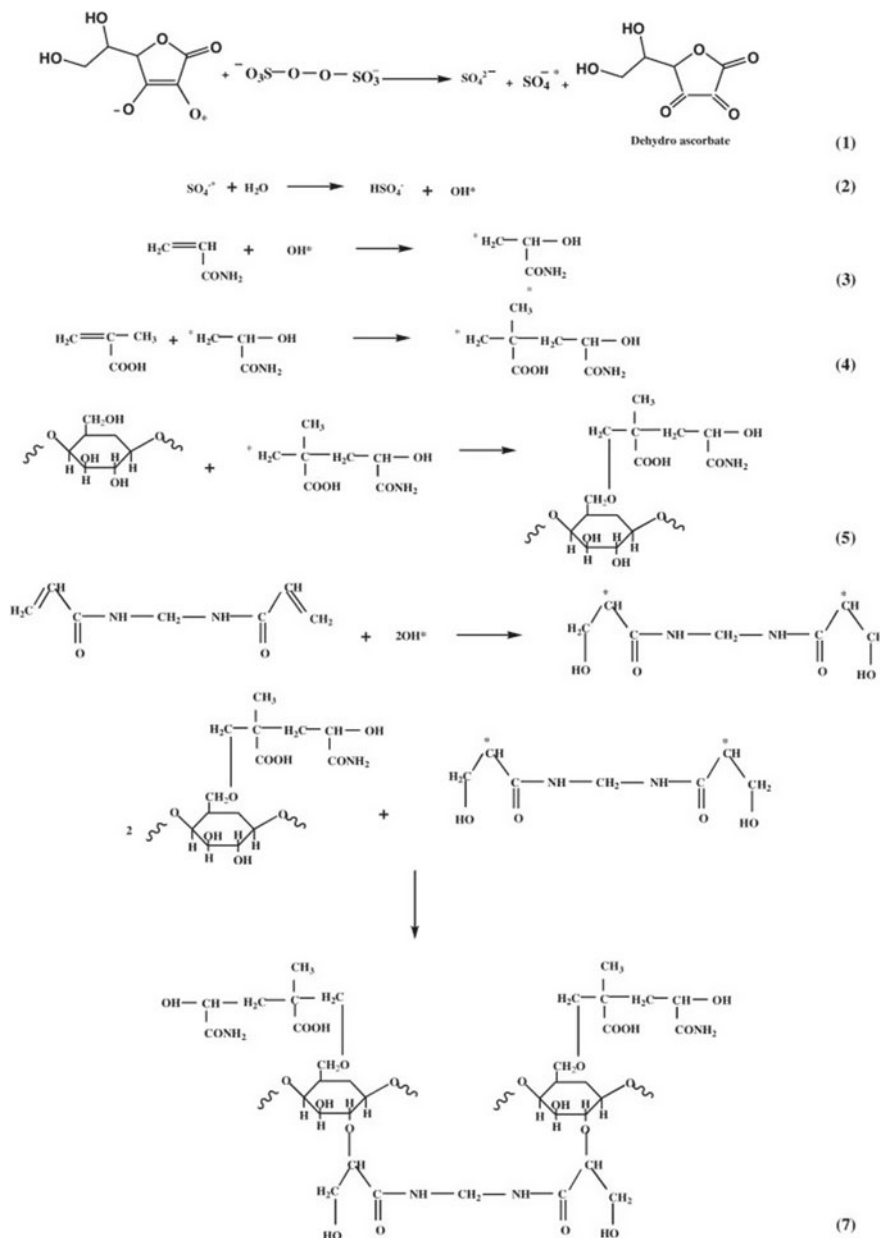
agent in the microwave-assisted graft co-polymerization method (Scheme 7.1) [69]. According to the group, this using MBA as the cross linker to establish links between different polymeric chains. [69].

