ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 15, No. 2 (2014)

Review

Use of Composite Sorbents for the Removal of Copper (II) ions from Aqueous Solution

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Received 08 August 2014, Revised 19 November 2014, Accepted 19 November 2014

Abstract

Composite adsorbents are synthesized from two or more materials with different chemical and physical properties in order to increase their selectivity and the reusability. Researchers have developed and applied several novel composite materials for enhancing the removal of heavy metal. In this review, extensive list of composites developed via advanced technologies with specified characteristics for the removal of Cu (II) ion are discussed. Emphases on their adsorption capacities, reusability, desorption and regeneration with improved mechanical strengths are presented. Conclusively, prospects and other challenges to be checked and addressed in future are outlined.

Keywords: Composite; Adsorption; Cu (II) ions; Desorption; Aqueous.

Introduction

Heavy metal pollution produced in industrial wastewater is a major issue throughout the world. In particular, Cu (II) ions, whose sources are metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray are used intensively [1]. The effect on human health and aquatic life are regarded as harmful, and of course are not biodegradable therefore, the removal in an effective manner from water and wastewater is, thus, ecologically very important.

Several researchers have reported and established technologies for the recovery of metals from wastewater, which include chemical precipitation [2], flotation [3], biosorption [4-6]. Among the various methods described, adsorption is the most promising method that has been successfully applied for the purification and recovery of Cu (II) ions from effluents, due to its high efficiency, easy handling and availability [7]. However, due to their low mechanic intensity, limited reusability and relative low adsorption capacity, there is a shift from expensive commercial activated carbon to low cost eco-friendly and readily available adsorbent [8].

The adsorption capacity of various adsorbents for Cu (II) ions removal has been reported, some of them are kaolinite, montmorrillonite, palm ash, zeolite, activated carbon fiber glycidyl methacrylate chelating resin containing Fe_2O_3 particles and alginate-activated carbon [9-12]. These adsorbents were effective, however, inability to separate the adsorbate from the adsorbent effectively after wastewater treatment has paved way for advanced technologies. Composites both inorganic and organic materials may be used as binding materials for effective removal of heavy metals [13]. Composites can be defined as natural or synthesized materials made from two or more materials with significantly different physical and chemical properties which remain separate and

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distinct at the microscopic or macroscopic scale within the material. Moreover, their high reactivity and excellent selectivity towards specific pollutant makes it a promising and attractive alternative adsorbent [14].

Composites are synthesized to combine the desired properties of the materials. In nano composite, nano particles (such as clay, metal, carbon nanotubes, e. t. c.) act as fillers in a matrix. Polymer–clay composites may offer combined properties; represent an improvement upon thermal, mechanical and porosity properties compared with the homogenous characteristics of the bare individual clay and polymer components [14]. In this review, the uses of different composites adsorbents obtained through various techniques by several researchers are reviewed; shortcomings and future challenges are discussed.

Ca-Alg$_2$/GO gel beads composite

Alginate materials have biocompatibility and relatively low cost compared to polymer materials [15]. Alginate is a binary heteropolymer containing varying proportions of 1, 4-linked α –L guluronic acid (G-blocks) and β–D–mannuronic acid (M-blocks) units in a pyranose form, arranged in linear blocks. Alginates are porous in structure with high affinity for various metals. Papageogiou *et. al.,* investigated the ability of calcium alginate (Ca-Alg$_2$) to adsorb Cu^{2+} ions from aqueous solutions and discovered the maximum adsorption capacity of Cu^{2+} ions was 88.95 mg/g, due to the high M- /G block ratio. Also, Gotoh *et. al.,* prepared alginate - chitosan hybrid gel beads and found the adsorption of Cu^{2+} ions on the beads very rapid, reaching equilibrium within 10 min with a maximum adsorption capacity of 70 mg/g [16].

