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Review

Adsorption of dyes and heavy metal ions by chitosan composites: A review

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ABSTRACT

Various adsorbents have been used to remove different types of dyes and heavy metal ions from wastewater especially those that are harmful to mankind. Activated carbons, plant or lignocellulosic wastes, clays and biopolymers are among the common adsorbents used. Chitosan, a type of biopolymer, is a good adsorbent to remove various kinds of anionic and cationic dyes as well as heavy metal ions. Chemical modifications that lead to the formation of chitosan derivatives, grafting chitosan and chitosan composites have gained much attention, extensively studied and widely reported in the literatures. This review provides relevant literature of the past ten years on the application of chitosan composites for removing dyes and heavy metal ions. A list of chitosan composites with their adsorption capacity and the experimental conditions has been compiled. This review also includes the mechanisms that might be involved during adsorption process.

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1. Introduction

The application of biopolymers such as chitin and chitosan is one of the emerging adsorption methods for the removal of dyes and heavy metal ions, even at low concentrations (Crini, 2006). Chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin, which is a polysaccharide consisting predominantly of unbranched chains of β-(1→4)-2-acetoamido-2-deoxy-D-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans (Wan Ngah & Isa, 1998). Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. (Kumar, 2000). Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites (Wu, Tseng, & Juang, 2001). Amino groups of chitosan can be cationized, after which they adsorb anionic dyes strongly by electrostatic attraction in the acidic media (Kumar, 2000). However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values (Chiou, Ho, & Li, 2004). To improve chitosan's performance as an adsorbent, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used (Crini & Badot, 2008). Cross-linking agents do not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties (Chiou et al., 2004).

Chitosan derivatives have been extensively investigated as adsorbents (Amit & Mika, 2009). Among them are chitosan derivatives containing nitrogen, phosphorus and sulfur as heteroatoms, and other derivatives such as chitosan crown ethers and chitosan ethylenediaminetetraacetic acid (EDTA)/diethylenetriaminepentaacetic acid (DTPA) complexes (Varma, Deshpande, & Kennedy, 2004). Recently, chitosan composites have been developed to adsorb heavy metals and dyes from wastewater. Different kinds of substances have been used to form composite with chitosan such as montmorillonite (Wang & Wang, 2007), polyurethane (Won, Lee, Jeong, Min, & Lee, 2009), activated clay (Chang & Juang, 2004), bentonite (Wan Ngah, Ariff, & Hanafiah, 2010), poly vinyl alcohol, poly vinyl chloride, kaolinite (Zhu, Jiang, & Xiao, 2010), oil palm ash (Hameed, Hasan, & Ahmad, 2008) and perlite (Kalyani, Ajitha, Srinivasa, & Krishnaiah, 2005). Chitosan composites have been proven to have better adsorption capacity and resistance to acidic environment (Veera, Krishnaiah, Jonathan, Edgar, & Richard, 2008). This review paper will highlight the application of chitosan composites as adsorbents, which includes the method of preparation, mechanisms and factors that can affect its adsorption capacity.

2. Dyes

The discovery of synthetic dyes overwhelmed the role of natural dyes in the society due to its low production cost, brighter colors, better resistance towards environmental factors and easy-to-apply factor. This has led to a higher consumption of synthetic dyes over natural dyes for most types of industrial applications. Synthetic dyes however are often highly toxic and carcinogenic. Dyes consist of two main groups of compounds — chromophores and auxochromes. Chromophores determine the color of the dye while the auxochromes determine the intensity of the color (Moussavi & Mahmoudi, 2009). Dyes have become one of the main sources of severe water pollution as a result of the rapid development of the textile industries. The release of the colorant effluent has triggered a major concern on the human health as well as marine lives. Inefficiency in delivering dyes onto textile fibers can cause the colorants, which contain harmful substances, being released together with the effluents. However, the treatment process to remove those harmful substances is not under consideration until their potential to raise an environmental issue is recognized.