Chemicals such as tri-propyleneglycol diacrylate (TPGDA) tetra-ethylene glycol dimethyl-acrylate (EGDMA), N, N-methylene-bis-acrylamide (MBA), and ethylene glycol dimethyl-acrylate are the most commonly used as crosslinkers in hydrogel synthesis [96]. However, these crosslinkers produce non-biodegradable hydrogels and are generally toxic [118]. Moreover, the resulting hydrogels are very brittle because of the lack of an effective strategy for energy dissipation and inner structural uniformity [108, 109]. As a solution, hybrid hydrogel systems comprising both physical and chemical interactions have been established by researchers to aid in energy dissipation and improve structural properties, respectively [19, 83]. For example, researchers constructed hybrid polymeric gels using poly(N-isopropyl acrylamide-co-itaconic acid) and non-poisonous octa-vinyl polyhedral oligomeric silsesquioxane (OV-POSS) crosslinkers. The analysis of the SEM and TGA (Fig. 7.1) results demonstrated that the surface of the non-hybridized NIPAM-co-IA (SEM image Fig. 7.1a) was not smooth. However, after crossing with various POSS amounts ((a) 8%, (b), 10%, and (c), 12%), the surface texture changed to a honeycomb-like structure with similar pores of different pore sizes as the POSS amount was raised. The group observed disruption of the honeycomb pattern at higher POSS content (12%), demonstrating that the level of homogeneity in the hybridized gel structure could be manipulated by varying the degree of crosslinking [27]. Their TGA thermogram (Fig. 7.1e) indicated that the thermal stability was enhanced through hybridization with POSS, in which the weight loss obtained for poly(NIPAM-co-IA) from 340 to 500 °C was higher compared to the weight loss achieved for the hybridized hydrogel at the same temperature [27].

7.2.2.3 Free Radical-Polymerization

Free radical polymerization is when free radicals are generated to which monomers bind progressively, and the polymer chain grows [13]. This technique combines crosslinking and grafting methods. In this process, an initiator breaks down by light, photon, or temperature to form a free radical [18]. The advantages of generating free radicals by photon are (1) cost-efficiency, (2) no chemical solvent is required, and (3) it offers improved time-based and spatial control of the reaction procedure [46]. Scheme 7.2 illustrates the synthesis of hydrogels through the free radical polymerization process. Firstly, free radicals are produced through an initiator (initiation). Next, the monomer interacts with the free radicals to create unoccupied functional sites (propagation), and lastly, crosslinking occurs to form a hydrogel (termination) [65].

The most commonly used technique in the polymer industry is free radical polymerization. This technique offers the advantage of easy operation, convenience, and the ability to design and prepare polymers for different uses. Impurities do not easily



Scheme 7.1 Mechanism for the graft co-polymerization of Gg with P(AAm-co-MAA). Reproduced with permission from [69]. Copyright 2015, Elsevier Science Ltd

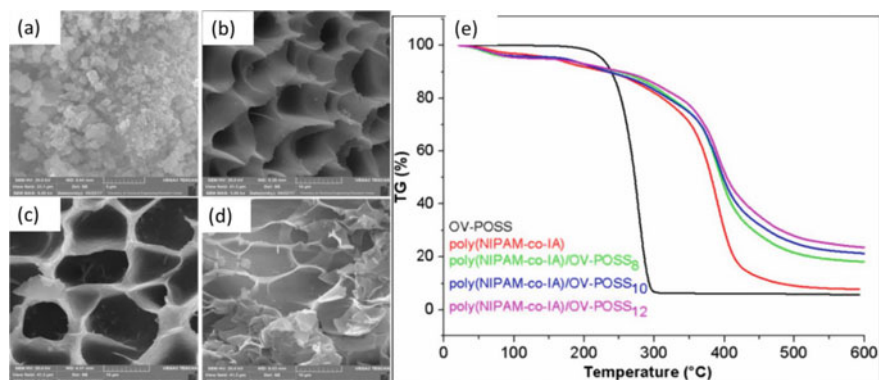


Fig. 7.1 SEM images of poly (NIPAM-co-IA) hydrogel (a) and hybrid poly (NIPAM-co-IA)/OV-POSS (8%, 10% and 12% POSS) (b–d), e TGA thermogram. Reproduced with permission from [27]. Copyright 2018, Elsevier Science Ltd

influence it. Free radical polymerization allows the achievement of in situ properties and well-characterized reaction kinetics [84].

7.2.3 Hybrid Hydrogels

It has been reported that hydrogel properties can be improved through generating hybrid hydrogel systems. Recently, many studies have incorporated nanofillers such as metal oxides [63], carbon-based materials [61, 62], and clay-based materials [65] into the hydrogel matrix during the polymerization process to produce a hydrogel nanocomposite with enhanced recovery and stability.