Moreover, Li and Ba investigated Ca-Alg$_2$/CNTs composite. It was found to have a high Cu^{2+} ion adsorption capacity of 84.9 mg/g in wastewater treatment applications [17]. Algothmi *et al.,* studied Ca-Alg$_2$/GO (prepared using sol gel chemistry technique) as a novel composite for the removal of Cu (II) ion in waste water [18]. Graphene oxide (GO) is the main structural element of graphite connected together via van der Waals forces. GO contains hydroxyl, epoxy, diol, ketone and carboxyl functional groups which are randomly assembled at edges and basal planes. Therefore, these functional groups make GO sheets strongly hydrophilic and compatible with biopolymers [19]. Naphthalene was also used as a drying agent as it causes less damage to the beads than other higher temperature dehydration methods and does not cause the dried beads to shrink [20]. The adsorption isotherm data was fitted using Langmuir isotherm. The maximum adsorption capacity is 60.2 mg/g at adsorption equilibrium of 45min. The adsorption kinetic data were described by pseudo second order kinetic equation showing that the Ca-Alg$_2$/GO has higher kinetic adsorption rate at 0.0179 g/mg. Fig. 1(a) and (b) shows the SEM images of Ca-Alg$_2$ and Ca-Alg$_2$/GO, respectively. In (Fig. 1a), there are limited porous structures observed in Ca-Alg$_2$ dehydrated beads while in (Fig 1b) more defined porous structures can be observed in Ca- Alg$_2$/GO gel beads (Fig. 1b), circled have pore sizes ranging from 1 to 5 µM.

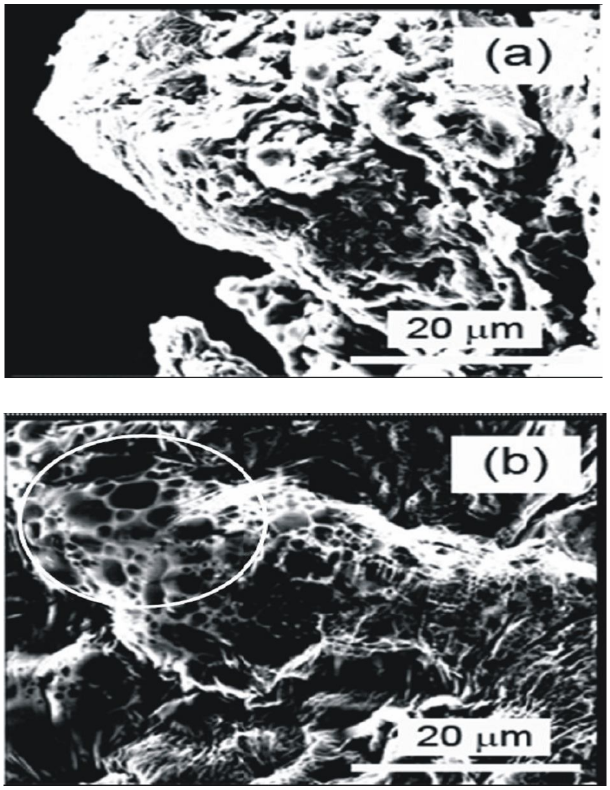

Figure 1. **FIB/SEM images of (a) Ca-Alg$_2$ and (b) Ca-Alg$_2$/GO gel beads after drying in molten naphthalene. Circled image in (b) indicates more defined porous structures in Ca-Alg$_2$/GO gel beads (b), circled have pore sizes ranging from 1 to 5 µM. [18] Reproduced with permission from publisher. Source.**

Diethylenetriamine-grafted poly(glycidyl methacrylate)

Diethylenetriamine-grafted poly (glycidyl methacrylate) adsorbent is an amine functionalized absorbent derived from diethylenetriamine (DETA) grafted onto poly (glycidyl methacrylate) (PGMA) micro-granules. The high content amine (amine groups) have been found to be one of the most efficient functional groups [17, 21] hence, positive effects on the effectiveness, capacity, selectivity and reusability of this adsorbent [22]. Different authors have reported amine-containing compounds being immobilized onto various substrates including polyacrylonitrile fiber, activated carbon [22], MCM- [22, 23], cellulose [24] for the removal of heavy metal. Paredes *et al.,* reported that polyglycidyl methacrylate has good mechanical strength and high reactivity of the epoxy groups for surface grafting, it is also used in column chromatography in industries.

Liu *et. al.,* reported that the grafting was achieved through a reaction between an amine group of DETA with an epoxy group of PGMA and the adsorbent showed excellent adsorption performance for copper ions at solution pH >3. Formation of surface complex with the neutral amine groups on the adsorbent and higher solution pH values resulted in better adsorption performance of Cu (II) ions on the adsorbent in the pH range of 1–5. Ionic strength improved maximum adsorption capacity was found to be 1.5 mmol/g at the solution pH value of 5, resulting into faster adsorption kinetics. The adsorption kinetics closely followed the pseudo-second-order kinetic model, indicating the importance of chemical adsorption in the process. Adsorption isotherm data were best fitted with the Langmuir–Freundlich isotherm model. Different HNO_3 solutions were used in desorption which showed that the acidic conditions greatly affected the desorption performance and 0.1 M HNO_3 solution achieved the best desorption efficiency, with 80 % of the desorption efficiency being completed in the first 1 min. PGMA-DETA adsorbent can be effectively reused five times for copper ion adsorption without any significant loss in the adsorption capacity [25].

