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REVIEW ARTICLE

# Modified Adsorbents for Removal of Heavy Metals from Aqueous Environment: A Review

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**Abstract**
The fatally ill consequences of the bioaccumulation of heavy metals in living beings call for an immediate remediation of wastewater. The adsorption is an effective and growing technique for the scavenging of the contaminants from the wastewater. Industrial waste/by-products are potential materials for the adsorptive scavenging of heavy metal ions such as Cu(II), Zn(II), Ni(II), Cr(III), Cr(VI), Cd(II), etc. in wastewater. The abundant and inexpensive industrial waste/by-products are a good alternative to costly adsorbents, which are available commercially and naturally. The major industrial by-products/waste includes slag, sludge, red mud, lignin and fly ash, which have contributed enormously to effective and economical treatment of wastewater containing heavy metals. This review reports the potential of industrial waste/by-products-based composites as the adsorbents for the removal of heavy metals from wastewater. Detailed investigations onto the adsorption mechanism and the role of the different adsorption parameters have also been discussed.

**Keywords** Industrial by-products · Composite · Adsorption · Heavy metal · Wastewater purification

## 1 Introduction

The industrial and domestic wastewaters contain a large number of organic and inorganic toxicants which are a serious threat to the living organism and ecosystem. Heavy metals are released into the environment either by industrial activity or as natural deposits (in the Earth crust) (Mohammed et al. 2011). Industrial activities, such as mining, metal finishing, plating, semiconductor and so forth are the major sources for the release of the heavy metals into the wastewater. The highly stable and water-soluble heavy metals are harmful to health above the permissible limit (Ahmad et al. 2016; Ansari et al. 2017; Barakat et al. 2016; Kumar et al. 2014). Such hazardous and toxic metal ions have a tendency for accumulation and carcinogenic effects on the living system. Therefore, it is essential to separate the heavy metals from industrial wastewater afore freeing it into the environment (Ahmad et al. 2013, Kumar et al. 2013a).

Several treatment methods have been applied for the elimination of the heavy metals from wastewaters such as solvent extraction, ion exchange, membrane filtration, precipitation, electrochemical, coagulation, etc. There are several disadvantages associated with these techniques such as high operation cost, use of larger amount of chemical, high sludge production, secondary pollution, etc. (Ahmad et al. 2015a, b; Barakat 2011, Neznakomova et al. 2018; Kumar et al. 2013a, 2017). Among the various methods used for heavy metal removal, adsorption is one of the best and low-cost method for wastewater purification. In the last decade, a variety of materials such as metal oxide, clay mineral, industrial and agriculture wastes, carbons, polymers and so forth have been used as adsorbents. Although, adsorption has become one of the most used techniques in the remediation of wastewater, it suffers from certain disadvantages namely low efficiency, low selectivity, and poor re-usability of the adsorbents.

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Hence, the preparations of new adsorbents with promising adsorption capacity are in need. One of the approaches involves the preparation of composites by reinforcing the waste materials into the developed matrix. Generally, the pro-adsorbent material forms the continuous phase while the reinforcing constituent forms the dispersed phase. Such reinforced modified composites possess higher specific and mechanical strength with high resistance to corrosion, oxidation and other chemicals. Such composites also possess large surface area and are applicable to diverse working environmental conditions (Khaskheli, et al. 2016; Kumar et al. 2013b). The growing concerns for the sustainable development of mankind, researchers are focusing on low-cost materials for adsorption applications. The use of low-cost materials such as industrial waste/by-products as adsorbent materials showed the potential for the removal of metallic ions. The recovery or removal of metal ions from the environment with waste-derived adsorbent can meet the dual purpose of valorization of wastes and remediation of contaminated wastewater (Ahmaruzzaman 2011; Devi and Saroha 2016; Siddiqui et al. 2016).

Industrial waste materials have been investigated as a source of low-cost adsorbents. The by-products or disposed materials, generated during various industrial activities, constitute the industrial waste. Such industrial waste materials possess several advantages, such as abundant availability, low cost, and least processing requirement. Industrial by-product/waste may consist of blast furnace slag (BFS), eggshell (EG), fly ash (FA), vineyard pruning waste, lignin and red mud (RM) and so forth (Ahmad et al. 2016; Ahmaruzzaman 2011; Devi and Saroha 2016). Ahmaruzzaman (2011), Ahmed and Ahmaruzzaman (2016) briefly summarized the adsorption properties of the various kinds of industrial waste/by-products used as an adsorbent for the wastewater purifications. In continuation of these reviews, this article is focused on the variety of the composite adsorbents based on the industrial waste/by-products for the scavenging of the heavy metals.

## 2 Industrial Waste-Based Composites Adsorbents

Solid waste/by-products from the variety of industries such as fly ash, vineyard pruning waste, slurry, sludge, red mud, lignin, coffee waste, rice husk, hen feather, eggshell and so forth have been explored as the possible low-cost adsorbents for the separation and scavenging of the organic and inorganic pollutants (Ahmaruzzaman 2011; Devi and Saroha 2016). In recent years, composite materials have gained more attention from the researchers due to their higher adsorption capacity and better reusability.

### 2.1 Sludge Based Composite

Sludge is produced during the wastewater treatment process. A large amount of the sludge is produced as a solid waste. The use of waste sludge as a low-cost adsorbent could be a good method to manage the sludge. Raw and modified sludge are widely explored for the decontamination of the wastewater (Devi and Saroha 2017). The potential of the modified sludge-based adsorbents has been widely investigated. A modified sludge biomass (MSB) (Ramteke and Gogate 2016) was immobilized on different supports including Ca-alginate (CA), phosphorylated polyvinylalcohol gel (PVA), activated carbon (AC) and chloromethylated cellulose (CMC) as shown in Fig. 1. The adsorption capacity of the prepared materials is in the order PVA-CMC-AC > PVA-CMC > PVA > CA (Ramteke and Gogate 2016). The major functional groups, including –OH and –NH, are involved in the ion-exchange mechanism for the retention of copper and hexavalent chromium. The regeneration of the biocomposites could be done with 20% $CaCl_2$ as the eluting agent. The results presented in Table 1 depicts that pure sludge is much efficient than the immobilized composites. This study revealed that modification of the materials is always not effective. The lower adsorption capacity of the immobilized sludge may be due to the blockage of the active sites present in the internal structure of the adsorbent. However, MSB-PVA-CMC-AC composite exhibited better removal for both Cu(II) and Cr(VI) as compared to other adsorbents.

The sludge, obtained from the water treatment plant, was coated with chitosan (Wan et al. 2013). The binding capacity of Cu(II) of the so-obtained biocomposite increased with increasing pH (pH 2–4). Both adsorption and chelation were responsible for the retention of Cu(II). A monolayer adsorption occurred on the surface active sites (rendered by the repeating amine group). Longer contact time resulted in the reduction of adsorption capacity, which may be due to other metal ions leaching out from the sludge that gains positive charge and competes with Cu(II) for adsorption. The blending of chitosan with sludge (for wastewater treatment) provided an adsorbent with the high surface area, which resulted in the enhanced monolayer adsorption of Cu(II). In acidic medium, the constituting $NH_2$ groups are prone to protonation and thus, the pro-bending sites are made unavailable for Cu(II), thereby decreasing the adsorption capacity. An enhanced sorption of Cu(II) was observed as the pH shifted from 2 to 4, whereby suggesting the gradual domination of the chelation mechanism over surface adsorption. However, at a prolonged contact time, the desorption of the retained Cu(II) occurs, which may be due to the other competitive cations leaching off the composite adsorbent.