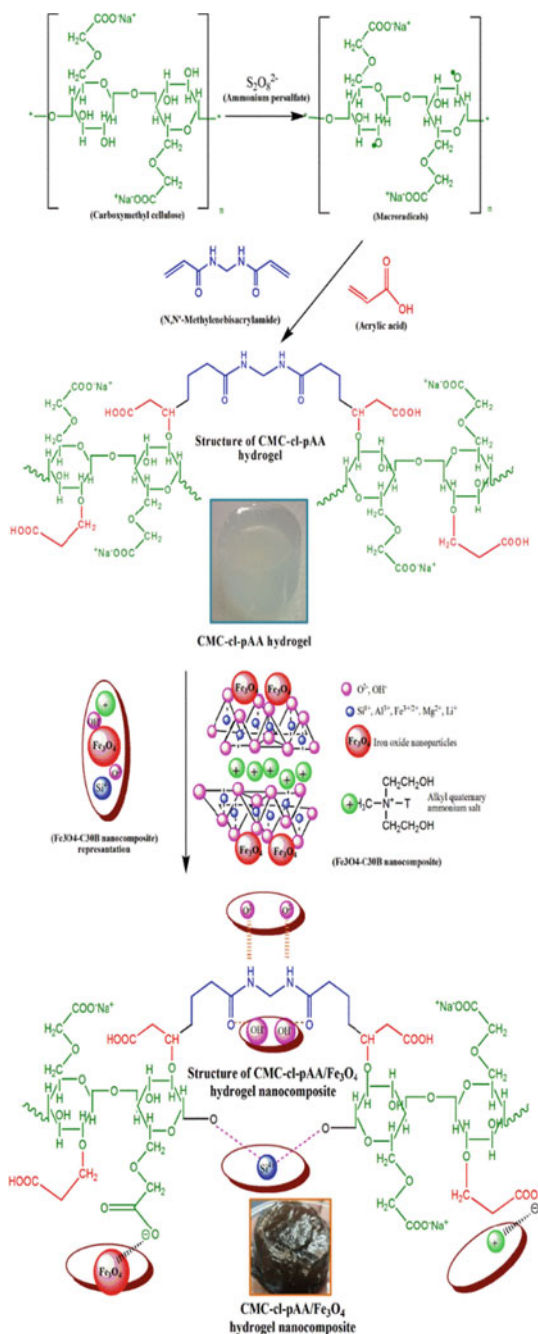
7.2.3.1 Modification of Hydrogels with Inorganic Materials

Depending on the intended application of the hydrogels, their physical properties can be enhanced through the incorporation of inorganic materials. For example, for use in removing contaminants from aqueous solutions, the hydrogel must be mechanically and thermally stable, especially for removing effluents from industries that utilize water for cooling reactions [22, 38]. Wherein the contaminants may be introduced at that point. Additionally, the hydrogels must be easy to recover.

7.2.3.2 Carbon-Based Hydrogels

Carbon-based hydrogel nanocomposites are hydrogels synthesized by incorporating nanofillers such as graphene oxide (GO), biochar, activated carbon, and carbon

Scheme 7.2 An overview of thermal free-radical polymerization and crosslinking. Reproduced with permission from [65]. Copyright 2020, Springer



nanotubes (CNTs) [11, 64, 95]. GO is a carbon material prepared by oxidizing graphene through chemical or thermal reduction processes. It contains highly hydrophilic groups such as hydroxyl, carboxylic, and epoxy groups that are essential for adsorbing dyes and toxic metals [8]. GO may interact with contaminants through pi-to-pi interactions, electrostatic interactions, or hydrogen bonding [107]. Owing to its outstanding mechanical, electrical and thermal properties, GO has attracted its use in the biomedical, energy and environmental field [31]. An example of a study is by [99]. The group prepared starch hydrogel infused with reduced graphene oxide and reported a high removal capacity of 1106.960 $\mu\text{g g}^{-1}$ for cationic dyes. The group also reported an improvement in the hydrogel pore size. In another study by [61, 62], xanthan gum-polyacrylic acid hydrogel was modified with reduced GO (XG-cl-pAA/rGO) for the removal of MB and MV [28]. The group reported an impressive removal capacity of 1052.63 mg/g and 793.65 mg/g at 25 °C for MB and MV, respectively. Additionally, the XG-cl-pAA/rGO hydrogel nanocomposite was reported to have easy recovery and recyclable.