Humic acid-immobilized polymer/bentonite composite

Humic acid-immobilized polymer/ bentonite composite, a novel product prepared by direct intercalation polymerization technique by immobilizing humic acid (HA) onto amine-modified polyacrylamide/bentonite. Anirudhan and Suchithra prepared amine-modified polyacrylamide/ bentonite. The multifunctional character is due to the presence of various phenolic, carboxyl and hydroxyl groups in addition to skeleton of aliphatic or aromatic units in weakly acidic to basic media. The adsorption of metal ion was enhanced by these carboxylic and phenolic groups through electrostatic interactions and surface complexation. The percentage loading increased to about 95 % with maximum monolayer adsorption capacity as high as 108.08 mmol /g, with a pH of 6.0 at 30^oC. The adsorption followed pseudo second order equation and rate constant decreases with increase in concentration of Cu (II) ions. Thermodynamic parameters showed that adsorption process is endothermic therefore influence of enthalpy change is prominent than entropy change. Large desorption and regeneration efficiency with 0.1 M HCl was recorded. Possibility of reuse for four cycles consecutively was reported [26].

Magnetic Cu (II) ion imprinted composite adsorbent

A novel method was studied to prepare magnetic Cu (II) ion imprinted composite (Cu (II) – MICA) to remove Cu (II) in wastewater treatment. This was achieved by synthesizing waste fungal mycelium from industry, chitosan (CS) and Fe_3O_4 nanoparticles combining with metal imprinting technology. Chitosan conjugated Fe_3O_4 nanoparticles for the removal of Cu (II) has been reported with a disadvantage of being nonselective [20]. Berger *et. al.,* reported Fe_3O_4 magnetic nanoparticles preparation and Cu (II) – MICA preparation, based on metal imprinting technique [11]. The character analyses indicated that the Cu (II) – MICA had a diameter of about 40 µm, with many tiny interspaces structure on the surface and possess amido and hydroxide groups which could chelate with Cu (II). The spinel structure of Fe_3O_4 did not change during the synthesis process. Cu (II)–MICA was nearly super paramagnetic while Ms and Mr values were 91.0 % and 92.4 % lower than that of Fe_3O_4. (Fig. 2) shows the preparation of Cu (II) MICA, with regeneration carried out by washing the adsorbent with 0.2M NaOH for 1.0 h.

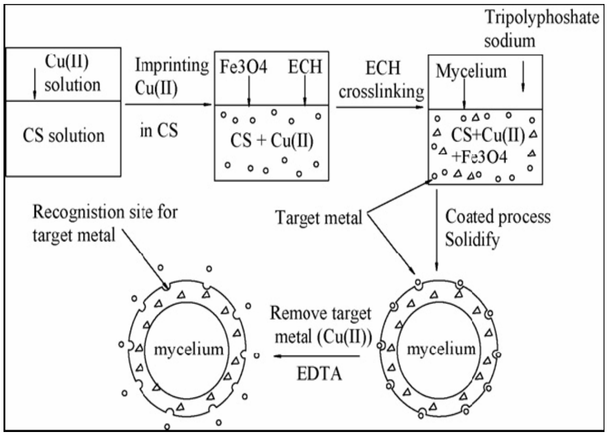

Figure 2. **preparation schematic of Cu (II)-MICA composite [27]. reproduced with permission from publisher. Source: Ren *et al.*, 2008.**

The Langmuir adsorption isotherm fit the adsorption equilibrium data most. The maximum adsorption capacity is 71.36 mg /g at 25 EC and pH 5.5. It also showed a metal ion affinity in the competitive conditions for Cu (II)> Zn (II)> Ni (II). Magnetic separation results showed that settling time was shortened by 180s. It can be used five times with an adsorption capacity loss of about 14–15 %. It is a cost-effective, easy separation adsorbent and has good practical prospects in the wastewater treatment industry. Kinetic studies showed that the adsorption process obeyed pseudo-second-order rate mechanism with an initial adsorption rate of 253.2 g/mg. (Table 1) reviews k_d, k and k values of Zn (II) and Ni (II) with respect to Cu (II). A comparison of the K_d values for the Cu (II) imprinted adsorbent with the control samples showed an increase in K_d for Cu (II) while K_d decrease for Zn (II) and Ni (II). This shows that imprinted beads indicate selectivity for the target molecule (i.e. Cu (II) ions) due to molecular geometry The Cu (II) sorption capacity of the Cu(II)-MICA was much higher than that for other metal ions and can be determined in the presence of Zn (II) and Ni (II) interference.