A sol–gel method (El-Deen and Zhang 2016) was followed to prepare a composite comprising of $TiO_2$

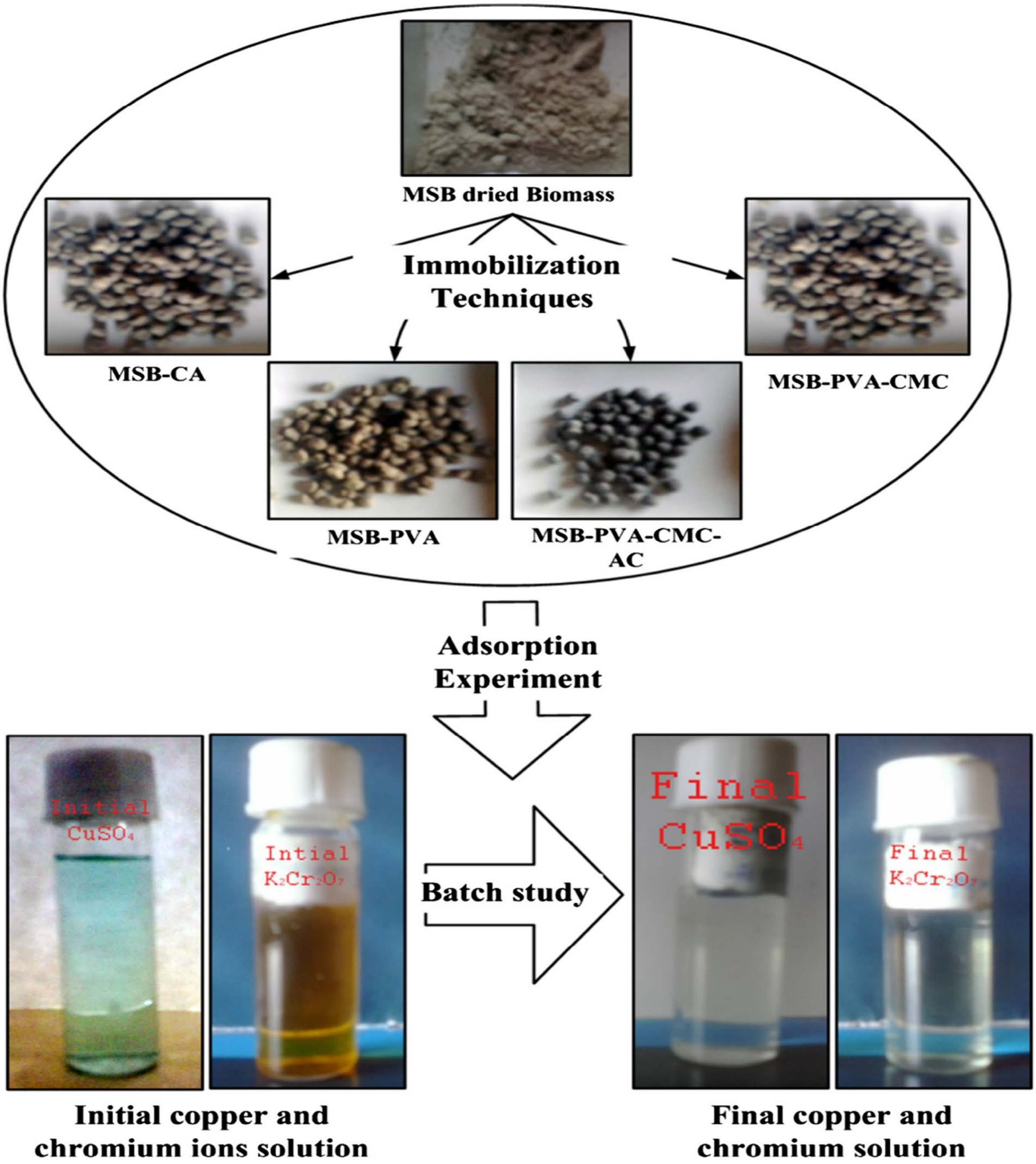

**Fig. 1** Immobilization of modified sludge biomass (MSB) using different immobilization approaches and subsequent application for metal removal (Ramteke and Gogate 2016)

nanoparticles and sewage sludge. This sorbent exhibited maximum adsorption capacity for Cd(II) at pH 6.0 and 3 h. The adsorption of Cd(II) onto the composite was governed by a combination of surface adsorption and intraparticle diffusion mechanism. A magnetic sludge composite was prepared by a facile co-precipitation method which has 78 $m^2\ g^{-1}$ surface area and 0.53 $cm^3\ g^{-1}$ pore volume (Wang et al. 2016). The composite was synthesized by immobilizing the $Fe_3O_4$ nanoparticles onto activated bio-sludge and employed for the removal of As(V) and Sb(V). The magnetic sludge composite was highly stable in acids and could be separated quickly from the solution by the application of a magnetic field. At pH 2.6, the positively charged protonated Fe species