CNTs are simply graphene sheets rolled up in cylinders of 1 nm in diameter [29]. As a result of their porous structure, large surface area, high tensile strength (0.15 TPa) and elastic modulus (0.91 TPa), CNTs have attracted interest in use for adsorption of pollutants such as dyes, dichlorobenzene, ethylbenzene, and some heavy metals [24, 117]. CNTs can be categorized into two forms, namely, single-walled CNTs (SWCNTs, which are made up of single layers of graphene sheets and multiwalled CNTs (MWCNTs), which are made up of multiple layers of concentric cylinders [4, 29]. Among recent studies that have used carbon-based materials to modify the properties of hydrogels, [62], reported that the incorporation of MWCNT's onto XG/PAA hydrogel improved the surface hydrophilicity and specific area of xanthan gum. The literature reports that although the incorporation of CNTs in gels improves the mechanical properties, the rate of degradation decreases, which is because carbon-based materials have high hydrothermal stability, which makes them resistant to harsh environments [60]. Another widely used carbon-based adsorbent and nanofiller are activated carbon/activated charcoal (AC). This material is reported to improve the surface properties, adsorption capacity, and porosity of adsorbent materials. A study by [45] reported a removal capacity of 60.9 mg/g for TH dye from wastewater using chitosan (CS) hydrogel modified with activated charcoal (CS/AC). Various carbon-based nanocomposite hydrogels and their adsorption properties for the removal of organic dye contaminants from aqueous solutions are listed in Table 7.3.

7.2.3.3 Clay-Based Hydrogels

Natural clays and their improved forms have recently been used for removing pollutants from water [15]. The most commonly used clays, especially for treating toxic metals and dyes, are modified kaolinite and montmorillonite [36]. However, these clays are difficult to regenerate and reuse because of their colloidal dimensions [113]. This prompted the functionalization of these clays—for example, the modification

Table 7.3 Carbon-based adsorbent hydrogels and their adsorption properties in removing contaminants from aqueous solution

Adsorbent	Cross-linker	Dye	Adsorption parameter				References
			q_e (mg/g)	pH	Dosage (mg)	Kinetics models	
CMC-AAm-GO	MBA	AB-133	185.4	6	100	–	[104]
XG-cl-pAA/o-MWCNTs	MBA	MB	521	6	30	Langmuir	[61]
XG-cl-pAA/rGO	MBA	MV MB	1052.6 793.6	5	10	Langmuir	[62]
Alg-KBC	Ca ²⁺	CV	2473.0	10	–	–	[77]
CS/CNTs beads	Alkaline mixture	CR	450.4	5	20	Langmuir	[17]
k-C-g-A/MWCNT	MBA	CV	118	5–8	200	Langmuir	[43]

of montmorillonite (MMT) to form Cloisite 30B. In a study where C30B clay was incorporated onto polypropylene (PP) grafted with maleic anhydride (PP-g-MA) and thermoplastic starch (TPS), it was reported that biodegradation studies performed in compost revealed that the presence of C30B improved the matrix biodegradability [1]. Modification of adsorbents by introducing functionalized clay components may improve both the physical and chemical properties of adsorbents [1, 113]. Other modifications with clay results improve the number of adsorbing active sites, enhanced porosity, and low levels of mineral impurities [1]. In a recent study, C30B was mixed with a culture obtained from an anaerobic sludge to remove hexavalent chromium, where the removal capacity of nearly 100% was obtained [58]. In our recent study, we reported the incorporation of C30B into magnetic carboxymethyl cellulose/poly(acrylic acid) to synthesize the hydrogel nanocomposite [65]. Our findings reported an increased crosslinking density and easy dispersion of magnetite (Fe_3O_4) nanoparticles into the hydrogel matrix due to the presence of the C30B component in the hydrogel. Another study by [81], prepared cellulose-MMT hydrogels for removing MB. The hydrogels had a maximum removal capacity of 1065 mg/g (Table 7.4). Their viscoelasticity studies from the sweep measurements (Fig. 7.2a) showed that when the storage modulus (G') < loss modulus (G''), the cellulose-MMT systems were in a viscous liquid form, however with increasing time when $G' > G''$, the materials were in a gel form. Figure 7.2b in this case revealed that increasing clay content decreased the gel formation. Figure 7.2c revealed that the storage moduli (G') of hydrogels containing clay was higher than that of unmodified hydrogel and was proportional to the clay content from 10 to 15 wt.%. However, the incorporation of clay increased the gel strength from 0.3 kPa to 4.7 kPa, as shown in Fig. 7.2d and e, which was approximately 16 times higher. Furthermore, the study reported that an increase in clay content from 10 to 15 wt.% reduced the swelling capacity of the hydrogel (Fig. 7.2f), reportedly due to a high degree of crosslinking. Furthermore, it was reported that the addition of modified clay containing 2,3-epoxypropyltrimethylammonium chloride increased the crosslinking density of the hydrogel networks, eventually resulting in enhanced storage modulus [81].