Table 1. **K_d, K and K values of Zn (II) and Ni (II) with respect to Cu (II) [27] Reproduced with permission from publisher.**

Metal ion	MNICA		Cu(II)-MICA		K^I
	K_d(mL/g)	k	k_d(mL/g)	K	
Cu(II)	124	-	210	-	-
Zn(II)	116	1.07	85	2.47	2.31
Ni(II)	58	2.13	37	5.67	2.6

Sewage sludge/industrial sludge-based adsorbent

Sewage sludge/industrial sludge-based is a complex adsorbent derived from industrial sludge consisting of sewage sludge and waste oil sludge was achieved by pyrolysis technique. The reason for the effectiveness of this composite was as a result of new chemical entities present on the surface such as basic pH, presence of catalytic centers based on iron and other transition metal forming solid state reaction, surface chemistry, porosity and high volume of pores. The condition of pyrolysis was adjusted in an inert atmosphere at 650 or 950^0C, either as single components or as 50:50 mixtures [28, 29]. The high removal ability of materials obtained at 650^0C is as a result of cation exchange reactions between calcium and magnesium in aluminosilicates, formed on their surface during heat treatment, and copper. On the other hand, Robertson and Leckie, 1998 indicate that the high degree of mineralization of the surface of the materials obtained at 950^0C promotes copper complexation and its surface precipitation as hydroxides or hydroxylcarbonate entities [30]. This is responsible for change in porosity [29].

Bentonite–polyacrylamide composite

Bentonite is effective due to its high swelling ability and cation exchange capacity. Bentonite is classified as a smectic soil composed of an expandable 2:1 type of alumino silicate clay mineral and also consists of flat particles with characteristic size of about 102 to 103 nm with negatively charged surface ions and sodium counter ions [31]. Bentonite was embedded in the polyacrylamide (PAAm) gel to form bentonite polycrylamide composite for the removal of Cu (II) ion. BENT PAAm performs effectively in the sorption of Cu (II) ion be due to its strong coordination between Cu(II) and the nitrogen on the surface of BENT–PAAm. The removal of Cu (II) ion increased from about 9 % to 97 % at pH ranging from 2.4 to 7, increased with increasing temperature, and decreasing ionic strength. The sorption of Cu (II) of BENT–PAAm was an endothermic and irreversible reaction. This composite showed higher adsorption capacity with increase from 29 to 33 mg/g at pH 6.2 and follows Langmuir Isotherm model. Ozcan *et. al,* revealed that E value is in the range of 8 – 16 kJ/mol [32], indicating that sorption is governed by chemical ion-exchange according to the theory of D–R mode. Both enthalpy and entropy change for BENT-PAAm is higher due to large activation energy [33].

Amine-functionalized silica magnetite composite

Amine-functionalized silica magnetite, $NH_2/SiO_2/Fe_3O_4$, was synthesized by surface modification of Fe_3O_4 with SiO_2 and N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TPED) containing amino functional groups with a cationic charge that can adsorb anionic pollutants by means of electrostatic attraction [19] TPED behaved as an anionic or cationic adsorbent. The pH value of the aqueous solution was adjusted to make amino groups protonic or neutral. The most efficient functional group for the removal of Cu (II) ion is neutral nitrogen of amine group with a lone pair electron [34, 35, 36]. Adsorption kinetic is best described by a pseudo- second order model and the derived activation energy for Cu (II) ions is 26.92 kJ and decreasing ionic strength mol^{-1}). In adsorption–desorption cycles, $NH_2/SiO_2/Fe_3O_4$, were repeated three times using the same amine magnetic adsorbent resulting in a loss of approximately 13.6 %. The optimum conditions to desorb cationic and anionic adsorbates from $NH_2/SiO_2/Fe_3O_4$ were provided by a solution with 0.1 M HNO_3 for Cu (II) ions [23].