**Table 1** Removal of heavy metals by various kinds of industrial by-product-/waste-based composite adsorption

| Adsorbent | metal ion | Experimental conditions | | | | Fitted models | | Adsorption capacity (mg/g) | References |
|---|---|---|---|---|---|---|---|---|---|
| | | Conc. (mg/L) | pH | Temp. | Adsorbent mass (g) | Kinetics | Isotherms | | |
| Free modified sludge biomass | Cu(II)<br>Cr(VI) | 100 | 5 ± 0.2 | 25 ± 0.2 | 0.1 | PFO | LM | 752.13<br>577.65 | Ramteke and Gogate (2016) |
| Modified sludge biomass-calcium alginate | Cu(II)<br>Cr(VI) | 100 | 5 ± 0.2 | 25 ± 0.2 | 0.1 | PFO | LM | 141.69<br>116.07 | Ramteke and Gogate (2016) |
| Modified sludge biomass-phosphorylated polyvinylalcohol gel | Cu(II)<br>Cr(VI) | 100 | 5 ± 0.2 | 25 ± 0.2 | 0.1 | PFO | LM | 307.89<br>204.83 | Ramteke and Gogate (2016) |
| Modified sludge biomass-phosphorylated polyvinylalcohol gel-chloromethylated cellulose-activated carbon | Cu(II)<br>Cr(VI) | 100 | 5 ± 0.2 | 25 ± 0.2 | 0.1 | PFO | LM | 614.91<br>410.45 | Ramteke and Gogate (2016) |
| Modified sludge biomass-phosphorylated polyvinylalcohol gel-chloromethylated cellulose | Cu(II)<br>Cr(VI) | 100 | 5 ± 0.2 | 25 ± 0.2 | 0.1 | PFO | LM | 604.91<br>404.45 | Ramteke and Gogate (2016) |
| Chitosan-coated sludge | Cu(II) | 100–2000 | 4.5 | | 2.5 | PSO | LM | 18.83 | Wan et al. (2013) |
| $TiO_2$/sewage sludge | Cd(II) | 5–100 | | 25 | 0.05 | PSO | LM | 29.8 | El-Deen and Zhang (2016) |
| Magnetic sludge | As(V)<br>Sb(V) | 0.01–0.5 | 2.6 | 50 | 1.4 | PSO | LM | 21.3<br>43.5 | Wang et al. (2016) |
| $CuFe_2O_4$/sludge | Sr(II) | | 10.25 | 50 | 0.05 | PSO | LM | 23.0 | Tu et al. (2016) |
| Ferric activated sludge | Pb(II) | | 5 | 25 | 0.06 | PSO | FM | 42.98 | Yang et al. (2016) |
| Bagasse/MWCNT composite | Pb(II) | 12.49–101 | 4.5 | 28 | 0.02 | EM | LM | 56.6 | Hamza et al. (2013) |
| Fly ash | Cr(VI) | 2–10 | 2 | 30 | 1.0 | – | LM | 1.3 | Banerjee et al. (2004) |
| Fly ash–Al | | | | | | | | 1.82 | |
| Fly ash–Fe | | | | | | | | 1.667 | |
| Fly ash | Hg(II) | 20–40 | 5.8 | 30 | 1.0 | – | LM | 11.0 | Banerjee et al. (2004) |
| Fly ash–Al | | | | | | | | 12.50 | |
| Fly ash–Fe | | | | | | | | 13.40 | |
| Steel slag/$Al(OH)_3$ | Cd(II) | 45–200 | 4 | 25 | 1.0 | PSO | LM | 10.16 | Duan and Su (2014) |
| Magnetic chitosan particles from steel slag | Ni(II)<br>Cu(II) | 100–1000 | | 25 | 1.0 | – | LM | 66.23<br>126.58 | Thuan et al. (2018) |
| Graphene/lignin/sodium alginate composite | Cd(II)<br>Pb(II) | 20–60<br>10–100 | 6 | 25 | 0.05 | PSO | LM | 80.32<br>224.72 | Zhou et al. (2018) |

*LM* Langmuir model, *FM* Freundlich model, *PFO* Pseudo-first order, *PSO* Pseudo-second order, *EM* Elovich model

forms outer-sphere complexes with As(V) and Sb(V) as $> FeOH_2^+ \cdot H_2AsO_4^-$ and $> FeOH_2^+ \cdot Sb(OH)_6^-$, respectively, and subsequently their dehydration may result in the formation of inner-sphere complexes (Fig. 2), as $> Fe–O–HAsO_3^-$ and $> Fe–O–Sb(OH)_5^-$, respectively. These inner complexes have stronger chemical bonds and are free of any interfering effects from co-existing anions, namely $Cl^-$, $NO_3^-$ and $SO_4^{2-}$. At $pH > 7$, the negatively charged surface of the composite repels the As(V) and Sb(V) anions, and hence restricts their further uptake. However, at $pH < 7$, the pro-active sites get reduced as the Fe species get leached out of the adsorbent, thereby decreasing the removal efficiency (Wang et al. 2016).

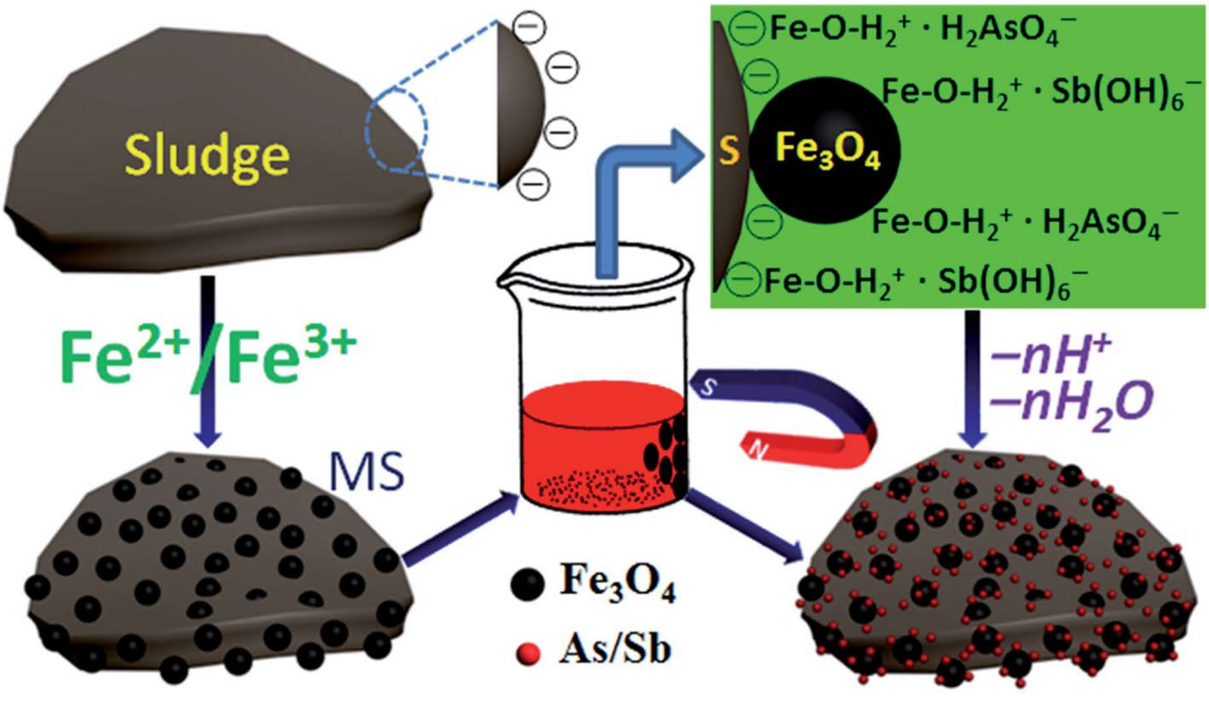

**Fig. 2** Schematic illustration of magnetic sludge (MS) synthesis and As(V)/Sb(V) removal (Wang et al. 2016)

The sludge discharged from the printed circuit board industry was used as a source for extracting Cu(II) through acid leaching and chemical exchange (with sacrificial $Fe^0$) (Tu et al. 2016). The extracted Cu(II) was then subjected to ferrite process to get $CuFe_2O_4$ nanocomposite, which was further employed for the removal of $Sr^{2+}$. The presence of co-existing metal ions including $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$ reduces the adsorption efficiency of $Sr^{2+}$. The routes of ion-exchange or outer-sphere complexation may be followed for its retention at $pH < 10$, while at $pH > 10$, inner-sphere complexation or surface precipitation may take place. This composite promises to remove the radiogenic $_{90}Sr$ nuclide from seawater, contaminated due to the release of $_{90}Sr$ after the 3/11 earthquake offshore of Japan. The composite magnetic nanoparticles ($CuFe_2O_4$) exhibited higher adsorption of $Sr^{2+}$ at $pH > 7.30$, thereby indicating the latter's stronger electrostatic interaction with hydroxyl groups comprising the adsorbent. Moreover, it was observed that at $pH > 10$, the retention of $Sr^{2+}$ (onto the composite) becomes independent of the ionic strength whereby suggesting the involvement of inner-sphere surface complexation or surface precipitation. However, at $pH < 10$, the dependency of the adsorption capacity on the ionic strength indicates the major pathways (for retaining $Sr^{2+}$) as ion-exchange and/or outer-sphere complexation. In presence of foreign/other coexisting cations, especially when the ratio of cation/$Sr^{2+}$ is greater than 100, a size-dependent resistance (of the other cations) against the uptake of $Sr^{2+}$ was observed. As for instance, $Mg^{2+}$was found to exert more hindrance, than $Ba^{2+}$, to the uptake of $Sr^{2+}$ onto the composite.