7.2.3.4 Metal Oxide-Based Hydrogels

Metal oxide-based nanoparticles have been reported to have a high density and restricted size, which are responsible for their fascinating and unique chemical and physical properties [7, 80]. Examples of metal oxides include titanium dioxide (TiO_2), iron oxide (Fe_3O_4), magnesium oxide (MgO), aluminium oxide (Al_2O_3). Owing to their nontoxic nature, high surface area, high chemical stability, and economical friendliness, Fe_3O_4 nanoparticles are widely used for the removal of toxic metals and organic pollutants from water [7, 80, 85, 97, 119]. Ion-oxide and zinc oxide nanoparticles are some of the most frequently used metal oxides in treating dyes from aqueous solutions [67].

Table 7.4 Clay-based adsorbent hydrogels and their adsorption properties in the removal of contaminants from aqueous solution

Adsorbent	Cross-linker	Dye	Adsorption parameter				References	
			q_e (mg/g)	pH	Dosage (mg)	Isotherm models	Kinetics models	
Agar/K-Carra	TEGDVE	MB	242.3	7	–	Langmuir	PSO	[26]
CMC-MMT	ECH	MB	1065	1–10	500	Langmuir	PSO	[81]
P(AA-co-AMPS)/MMT	MBA	MB	192	10	–	Redlich–Peterson	PSO	[42]
CS-g-IA/BT	MBA	MB	500	6	30	Langmuir	PSO	[90]
clay/PNIPAm	LMSH	CV	4.71	8.9	–	–	–	[115]
SH/PAM/clay	MBA	MB	800	–	–	–	–	[111]

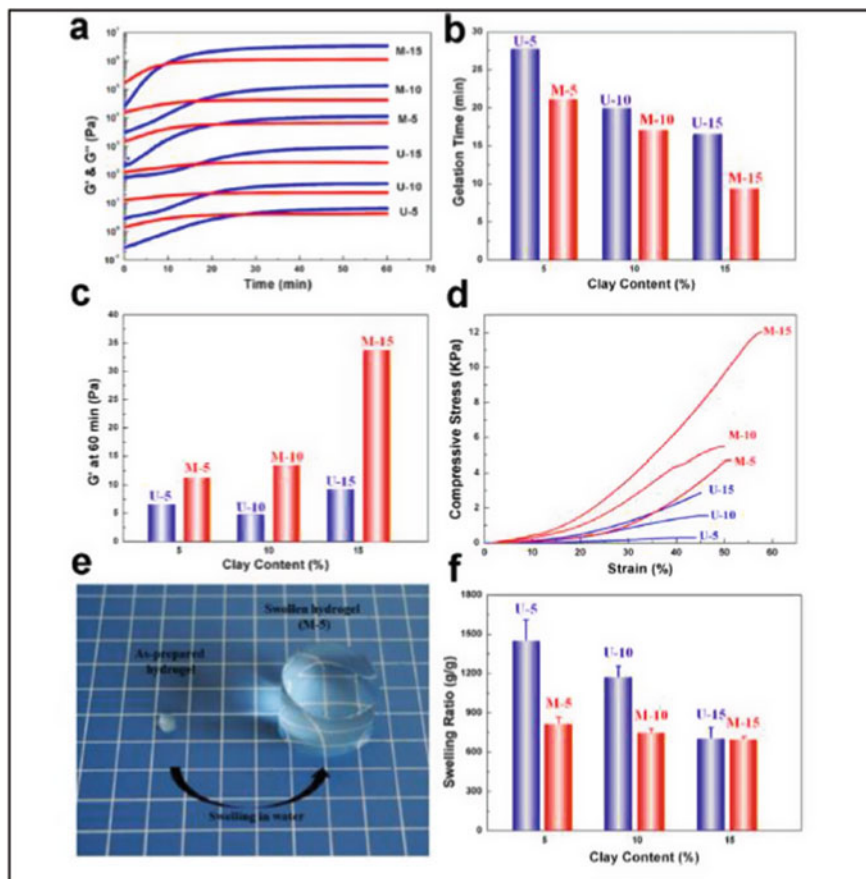


Fig. 7.2 a Time dependence of storage modulus (G') and loss modulus (G''), b Gelation time c G' at 60 min d Compressive-strain curves e Photographs of M-5 f The swelling ratio performed using distilled water. Reproduced with permission from [81]. Copyright 2016, American Chemical Society