Pectin iron oxide magnetic nanocomposite adsorbent

Pectin, a component of higher plant cell walls is a structural polysaccharide with partially esterified polygalacturonic acid (PGA) [37]. Therefore, pectin can be used as bio-sorbent to remove Cu (II) ions from aqueous solutions. Pectin coated Iron oxide magnetic nano composite (PIOMN) adsorbent is prepared by iron salt co-precipitation method, followed by the direct encapsulation without cross linking with calcium ions. This method is promising due to complexation and decreasing ionic strength. When polyglacturonic acid (PGA) binds with Cu (II) it strengthens Cu-pectin interactions [38]. Mata *et. al.,* studied adsorption behavior of Cu (II) ions from waste water by Sugar-beet pulp pectin [39]. They use sugar beet-pulp pectin Xerogels for copper removal in a fixed bed column [40]. Sahu et al., also studied pectin coated iron oxide magnetic which was prepared by co-precipitation method, encapsulation and cross linking with calcium iron [41]. A binding method using glutatradehyde and adapic acid has been used to synthesize pectin iron oxide magnetic nano composites [42]. These nano composites have the advantages of pectin and magnetic properties. Gong *et. al.,* studied PIOMN adsorbent. The sorption kinetic data fitted best to pseudo second order model. Sorption Isotherms were described by both Langmuir and Freundlich equation with maximum adsorption capacity of 48.99 mg/g. Scanning Electron Microscope studies shows the diameter of PIOMN has 77 ± 5nm with a spherical shape. This adsorbent increases with increasing pH, confirming ion exchange and electrostatic force mechanism during adsorption process. Furthermore, desorption studies were investigated with 0.1 M HNO_3, 0.01 M EDTA and 0.1 M NaOH respectively. The adsorbent regenerated using 0.01 M EDTA is the most efficient, releasing 93.70 % of its original capacity after the first regeneration cycle, it reached 58.66 % of the original capacity after the fifth cycle [36].

Carboxymethyl - cyclodextrin conjugated magnetic nanoparticles

Cyclodextrin is a cyclic oligosaccharide consisting of seven -d-glucose units connected through - (1,4) linkages with a toroidal structure, truncated cones containing a polar cavity with primary hydroxyl groups lying outside and the secondary hydroxyl groups inside [43, 44]. Cyclodextrins can form inclusion complexes with a wide variety of organic and inorganic compounds in its hydrophobic cavity [44].

The novel nano adsorbent caboxylmethyl - cyclodextrin conjugated magnetic nanoparticles (CMCD-MNPs) are prepared by grafting Carboxymethyl - cyclodextrin onto the magnetite surface via carbodiimide method. Aqueous solubility and metal complexation potential can be altered by substituting functional groups on the outside of the cyclodextrin [45]. Moreover, metal ion complexes with cyclodextrins could have a wide range of applications in catalysis and molecular identification [46]. Hu *et. al.,* showed that the grafted CD on the MWCNT/iron oxides showed enhancement of the adsorption capacity because of the strong complexation abilities of the multiple hydroxyl groups in CD with the lead ions [47]. Furthermore, Anirudhan and Suchithra studied CMCD-MNPs, the kinetics of Cu (II) adsorption follows the pseudo second order model. The equilibrium data are fitted well by Langmuir model, adsorption of Cu (II) ions reached his equilibrium within 30 minutes and 90 % was adsorbed in 15 minutes. The adsorption of Cu (II) onto CMCD-MNPs was found to be temperature dependent. The maximum adsorption capacity for Cu^{2+} ions is estimated to be 47.2 mg/g at 25°C. The analyses of FTIR and XPS reveal that the oxygen atoms on CMCD-MNPs are the main binding sites in the formation of complexes. Treatment with citric acid and Na_2 EDTA solution for desorption of Cu (II) on CMCD-MNPs was effective [26].

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide formed from seven glucose molecules by -1-4-glucosidic linkages, giving a micro-environment of a chiral, hydrophilic outside and a hydrophobic interior cavity [48, 49]. More over, renewable, biodegradable characters and large number of active hydroxyl groups selectively makes cyclodextrin a promising adsorbent for Cu (II) ion removal from waste waters [50]. Zhao *et. al.,* investigated chemical modification of cyclodextrin through esterification and oxidation reactions and cross-linking of hydroxyl outside the interior cavity to produce the enhanced adsorption functions on heavy metal ions [3]. Cyclodextrin adsorbent CDA is a co-polymer resin formed from acrylic acid (AA) and Acrylamide (AM) by inverse suspension and redox titrations to remove Cu (II) ion from waste water. CDA hydrogel exhibited typically three-dimensional cross-link network structure. The significant increase in the adsorption capacity when the pH of the solution and the ionic strength increased was 107.37mg/g at 80 mg/l concentration of Cu (II) ion. Experimental data fitted best with the Freundlich equation model. The kinetic model results indicate that adsorption of Cu (II) ions onto the CDAA fits the quasi-second-order and Elovich equations [5].