In another reported work (Yang et al. 2016), a mixture of sludge, from the municipal wastewater treatment plant, and ferric sulfate was subjected to pyrolysis to get a ferric-activated sludge biocomposite. Thus, a biocomposite with the enhanced surface area and high pore volume (due to increased mesopores and macropores) resulted in elevated adsorption capacity for $Pb^{2+}$ at pH 4–6. The mode of adsorption of $Pb^{2+}$ onto the biocomposite includes ion-exchange, precipitation and surface complexation (as $Fe\text{–}OPb^{2+}$). During ion exchange, $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$, were replaced by $Pb^{2+}$ and thus the former was released into the contacting medium (at pH 5). It was observed that $Pb^{2+}$ was precipitated into $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite), $Pb_2SiO_4$ and $Pb(SO_4)$. The authors also reported that leaching of $Pb^{2+}$ from the adsorbent depends on the availability of carbonate (within the adsorbent) to form $Pb_3(CO_3)_2(OH)_2$ precipitate according to the following reaction:

$$2HCO_3^- + 3Pb^{2+} + 4OH^- \rightarrow Pb_3\left(CO_3\right)_2(OH)_2 + 2H_2O \qquad (1)$$

The formation of $Pb^{2+}$ complex with the $\pi$–electrons of C=C groups, as well as, with iron hydroxides (as $Fe\text{–}OPb^+$) has been reported.

A composite was prepared by combining multi-walled carbon nanotube (MWCNT) with glutaraldehyde-crosslinked sugarcane bagasse (Hamza et al. 2013). The presence of MWCNT imparted mechanical robustness and enhanced metal-binding properties into the biocomposite, so that it could be used in harsh industrial environments. Moreover, the oxidation of MWCNT would introduce more oxygen-containing functional groups and hydrophilicity into the adsorbent. The entropy-driven adsorption, onto the biocomposite, reached its maximum capacity for Pb(II) in 120 min at pH 4.5.

## 2.2 Poultry Industry Waste Based Composite

The use of the poultry industry waste materials, like feathers and eggshell, as adsorbent materials for the removal of various kinds of organic and inorganic pollutants has been investigated. Annually, around 8.5 billion tons of waste is produced worldwide by the poultry based industries. The feather comprises of about 1.3% fat, 7.9% water and 91% protein with a large number of functional groups. These functional groups help in the binding of heavy metals during the adsorption process (Agrahari and Wadhwal 2010; Gao et al. 2014; Kumari and Sobhab 2016).

The synthesis of a biocomposite involving the barbs of *Dromaius novaehollandiae* and chitosan for the removal of Pb(II) is reported by Kumari and Sobhab (2016). Although the amino, hydroxyl, carboxyl and thiol groups (constituting the protein) get embedded within the matrix, the exposed amino and alcohol groups (contributed by chitosan) offer the active binding sites. The adsorption of Pb(II) onto the biocomposite occurred through complexation (with N and O groups), chemisorptions and ion-exchange at an optimum medium of pH 4.4. The adsorption of the Pb(II) was endothermic in nature and optimum removal was observed at 30 °C while following the pseudo-second-order kinetics. Moreover, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models were fitted to the experimental data and the Chi-square test indicated that the Langmuir model was the best fit to the experimental data. About 93.4% of Pb(II) was removed with the composite, constituting feathers of Dromaius novaehollandiae and chitosan, at pH 4. The adsorption of Pb(II) may have occurred due to its entrapment into the nanoporous network, as well as, electrostatic interaction with the constituting carboxylic groups. However, at $\mathrm{pH} < 4$, the competing $H_3O^+$ keeps Pb(II) from binding. Again at pH 4–9, the excessive presence of hydroxyl groups hinders the adsorption of Pb(II), by forming Pb(II) hydroxyl complexes.

Ahmad et al. (2012) synthesized the iron-oxide-coated eggshell composite via a facile co-precipitation method for the separation and removal of Cu(II). The uptake of the Cu(II) was found to depend on the solution pH and the initial metal ion concentrations. The results revealed that the maximum uptake of Cu(II) was observed at pH 6 and within 200 min. Moreover, the reusability of the spent composite was done with HCl solution. The optimum uptake was observed to be 44.843 mg/g and a decrease Cu(II) in removal was observed in the existence of Pb(II) and Ni(II).

## 2.3 Fly Ash-Based Composite

Fly ash is an industrial solid waste material mainly produced from the burning of the municipal waste, fossil fuel, thermal power plants, and other industries. Depending on the source of the materials being used for burning, the composition of fly ash may change. Generally, the main constituents of the fly ash are $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$, etc. (Lee et al. 2017). Banerjee et al. (2004) utilized the Fe and Al impregnated fly ash for the scavenging of Cr(VI) and Hg(II) from the wastewaters. The adsorption of both the metals was higher on the modified fly ash in comparison to the pure fly ash and the sorption of Cr(VI) and Hg(II) followed the Langmuir isotherm model. The adsorption of both Cr(VI) and Hg(II) metals was depended on the initial metal ion concentration and adsorption at high temperatures was favorable. The adsorption of both Cr(VI) and Hg(II) metals occurred through surface-complexation and ion-exchange reactions.

Adamczuk and Kołodynska (2015) synthesized the fly ash-coated chitosan for the removal of anionic and cationic metallic pollutants and investigated the kinetics, thermodynamic and isotherm for the metal ion adsorption. The removal of the metal ions obeyed the pseudo-second-order kinetics and Freundlich isotherm model. The maximum uptake of the Cr(III, VI), Cu(II), Zn(II) and As(V) was found to be 36.22, 28.65, 55.52 and 19.10 mg/g, respectively.

A cementitious composite, constituting fly ash and iron oxide nanoparticles involving the binder (NaOH and $Na_2SiO_3$), was prepared by the Maiti et al. (2018) for the scavenging of metallic ions and degradation of the organic dyes. The adsorptive removal of the Pb(II), Cu(II), Cd(II) and Cr(III) at the various studied parameters is shown in Fig. 3. As Fig. 3 depicts, the uptake of the metals ions rises with the increase in the initial solution pH, solution temperature, reaction time and initial metal ions concentrations. The highest adsorption was observed for Pb(II) (82.2 mg/g) while Cr(III) exhibited the lowest affinity (24.6 mg/g) for the composite adsorbent.