Amongst the most promising metal-oxides are magnetite (Fe_3O_4) nanoparticles. Magnetite nanoparticles also called black iron oxide amongst other transition metals, have the strongest magnetism and are stable at ambient temperatures [59]. Magnetite is prepared from the coprecipitation of iron oxide salts that result in an inverse spinel crystal structure consisting of half of the Fe^{3+} in tetrahedral coordination and the other half Fe^{2+} ions in octahedral coordination (Fig. 7.3a) [32, 59, 86]. The coprecipitation method is the most useful and suitable technique in preparing magnetite at both lab-scale and industrial scales [53]. Due to their cheap synthesis costs, susceptibility, stability, high porosity, magnetic properties, biocompatibility, and easy chemical modification, MNP's have attracted much use in the wastewater

treatment field [32, 59, 67, 85, 86]). The introduction of MNPs into polymer structures to produce nanocomposite hydrogels leads to a hybrid hydrogel with advantages of both components, thus improved chemical and physical properties. An example of such hybridized hydrogel is Fe_3O_4 -g-pAA hydrogel synthesized via radical polymerization in the presence of MBA crosslinker, which resulted in a highly adsorptive hydrogel of 507.7 mg/g removal capacity for MB [82], as shown in Table 7.5. However, according to Flory's theory, the swelling degree of a hydrogel depends on the density of crosslinking, the ionic osmotic pressure, and the attraction of the gel for the liquid [50].

When the crosslinking density is high, the space between the polymer chains decreases, making the gel to be stiff due to tiny nonexpendable pores [50]. Additionally, an increase in the amount of MNPs increases the thermal properties but consequently reduces the swelling capacity as the Fe^{3+} from the incorporated MNPs may act as a physical crosslinking agent [82, 87]. Additionally, in a study by [65] in the removal of MB using CMC-cl-pAA/ Fe_3O_4 -C30B, the group reported a decreased removal capacity with improved stability for modified HNC compared to non-modified CMC-cl-pAA hydrogel as a consequence of incorporating metal oxide nanoparticles. The most significant advantage of incorporation MNPs into the hydrogel matrix is the improved stability and easy recovery of the material after application [10]. Another prevalent metal oxide is zinc oxide (ZnO) which can be found in nature as a zincite mineral; however, the majority of it is prepared synthetically. Its crystal structure can be found in a hexagonal wurtzite form of cubic zinc blend form (Fig. 7.3b). The form that is most stable and commonly found at ambient temperature is the wurtzite structure Fig. 7.3b [98]. ZnO is commonly used for treating skin-related problems such as nappy rash, dandruff, and incorporation in ointments used in wound dressing [98]. Other applications of ZnO include the use in catalysis, batteries, sensors, and adsorption of contaminants [3, 30, 73, 112]. Their application as adsorbent material was reported in a study by [49], where a guar gum adsorbent hydrogel incorporated with ZnO nanoparticles was used for removing chromium (VI) from water. The group reported that incorporating ZnO nanoparticles improved the recovery of the adsorbent from the aqueous solution after the removal of Cr (VI) [49]. In another study, CMC hydrogel was modified with ZnO for antimicrobial activity, which was influenced by their inexpensiveness and lack of colour [54].