High strength hydrogel

Hydrogel-based adsorbents are easy loading; it captures cations with simple chemicals in most cases, reusable and has the possibility of semi-continuous operation [51]. Moreover, they are functionalized with amino, hydroxyl, carboxyl, imidazole and hydrazine groups to demonstrate high capacities in removal of metal ions from aqueous solutions due to their complexing abilities [52]. The thermal, hydrolytic and chemical stabilities of hydrogels make them very promising in the field of water purification [53]. Katime *et. al.,* and Trakulsujarichok *et. al.,* reported that wettability and high swelling can facilitate adsorption of target metals because the swelling of three dimensional networks likely give specific surface area and more functional group exposed are readily approachable; while limitation in the mobility of functional group occurs by coordination resin which are poorly swollen in water [54, 55].

Poly (vinylpyrrolidone/ acrylic acid (PVP/AAc) co-polymer hydrogels was prepared to remove Cu (II) ions from aqueous solution with maximum adsorption capacity of 0.36 mmol/g [56]. Also, Cavus studied non-competitive removal of metal ions by poly (acrylic acid-co-methacrylamide) gels and found that the maximum adsorption capacity of the hydrogels was 0.64 mmol Cu^{2+} /g dry hydrogel. Lack of being reusable coupled with poor mechanical strength caused by highly swollen network is one of the serious drawbacks hindering the actual applications of hydrogels in metal ion removal.

Wang *et. al.,* investigated mechanically strong hydrogel prepared by photo initiated polymerization of oligo (ethylene glycol) methacrylate (OEGMA), 2-vinyl-4,6-diamino-1,3,5-triazine (VDT) and cross-linker N,N – methylene bisacrylamide (MBAA). A series of

P(OEGMA-co-VDT) hydrogels whose schematic molecular structure is depicted in (Fig. 3). Mechanical properties of the hydrogel are strengthened by the introduction of monomer VDT through self-bonding of diaminotriazine, therefore enhancing the adsorption of copper ion onto the hydrogel by chelation between amino group and the metal ion. The experimental adsorption data fits Langmuir isotherm most, the maximum adsorption capacity was calculated to be 1.1 mmol/g. 1 M HCL aqueous solution will desorbed Cu (II) ion from the hydrogel with the desorption efficiency of 99 %. Moreover, desorption capacity is maintained above 90 % with no significant loss in mechanical properties after six adsorption – desorption cycles [57].

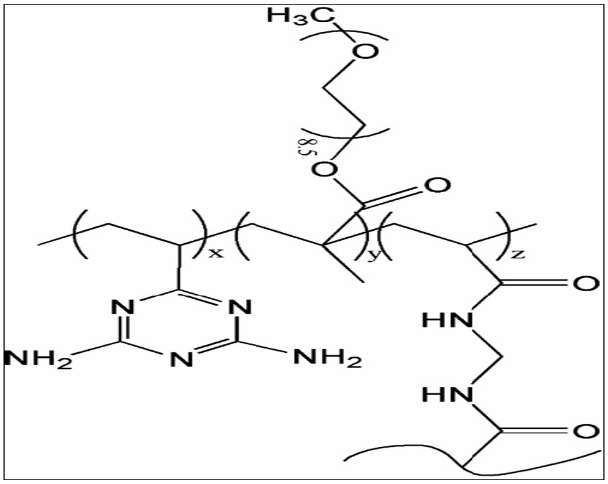

Figure 3. **Schematic molecular structure of P(OEGMA-co-VDT) hydrogel [57]. Reproduced with permission from publisher.**

Macroporous bead adsorbents based on poly(vinyl alcohol) / Chitosan (PVA/CS)

Poly(vinyl alcohol) (PVA) is a water-soluble material containing large amounts of hydroxyl groups. PVA has many advantages such as low cost, non-toxicity, biocompatibility, high durability and chemical stability [58, 59]. The macroporous PVA-based beads also showed a good removal for heavy metal from aqueous solution [60]. A lot of poly(vinyl alcohol) synthesized with different material has been investigated by different researchers. Yanfeng *et al.*, studied PVA/CS bead composites adsorbents, which were prepared by the interpenetrating polymer network (IPN) and cross linking process. It was discovered that the amino group and the hydroxyl group present in the PVA / CS bead adsorbent exhibits a synergistic effect on removal of heavy metals from wastewaters. The equilibrium data of Cu (II) ion were best fitted the Freundlich isotherm best while adsorption kinetics followed the pseudo-second-order kinetic model. In thermodynamics studies, adsorption process was found to be feasible and endothermic in nature. Initial metal concentration, contact time, pH, temperature and ionic strength were some of the factors that affect the adsorption process. After five cycles of adsorption–desorption operations, the re-adsorption capacities attained 76 – 88 % of initial adsorption values [61].