## 2.4 Red Mud-Based Composite

Red mud is a highly alkaline by-product from the alumina production industry, majorly constituting Al, Fe, Si $TiO_2$ and other metal oxides. The annual production of the red mud is around 90 million tons worldwide (Rashad 2013). Due to the presence of these metal oxides, red mud shows a good adsorption for the separation and removal of the organic and inorganic contaminants from effluents. Although a lot

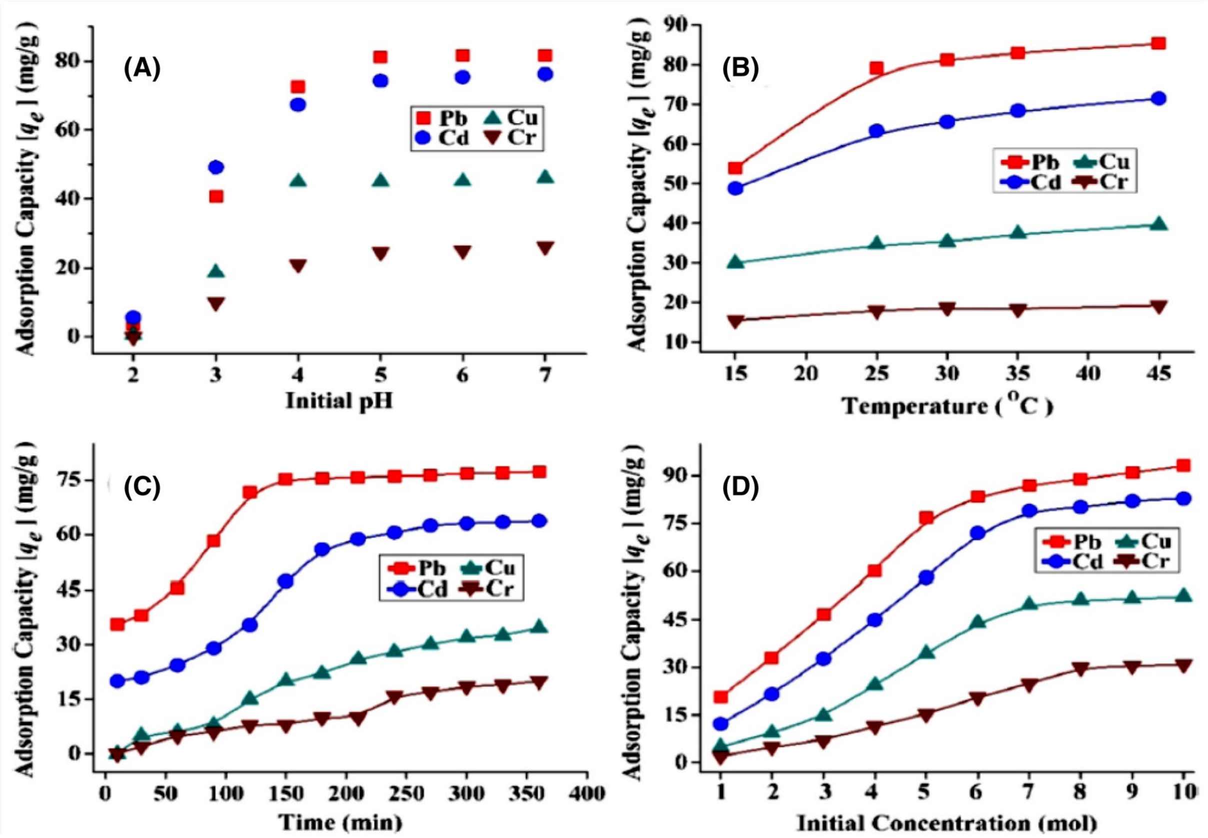

**Fig. 3** Effects of **a** pH, **b** temperature, **c** time, and **d** initial concentration on adsorption performance (Maiti et al. 2018)

of works have already been published on the use of pure red mud as an adsorbent, very few articles have been reported on the red mud-based composite adsorbents.

Khan et al. (2015) used the iron oxide-activated red mud for the elimination of the Cd(II) at the optimized experimental conditions such as pH 6, interaction time 1.5 h at the 298 K and the optimum uptake of Cd(II) was 117.64 µg/g. The adsorption of Cd(II) was spontaneous in nature and followed the pseudo-order kinetics with intra- and film diffusion mechanism. Around 91% of the Cd(II) could be recovered from the saturated adsorbents, while the regenerated adsorbent was effectively capable of removing Cd(II) up to five cycles.

Carbon nanotubes (CNTs) are well known-adsorbent with high adsorption capacity but its agglomeration properties hindered its applications at large scale. In order to overcome this problem, several authors used the composite of the CNTs to enhance its properties and to avoid the agglomeration (Gupta et al. 2013; Kumar et al. 2013b).

Abbasi et al. (2016) synthesized the red mud/carbon nanotube composite by chemical vapor disposition method where the red mud was used as a catalyst. The so-obtained red mud/carbon nanotube composite was explored as a sorbent for the scavenging of Pb(II) ions. The results showed that the red mud/carbon nanotube composite (78 $m^2/g$) has a higher surface area compared to the pure red mud (11 $m^2/g$). Therefore, the adsorption capacity of the composite was higher than the red mud and 0.05 g composite showed the highest adsorption at pH 5 within 50 min of the equilibrium time.

A ternary hybrid composite of the red mud with iron oxide and alginate/chitosan was synthesized by García et al. (2017). The results showed that the chitosan-immobilized materials showed the highest removal of As(V) at 100 mg/g with the adsorbent dose of 2.5 g/L at pH 7. The results were best fitted to the Freundlich isotherm and pseudo-second-order kinetics.

## 2.5 Slag-Based Composite

Slag is the solid by-product that remains after the separation of the metal from the ore. Slag is mostly a mixture of various metal oxides and silicon oxides. It has been reported in the literature that the slag can be used for the removal of the nutrients, organic pollutants and metals ions. Generally, the porosity and the surface area of the slag is poor. Therefore, its internal surface sites cannot be used properly for the removal of the pollutant species, thereby resulting in low adsorption capacity. Several activation methods have been applied to enhance the adsorption properties of the slag. The synthesis of the slag-based composite is the most effective approach to enhance its sorption performance (Thuan et al. 2018).

Iron oxide-loaded melted slag, for the removal of As(II) and As(V), was synthesized by Zhang and Itoh (2005). The metal ions uptake potential of the modified slag composite was 2.5 and 3 times higher than FeOOH for As(II) and As(V), respectively. The role of the FeOOH and Ca and other components in the slag for the arsenic binding is as follows:

$$\mathrm{FeOOH} + 3\mathrm{H_2AsO_4^-} + 3\mathrm{H^+} = \mathrm{Fe\left(H_2AsO_4\right)_3} + 2\mathrm{H_2O}, \tag{2}$$

$$2\mathrm{H_2AsO_3^-} + \mathrm{Ca^{2+}} + n\mathrm{H_2O} = \mathrm{Ca\left(H_2AsO_3\right)_3} \cdot n\mathrm{H_2O}\ (\mathrm{pH} = 9 - 12), \tag{3}$$

$$2\mathrm{H_2AsO_4^-} + \mathrm{Ca^{2+}} + n\mathrm{H_2O} = \mathrm{Ca\left(H_2AsO_4\right)_3} \cdot n\mathrm{H_2O}\ (\mathrm{pH} = 2 - 7), \tag{4}$$

Duan and Su (2014) used aluminum hydroxide for the modification of the steel slag by mixing both in 4:3 mass ratios and heated at 700 °C for 2 h. The modified steel slag was applied as an adsorbent material for Cd(II) removal in the batch adsorption process. The applied models showed that the pseudo-second-order and Langmuir isotherm model are more suitable to describe the ongoing adsorption process. The authors suggested that Cd(II) removal by modified steel slag involved chemisorption including precipitation and coordination reactions.