Another widely used metal-oxide is TiO_2 , a semiconductor [25, 75]. There exist three forms of TiO_2 , namely, anatase, rutile, and brookite. Amongst the three forms, anatase has been reported to be more photoreactive thus its wide use in photocatalytic degradation during water treatment studies [34]. This is because TiO_2 as a photocatalyst is chemically stable, non-toxic, cost-effective, and remains stable during irradiation [9, 47, 74]. Various techniques have been used to synthesize titanium dioxide, namely, low-temperature dissolution-precipitation, gas-phase pyrolysis, ultrasonic spray pyrolysis, sol-gel, ultrasonic spray pyrolysis, and combustion synthesis [76]. TiO_2 -based nanomaterials have been used in fields such as drug delivery, medical research, self-cleaning, producing antibacterial materials, and energy storage [51, 9]. As nanoparticles for water treatment, TiO_2 offers a high surface area, which is very important in the sorption of contaminants from aqueous solutions [37]. A study

Table 7.5 Metal oxide-based adsorbents for organic dyes removal

Adsorbent	Cross-linker	Dye	Adsorption parameter			Kinetics models	References
			q _e (mg/g)	pH	Dosage (mg)		
Fe ₃ O ₄ /p (Am-co-Na Ac)	MBA	MB	641	7	50	PSO	[7]
pAA-grafted MNPs	MBA	MB	507.7	4	20	PSO	[82]
CMC coated Fe ₃ O ₄ @SiO ₂ nanocomposite	–	MB	22.7	11	30	PSO	[120]
Fe ₃ O ₄ /CA gel beads	CaCl ₂	MV	713	–	20–40	modified Langmuir–Freundlich	[6]
ZnO–clay–alginate hydrogel beads	Clay	CR	546.89	5–7	200	Temkin	[103]
ZnO-PPy nanocomposite	–	BG	140.8	–	50–200	Langmuir	PSO
Fe ₃ O ₄ -CS-Clay	Clay	MB	82	9–12	500	–	–
chitosan/silica/ZnO NC	–	MB	293.3	–	–	Langmuir	PSO
SA-poly (AA)/ZnO	MBA	MB	579.2	6	10	Langmuir	PSO
CMC-cl-pAA/Fe ₃ O ₄ -C30B	MBA	MB	1081.6	7	10	Langmuir	PSO
TiO ₂ /p(Aam-co-AA)	UV radiation	MB	2.22	–	–	–	PFO
Gg-cl-PAAm/TiO ₂	MBA	MB	1305.5	7	–	Langmuir	PSO
SA/AA/TiO ₂	MBA	MV	1156.6	2–3	–	Langmuir	PSO

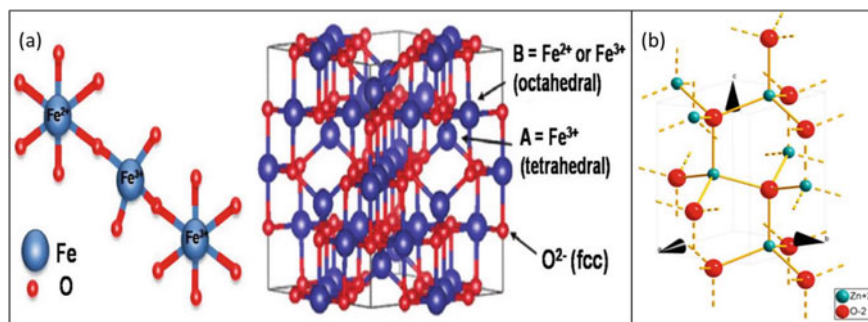


Fig. 7.3 Structures of Fe₃O₄ and ZnO [67]. Reproduced with permission from [98]. Copyright 2017, Walter de Gruyter GmbH

by [102] reported that an increase in the TiO₂ content from 0.05 g to 0.2 g in SA-cl-poly(AA)-TiO₂ O/I hydrogel nanocomposite increased anionic centres and the intrinsic charge repulsion within the hydrogel matrix, consequently enhancing the removal capacity for MB.

7.3 Conclusions

In conclusion, this chapter discusses recent studies applied for removing different types of dyes from an aqueous solution using biopolymer-based HNCs. Owing to various advantages such as low cost and easy design, the adsorption method is recognized as the most promising treatment technique for the removal of dyes. This work briefly discussed hydrogels, their classification, methods of synthesis and modifications with inorganic components to improve on their drawbacks. This contribution emphasized the importance of incorporating carbon compounds, clay content, and metal oxide nanoparticles in hydrogels for the removal of dyes. Additionally, various modified hydrogel nanocomposites are summarised in table form for easy study and comparisons depending on which content was used to modify them.

Acknowledgements This research was supported by the National Research Foundation (NRF) under the Thuthuka programme (UID. 117727), and the University of Limpopo (R202, R232, R355), South Africa.

Conflicts of Interest There are no conflicts of interest to declare.

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