Iron oxide-coated zeolite

Natural zeolite, an alumino silicate mineral, possesses characteristics of large surface area, strong capability of ion exchange and adsorption due to their particular tetrahedral pore framework. Also, they are one of low-cost and easily obtainable materials which have been used as adsorbent for removal of heavy metals [62, 63]. In order to enhance the sorption capacity of natural zeolite for heavy metal ions, some metal oxides such as manganese, aluminum oxides having higher affinity towards metal were used [64]. Manganese oxide coated Zeolite (MOCZ) used to adsorb Cu (II) ion [4]. Thomas model was found to be suitable for describing the adsorption process of the dynamic behavior of the MOCZ column. The total adsorbed quantities, equilibrium uptake and total percentage of Cu (II) ions removal related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different conditions. The removal of copper and lead ion by MOCZ columns was in descending order: Pb (II) > Cu (II). The adsorbed copper and lead ions were easily desorbed from MOCZ with 0.5 mol^{-1} HNO_3 solution. Han studied iron oxide coated on the surface of zeolite which was a promising adsorbent for the removal of Cu (II) ion. The initial region of breakthrough curve was defined by Adams –Bohart model while Thomas described the whole breakthrough process. Adsorption process strongly depends on the flow of rate, the initial Cu (II) concentration and depth. The mass transfer model provides a good agreement with experimental data. The saturated column was regenerated by 1 mol^{-1} hydrogen chloride solution and IOCZ could be reused in Cu (II) ion removal [4].

Chemically functionalized silica gel

Silica gel has large surface area and is easily modified, which makes it an effective carrier. AMPS have amide, sulfonic, and carbonyl groups that could bind metal ions thereby making AMPS a functional polymer. Also, others such as amine group have been reported by Haung et. al., Glerup et. al. and Zoubolis *et. al.,* as one of the most efficient functional group in removing metal ions [5, 33, 65]. Deng *et. al.,* investigated on poly acrylonitrile as effective function al group for the adsorption of Cu (II) ion [21]. Torress also studied on cellulose an effectual material for the removal of Cu (II) ion [24]. Moreover, Wang et al., investigated the grafting of AMPS(2 – acrylamido-2-methylpropanesulfonic acid) on silica gel to obtain adsorbent which functions with methacryloxypropyl trimethoxy silane reagent. The adsorption capacity increased with increasing pH while the adsorption kinetics showed that the data fitted well, the pseudo second order kinetic model. The adsorption obeyed both Freundlich and Langmuir Isotherms. The Thermo gravimetric analysis shows that surface modification reaction introduced some organic functional groups onto the surface of silica. The maximum copper (II) ion capacity was 19.9 mg/g. HNO_3 solution was used as the desorbing solution and the adsorption capacities remain stable after three adsorptions and desorption respectively [57].

Magnetite polyvinyl acetate coupled with ligands of imiodiacetic acid (M-PVAC-IDA)

Recently, adsorption materials with large specific external surface area, easy recycling, and high reusability has been of great interest [66, 67]. MPA is essentially non-porous, thus preventing the clog problem and having good regeneration ability. Yoshitake *et. al.,* synthesized magnetic polymer adsorbent (MPA) of micro-size to recover Cu (II) ions from the aged pickling solution in the PCB plant [68]. Dauer and Dunlop investigated super-paramagnetic Fe_3O_4 (magnetite) prepared by the chemical co-precipitation method coated with polyvinyl acetate (PVAC) to form MPA of magnetite- PVAC (M-PVAC) via the suspension polymerization with vinyl acetate (VAC) [69]. Tseng *et. al.,* studied the synthesis of micro-size magnetic polymer adsorbent (MPA) coupled with metal chelating ligands of iminodiacetic acid (IDA) for the removal of Cu (II) ion. Super-paramagnetic Fe_3O_4 called magnetite was prepared via chemical co-precipitation method, and then coated with polyvinyl acetate (PVAC) through suspension polymerization with vinyl acetate (VAC), yielding magnetite-PVAC (denoted as M-PVAC). Introduction of functional groups on the surface of super-paramagnetite particles of M-PVAC, without demolishing the magnetite within the particles through several sequential procedures such as alcoholysis, epoxide activation and coupling were subsequently employed [70].

Also, the micro-size M-PVAC coupling with chelating ligands of IDA (denoted as M-PVAC-IDA) was prepared with the desired chemical properties. Micro-size of about $1\mu m$ and specified functional groups of metal chelating ligands of M-PVAC-IDA can provide large specific area of external surface and absorbability of metal ions of adsorbent, which are essential to adsorption. Moreover, after the use, M-PVAC-IDA was separated from the solution via applied magnetic force [70]. The summary of the maximum capacity of the different composite adsorbents are shown below in (Table 2).