## 2.6 Lignin-Based Composite

Lignin is a natural biopolymer which is largely produced in the biorefineries, pulp and paper, etc. industries and mainly composed of propyl-phenolic subunits having a variety of functional groups which depend on the origin of biomass from the lignin is extracted. The functional groups present on lignin act as the active sites for the binding of the pollutant species (Nair et al. 2014; Valls and Hatton 2003).

As reported by Nair et al. (2014), a solid waste of paper industries and cellulosic bioethanol industries, namely lignin, was impregnated into chitosan. The two components were held by weak bonding among 1,4-glycosidic linkage, amide, and hydroxyl of chitosan, and ether and hydroxyl groups of lignin. The composite with an equal ratio of its two components (chitosan and lignin) revealed the optimum removal of organic dyes and Cr(VI). In acidic conditions (at pH 5.9), the dye and Cr(VI) were retained by virtue of the electrostatic/chemical interaction of the constituents, namely protonated –NH and –OH groups of the adsorbent, with the carbonyl/sulfate and $\mathrm{HCrO_4}^-$ of dye and Cr(VI), respectively. A proposed mechanism for Cr(VI) adsorption is shown in Fig. 4. The authors reported that the prorogated

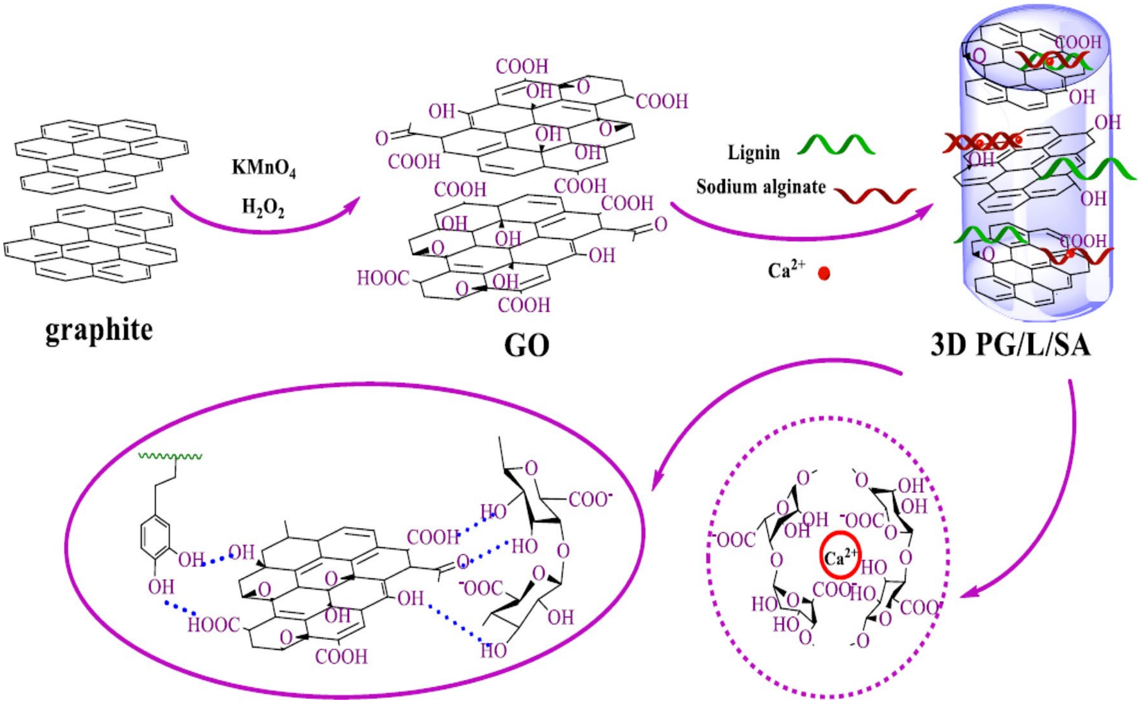

**Fig. 4** Schematic illustration of fabrication process and formation mechanism of 3D PG/L/SA (Zhou et al. 2018)

amine and hydroxyl groups attract the $HCrO_4^-$ anions electrostatically.

Zhou et al. (2018) recently synthesized the 3D nanocomposite graphene/lignin/sodium alginate by a hydrothermal method in aqueous solution for the scavenging of the Cd(II) and Pb(II). A schematic diagram of the synthesis of graphene/lignin/sodium alginate is shown in Fig. 5. The adsorption properties of graphene/lignin/sodium alginate were much higher than graphene and the optimum uptake capacity of Cd(II) and Pb(II) was 79.88 and 225.24 mg/g. The application of the prepared composite was also tested on the real sample (collected from the local smelter) whereby almost 100% scavenging for both metal ions was observed, while a comparatively lower adsorption for Cd(II) (28.41%) and Zn(II) (32.86%) was observed due to the presence of higher initial concentrations in wastewater.

Vecino et al. (2014) synthesized an alginate–vineyard pruning waste composite, for the separation and scavenging of a variety of nutrients and micronutrients from the winery wastewater using the batch adsorption method. The authors