Wastewaters containing dyes are difficult to remove because of their inert properties. Another difficulty found during the removal of dyes is the low concentration of dye molecules in wastewater. The high cost to remove trace amounts of impurities causes the conventional methods of removing dyes become unfavorable to be applied at a large scale (Crini & Badot, 2008). Other conventional methods of removing dyes from wastewater such as adsorption, adsorption on activated carbons, coagulation and flocculation (Shi, Li, Wang, Feng, & Tang, 2007), reverse osmosis (Al-Bastaki, 2004), activated sludge (Junior, Bailod, & Mihelcic, 2005), bacterial action (Tony, Goyal, & Khanna, 2009), chemical oxidation (Arslan, Balcioğlu, & Bahnemann, 2000), ozonation (Wang, Yediler, Lienert, Wang, & Kettrup, 2003), and physical methods like membrane filtration (Akbari, Remigy, & Aptel, 2002), ion exchange (Labanda, Sabaté, & Llorens, 2009) and electrochemical techniques (Raghu & Basha, 2007) are either expensive or ineffective (Popuri, Vijaya, Boddu, & Krishnaiah, 2009). Recently, adsorption techniques using chitosan composites have been developed to adsorb dyes as an alternative to conventional wastewater treatment processes (Mouzdahir, Elmchaouri, Mahboub, Gil, & Korili, 2010). The list of chitosan composites that have been used to remove dyes in wastewater is summarized in Table 1. In the following sections, chitosan composites that have been developed to remove dyes will be discussed separately.

2.1. Chitosan/montmorillonite composites

Wang and Wang (2007) reported the use of montmorillonite (a natural phyllosilicate) in forming chitosan composites for the removal of Congo Red. The details of the structures of chitosan montmorillonite composites will be discussed in Section 3.7. The effects of different molar ratios of chitosan and montmorillonite were studied by Wang et al. (2004). They found that molar ratio of chitosan to montmorillonite could influence the chemical environment of the composites and hence the adsorption properties. Increment in the molar ratio of chitosan to montmorillonite increases the adsorption capacity of Congo Red until the molar ratio exceeds 1:1 after which the adsorption remains almost constant. There are two possible reasons for this scenario. Firstly this could be due to the balancing of the initial negative charge of montmorillonite by chitosan which would enhance the adsorption capacity of Congo Red. Secondly, it may be caused by the montmorillonite being saturated by the amount of intercalated chitosan.

X-ray diffraction (XRD) analysis showed that chitosan intercalated into montmorillonite interlayer led to the destruction of montmorillonite crystalline structure. Wang and Wang (2007) suggested two mechanisms of adsorption — electrostatic interaction and chemisorption. Electrostatic interaction happened due to the protonation of amine group in chitosan and the anionic dyes at low pH. Above pH 7, the excessive amount of hydroxyl ions would compete with the anionic dyes for the active site, hence reducing the adsorption of anionic dyes. The significant amount of adsorption at higher pH would indicate that chemisorption also took place. Kinetic studies showed that the adsorption of Congo Red on chitosan/montmorillonite composites was better described by the pseudo-second order model. This suggested that the adsorption rate was influenced by structural properties of the adsorbent (Wan Ngah & Kamari, 2009). The Langmuir isotherm suggested monolayer coverage of Congo Red with an adsorption capacity of 54.52 mg/g, and this value was almost similar to the experimental value (53.42 mg/g) (Wang & Wang, 2007).

Table 1
Adsorption capacities and experimental conditions of chitosan composites for various synthetic dye removal from wastewater.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	pH	Temperature (°C)	Kinetic model	Isotherm	Reference
Chitosan/montmorillonite	Congo Red	53.42	7.0	30	Pseudo-second-order	Langmuir	Wang and Wang (2007)
Chitosan/polyurethane	Acid Violet 48	30.00	7.0	30	Pseudo-second-order	Langmuir	Won et al. (2009)
Chitosan/activated clay	Methylene blue	330.0	7.1	30	Pseudo-second-order	Freundlich	Chang and Juang (2004)
Chitosan/activated clay	Reactive dye RR222	1912	6.5	30	Pseudo-first order	Freundlich	Chang and Juang (2004)
Chitosan/bentonite	Tartrazine	294.1	2.5	47	Pseudo-second-order	Langmuir	Wan Ngah, Ariff, and Hanafiah (2010)
Chitosan/bentonite	Malachite Green	435.0	6.0	37	Pseudo-second-order	Langmuir	Wan Ngah, Ariff, Hashim, et al. (2010)
Chitosan/oil palm	Reactive Blue 19	909.1	6.0	50	Pseudo-second-order	Redlich–Peterson	Hameed et al. (2008)
Chitosan/kaolin/γ-Fe_2O_3	Methyl orange	–	6.0	–	–	–	Zhu et al. (2010)