Table 2. **Adsorption capacities of composite for the removal of Cu (II) ion using different adsorbents.**

Adsorbents	Maximum Capacity	References
DETA-PEGA	1.5mol/g	25
GA-MNP	38.5mg/g	7
Cu(II)-MICA	71.36mg/g	24
BENT- PAA m	33mg/g at pH 6.2	60
$NH_2/SiO_2/Fe_3SO_4$	10.41mg/g	23
CmCD-MNPs	47.2mg/g	70
HA-AM PAA-B	108.08mg/g	29
Sewage /industrial sludge	50mg/g	13
β-cyclodextrin	18.93-107.37mg/g	5
$Ca-Alg_2/GO$ gel beads	60.2mg/g	18
OEGMA/VDT	1.1mmol/g	57
M-PVAC-IDA	0.12mmol/g	70
AMPS-Silica	19.9mg/g	14
PVA/CS	238.45mg/g	17
PIOMN	48.99mg/g	36

Diboron trioxide / titanium dioxide

Titanium dioxide has been widely used as photocatalytic material for removing toxic chemicals from waters. However, certain limitations exist in using bare TiO_2 in photocatalytic reactors. As a result of small size (about 4–30 nm) TiO_2 aggregates rapidly in a suspension losing its effective surface area as well as catalytic activity [14]. Several researchers have made attempt to immobilize fine TiO_2 on porous adsorbent materials such as silica, activated carbon, alumina clay and zeolites etc. using sol-gel route to produce composites adsorbent [71, 72, 73]. Yoneyama and Torimoto also dispersed TiO_2 on the surface area vermiculite to prepare composite adsorbent for the decomposition of textile dye [74]. Al-Rashidi *et al.,* synthesized TiO_2 with diborontrioxide at the nano-size used to remove Cu (II) ions from water by adsorption. Nanoparticle materials of interest are of sizes below 50 nm. The adsorption kinetics was well explained by pseudo second order kinetic model. The sorption particle was best fitted to Freudlich model therefore suggesting that the copper uptake is a chemi-sorption process. An intra particle diffusion based Weber–Morris model was applied to evaluate the rate-limiting steps which suggested that pore diffusion controlled the overall sorption process [75].

Polyamine functionalized copper

High content of amine (amine groups) was discovered to be one of the most efficient functional groups [17] therefore, effects on the effectiveness, capacity, selectivity and reusability of this adsorbent has been positive [22, 76]. Different authors have reported amine-containing compounds being immobilized onto various substrates including polyacrylonitrile fiber, activated carbon [22]. Yu *et. al.,* investigated immobilizing copper chelating agent: triethylenetetramine and tetraethylenepentamine onto macroporous poly (GMA-co-TMPTMA) microspheres. The adsorbent is of good specificity to Cu (II) ion but have weak adsorption towards other metal ions such as Fe^{2+}, Mg^{2+}, Zn^{2+} and Ca^{2+}[77].

Prospects and future challenges

Although the use of these composite reported in the literature have increasingly improved the pace of Cu (II) ion removal in waste water, there are still some gaps to be filled. Some of these are suggested below:

(1) The potential of composite adsorbents under multi-component pollutants needs to be assessed. This would make a significant impact on the potential commercial application of composite adsorbents to industrial systems.
(2) Diversity in the use of each sorbent for considerable removal of other contaminants (heavy metals) not only selective detoxification of copper ion, should be investigated to further contribute to environmental protection.
(3) Further feasibility studies in utilizing these composites on commercial scale need to be checked, avoiding limitation to laboratory scale batch studies.
(4) Great concern for environmental friendly disposal of pollutant laden adsorbent should not be ignored.
(5) Further investigation of these adsorbent with real industrial effluents is required to bring about improvement in the field of adsorption.

Conclusion

This review focus on recent developments of wide varieties of composite adsorbents (clay particles and polymers forming complexes with metal ion and amine groups) in the application of wastewater treatment for copper ion removal. It should be noted that the maximum adsorption capacities reported identifies a promising effect of these composites materials in Cu (II) ion detoxification. The developed sorbents are robust enough to withstand multiple handling and can release the metal ion in response to external stimuli (separation) and then re-adsorbed repeatedly with little or no loss of mechanical strength therefore contributing to economic feasibility.

Acknowledgements

The corresponding author acknowledges the support obtained from Third World Academy of Science (TWAS) in form of grant; Research Grant number: 11-249 RG/CHE/AF/ AC_1_UNESCO FR: 3240262674.

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