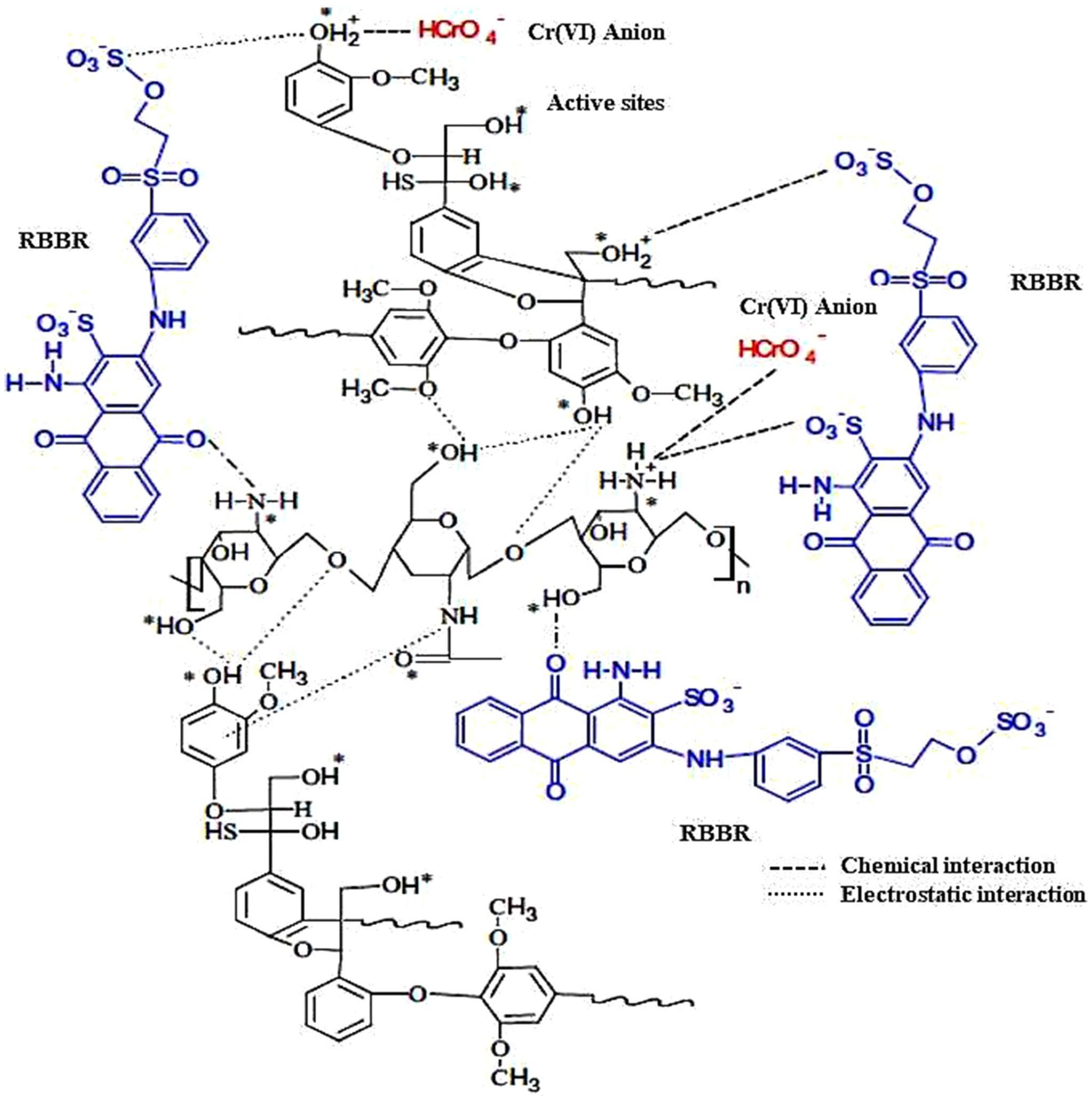

**Fig. 5** Mechanism of RBBR and Cr(VI) adsorption on 50ChAL composite. Asterisks (*) denote possible adsorption sites (Nair et al. 2014)

observed that the adsorbent, which was prepared by a mixture of 5 and 0.5% sodium alginate and vineyard pruning waste with 0.05 M $CaCl_2$, gave the best adsorption results and the removal of Mg(II) was 5.9 mg/g while 0.3 mg/g for Zn(II). Recently, Bustos et al. (2018) again used the winery industry waste (bio-oxidized grape marc) as an adsorbent by encapsulating it with calcium alginate for the removal of $CuSO_4$. The adsorbent exhibited fast removal whereby around 97.2% of $CuSO_4$ was removed within 5 min, while a maximum removal efficiency of 2785 mg/g was observed. Another interesting factor, observed by the authors, was that the sulfate ions were removed through precipitation as calcium sulfate.

## 3 Conclusions and Future Prospects

The abundant availability and low cost are the two major advantages of industrial waste-based adsorbents. The process of adsorption, by industrial waste, exhibited increment with increasing pH, reaction period, and adsorbent mass, while the reduction was observed with increasing particle size and ionic strength. The varying composition of the industrial waste-based adsorbents exhibited diversified physiochemical conditions for efficient adsorption. As for instance, every metal ion exhibited its own specific preferable pH range for maximum adsorption. The adsorption of the various heavy metals depends on the experimental conditions and nature of the adsorbents. This review revealed that industrial waste/by-products are good adsorbents for the removal of the heavy metals and can be used at a large scale for the wastewater purifications.

It is evident that recycling (of industrial waste) reduces the need for raw materials whereby reducing greenhouse-gas emissions and pollutants. It contributes to the conservation of resources, saving energy as well as the reduction of demand for landfill space. The performance of industrial waste-based adsorbent exhibited a strong dependency on its origin, chemical composition as well as morphology. Exploration of new dimensions, of industrial waste-based adsorbents, is required for enhancing its quantitative selectivity for target heavy metals. Hence, a sincere and committed effort is required for designing and modifying the adsorption system, especially for those involving the abundant low-cost industrial waste. Engineering of the constituents, of industrial waste, in the macro-, micro- and nano-level may open a new avenue for removal of heavy metals in complex environmental and/or biological conditions.

## References

Abbasi SM, Rashidi A, Ghorbani A, Khalaj G (2016) Synthesis, processing, characterization, and applications of red mud/carbon nanotube composites. Ceram Int 42:16738–16743

Adamczuk, Kołodynska D (2015) Equilibrium thermodynamic and kinetic studies on removal of chromium, copper, zinc, and arsenic from aqueous solutions onto fly ash coated by chitosan. Chem Eng J 274:200–212

Agrahari S, Wadhwal N (2010) Degrdation of chicken feather a poultry waste product by keratinolytic bacteria isolated from dumping site at Ghazipur poultry processing plant. Int J Poult Sci 9:482–489

Ahmad R, Kumar R, Haseeb S (2012) Adsorption of $Cu^{2+}$ from aqueous solution onto iron oxide coated eggshell powder: evaluation of equilibrium, isotherms, kinetics, and regeneration capacity. Arabian J Chem 5:353–359

Ahmad R, Kumar R, Laskar A (2013) Adsorptive removal of $Pb^{2+}$ from aqueous solution by macrocyclic calix [4] naphthalene: kinetic, thermodynamic, and isotherm analysis. Environ Sci Poll Res. 20:219–226

Ahmad SSHM, Chuong CS, Khatoon A, Wani WA, Kumar R, Rafatullah M (2015a) Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater. RSC Adv 5:30801–30818

Ahmad A, Siddique JA, Laskar MA, Kumar R, Khatoon A, Setapar SHM (2015b) New generation amberlite XAD resin for the removal of metal ions: a review. J Environ Sci 31:104–123

Ahmad A, Khatoon A, Mohd-Setapar SH, Kumar R, Rafatullah M (2016) Chemically oxidized pineapple fruit peel for the biosorption of heavy metals from aqueous solution. Desal Water Treat 57:6432–6442

Ahmaruzzaman M (2011) Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. Adv Colloid Interface Sci 166:36–59

Ahmed MJK, Ahmaruzzaman M (2016) A review on potential usage of industrial waste materials for binding heavy metal ions from aqueous solutions. J Water Pro Eng 10:39–47

Ansari MO, Kumar R, Ansari SA, Ansari SP, Barakat MA, Alshahrie A, Cho MH (2017) Anion selective pTSA doped polyaniline@graphene oxide-multiwalled carbon nanotube composite for Cr(VI) and Congo red adsorption. J Colloid Interface Sci 496:407–415

Banerjee SS, Joshi MV, Jayaram RV (2004) Removal of Cr(VI) and Hg(II) from aqueous solution using fly ash and impregnated fly ash. Sep Sci Technol 39:1611–1629

Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arab J Chem 4:361–377

Barakat MA, Al-Ansari AM, Kumar R (2016) Synthesis and characterization of Fe–Al binary oxyhydroxides/MWCNTs nanocomposite for the removal of Cr(VI) from aqueous solution. J Taiwan Inst Chem Eng 63:303–311

Bustos G, Calvar S, Vecino X, Cruz JM, Moldes AB (2018) Industrial symbiosis between the winery and environmental industry through the utilization of grape marc for water desalination containing copper(II). Wat Air Soil Pollut 229:36

Devi P, Saroha AS (2016) Improvement in performance of sludge-based adsorbents by controlling key parameters by activation/modification: a critical review. Cri Rev Environ Sci Technol 46:1704–1743

Devi P, Saroha AK (2017) Utilization of sludge based adsorbents for the removal of various pollutants: a review. Sci Tot Environ 578:16–33

Duan J, Su B (2014) Removal characteristics of Cd(II) from acidic aqueous solution by modified steel-making slag. Chem Eng J 246:160–167

El-Deen SEAS, Zhang FS (2016) Immobilisation of $TiO_2$-nanoparticles on sewage sludge and their adsorption for cadmium removal from aqueous solutions. J Exper Nanosci 11(4):239–258

Gao P, Li K, Liu Z, Liu B, Ma C, Xue G, Zhou M (2014) Feather keratin deposits as biosorbent for the removal of methylene blue from aqueous solution: equilibrium, kinetic and thermodynamic studies. Water Air Soil Poll 225:1946

García ML, Cabanas MM, Teresa Vilariño T, Lodeiro P, Barro PR, Roberto H, Barriada JL (2017) New polymeric/inorganic hybrid sorbents based on red mud and nanosized magnetite for large scale applications in As(V) removal. Chem Eng J 311:117–125

Gupta VK, Kumar R, Nayak A, Barakat MA, Saleh TA (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv Colloid Interface Sci 191–193:24–34

Hamza IAA, Martincigh AABS, Ngila JC, Nyamori VO (2013) Adsorption studies of aqueous Pb(II) onto a sugarcane bagasse/multi-walled carbon nanotube composite. Phys Chem Earth 66:157–166

Khan TA, Chaudhry SA, Ali I (2015) Equilibrium uptake, isotherm and kinetic studies of Cd(II) adsorption onto iron oxide activated red mud from aqueous solution. J Mole Liq 202:165–175

Khaskheli MI, Memon SQ, Chandio ZA, Jatoi WB, Mahar MT, Khokhar FM (2016) Okra leaves—agricultural waste for the removal of Cr(III) and Cr(VI) from contaminated water. Am J Anal Chem 7:395–409

Kumar R, Ansari MO, Barakat MA (2013a) DBSA doped polyaniline/multi-walled carbon nanotubes composite for high efficiency removal of Cr(VI) from aqueous solution. Chem Eng J 228:748–755

Kumar R, Kumar M, Ahmad R, Barakat MA (2013b) L-methionine modified Dowex-50 ion-exchanger of reduced size for the separation and removal of Cu(II) and Ni(II) from aqueous solution. Chem Eng J 218:32–38

Kumar R, Khan MA, Haq N (2014) Application of carbon nanotubes in heavy metals remediation. Cri Rev Environ Sci Technol 9:1000–1035

Kumar R, Barakat MA, Alseroury FA (2017) Oxidized g-$C_3N_4$/polyaniline nanofiber composite for the selective removal of hexavalent chromium. Sci Rep 7:12850

Kumari AR, Sobhab K (2016) Removal of lead by adsorption with the renewable biopolymer composite of feather (Dromaiusnovaehollandiae) and chitosan (Agaricusbisporus). Environ Technol Innov 6:11–26

Lee Y, June TS, Zhang S, Ahn J, Park MB, Ahn WS (2017) Synthesis of nanoporous materials via recycling coal fly ash and other solid wastes: a mini review. Chem Eng J 317:821–843

Maiti M, Sarkar M, Malik MA, Xu S, Li Q, Mandal S (2018) Iron oxide NPs facilitated a smart building composite for heavy metal removal and dye degradation. ACS Omega 3:1081–1089

Mohammed AS, Kapri A, Goel R (2011) Heavy metal pollution: source, impact, and remedies. In: Khan M, Zaidi A, Goel R, Musarrat J (eds) Biomanagement of metal-contaminated soils. Environmental pollution, vol 20. Springer, Dordrecht

Nair V, Panigrahy A, Vinu R (2014) Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater. Chem Eng J 254:491–502

Neznakomova M, Boteva S, Tzankovn L, Mohamed E (2018) Nonwoven textile materials from waste fibers for cleanup of waters polluted with petroleum and oil products. Earth Syst Environ 2:413–420

Ramteke LP, Gogate PR (2016) Treatment of water containing heavy metals using a novel approach of immobilized modified sludge biomass based adsorbents. Sep Purif Technol 163:215–227

Rashad AM (2013) Alkali-activated metakaolin: a short guide for civil engineer—an overview. Constr Build Mater 41:751–765

Siddiqui S, Otaif K, Laskar MA (2016) Characterization and efficacy of a new generation scavenger of heavy metal pollutant: a green method of remediation of wastewater. Int J Environ Sci Technol 13:2951–2960

Thuan LV, Chau TB, Ngan TTK, Vu TX, Nguyen DD, Nguyen MH, Thao DTT, Hoai NT, Sinh LH (2018) Preparation of cross-linked magnetic chitosan particles from steel slag and shrimp shells for removal of heavy metals. Environ Technol 39:1745–1752

Tu YJ, You CF, Zhang Z, Duan Y, Jing F, Xu D (2016) Strontium removal in seawater by means of composite magnetic nanoparticles derived from industrial sludge. Water 8:357

Valls RG, Hatton TA (2003) Metal ion complexation with lignin derivatives. Chem Eng J 94:99–105

Vecino X, Devesa-Rey R, Moldes AB, Cruz JM (2014) Formulation of an alginate-vineyard pruning waste composite as a new eco-friendly adsorbent to remove micronutrients from agroindustrial effluents. Chemosphere 111:24–31

Wan MW, Wang CC, Chen CM (2013) The adsorption study of copper removal by chitosan-coated sludge derived from water treatment plant. Int J Environ Sci Develop 4:545–551

Wang L, Wang J, Zhang R, Liu X, Song G, Chen X, Wang Y, Kong J (2016) Highly efficient As(V)/Sb(V) removal by magnetic sludge composite: synthesis, characterization, equilibrium, and mechanism studies. RSC Adv 6:42876

Yang X, Xu G, Yu H (2016) Removal of lead from aqueous solutions by ferric activated sludge-based adsorbent derived from biological sludge. Arab J Chem. https://doi.org/10.1016/j.arabjc.2016.04.017 **(in Press)**

Zhang FS, Itoh H (2005) Iron oxide-loaded slag for arsenic removal from aqueous system. Chemosphere 60:319–325

Zhou F, Feng X, Yu J, Jiang X (2018) High performance of 3D porous graphene/lignin/sodium alginate composite for adsorption of Cd(II) and Pb(II). Environ Sci Pollut Res 25:15651–15661