2.2. Chitosan/polyurethane composites

Won et al. (2009) used polyurethane to form chitosan composites in adsorbing Acid Violet 48. Polyurethane has various applications such as insulator in walls and roofs, flexible foam in upholster furniture, medical devices and foot wears (Zia, Bhatti, & Bhatti, 2007). From the literatures, it was found that polyurethane foams contain high surface area and porous structures, which enable it to act as matrix materials to immobilize various kinds of adsorbents such as activated carbon, zeolites and hydroxyapatite in removing heavy metal ions from aqueous solution (Jang, Min, Jeong, Lyoo, & Lee, 2008; Moisés, João, Ana, Manuela, & João, 2006). The preparation of chitosan/polyurethane composites is different from other methods, as chitosan does not undergo dissolution using acetic acid. According to Lyoo, Lee, Jeong, Min, and Lee (2009), at 0.25 wt% of glutaraldehyde concentration, chitosan was found to be most efficient in immobilizing into the polyurethane matrix foam. The scanning electron microscope (SEM) image revealed the composites to have open structures which had been proven in previous literatures (Jang et al., 2008; Moisés et al., 2006). The open structures of the composites enhance the accessibility of acid dyes into the chitosan adsorbent which had been immobilized in the composite foams (Lyoo et al., 2009). A comparison was also made between neat polyurethane foams and chitosan/polyurethane composites in the adsorption of acid dyes. It was found that the adsorption capacity of neat polyurethane was comparably lower. This indicated that the amine groups in the neat polyurethane could not react specifically as an active site to adsorb dye.

2.3. Chitosan/activated clay composites

Clay has a wide variety of uses due to its chemical and physical properties, variety of surfaces and also specific surface area (Lin, Juang, & Wang, 2004). Modified clays have been used as catalysts in organic synthesis (Sandeep & Man, 1997), as adsorbent to remove 2,4,6-trichlorophenol (Hameed, 2007) and paraquat (Tsai, Lai, & Hsien, 2003). Modified clays were also used to adsorb dyes (Mouzdahir et al., 2010) and heavy metals (Mabrouk & Mourad, 2010). Clays are rich in phyllosilicate minerals consisting of silicon, aluminum oxide and hydroxides. Clay consists of layers which are negatively charged. The negative charge is usually balanced by the interlayer cations such as Na^+ and K^+ (Mabrouk & Mourad, 2010). The water molecules intercalated in between the layers lead to the expansion of the structure, thus the dissolved compound may have diffused into the interlayer space (Lin et al., 2004).

Chang and Juang (2004) studied the chitosan/activated clay composites. The authors studied the specific gravity of the composite beads. Specific gravity for chitosan beads and composite with 50 wt% clay were 1.0055 and 1.0197, respectively. Based on specific gravity values, Chang and Juang (2004) concluded that the addition of activated clay could enhance the ability of chitosan to agglomerate and improve the hardness of the beads based on the Stokes Laws. This is important in beads formation because it facilitates the separation of the adsorbents from the solution without swelling. In the adsorption studies of methylene blue and reactive dye (RR22), the chitosan composites had a comparable adsorption in comparison to chitosan beads.

2.4. Chitosan/bentonite composites

Bentonite contains a high proportion of swelling clays. It mainly composed of montmorillonite with a composition of SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, Na_2O, and K_2O (Holzer et al., 2010; Li, Yue, Sun, Su, & Gao, 2010). Bentonite is a 2:1 type aluminosilicate, the unit layer which consists of one Al^{3+} octahedral sheet between two Si^{4+} sheets (Wei et al., 2009). Bentonites have been used to remove aromatic organics from oily liquid wastes (Saeid, Mark, Warren, & Andrew, 1997), 3-hydroxybenzaldehyde (Hülya, 2008) and 2-naphthol (Wei et al., 2009). Wan Ngah, Ariff, and Hanafiah (2010), prepared crosslinked chitosan/bentonite composites to adsorb tartrazine, a dye which contains azo group that is harmful to living things. The chitosan composites, crosslinked with epichlorohydrin were able to improve the chitosan performance as an adsorbent (Crini & Badot, 2008). A crosslinking agent can stabilize chitosan in acid solutions so that chitosan becomes insoluble. According to Wan Ngah, Ariff, and Hanafiah (2010), the pH of the tartrazine plays a crucial role in the adsorption process. At pH lower than pH_{ZPC}, the surface of the adsorbent would carry positive charge and tartrazine molecules would be attracted. As pH increased, the surface of the adsorbent carried more negative charges. This would result in repulsion between tartrazine and the adsorbent surface, resulting in the decrease of adsorption capacity.

Adsorption of tartrazine was best described by the pseudo-second order model. This showed that the rate limiting step was due to chemical adsorption. As much as 294.1 mg/g of tartrazine could be adsorbed as determined by the Langmuir model. Wan Ngah, Ariff, and Hanafiah (2010) also carried out desorption studies and found that the beads showed poor recovery as it was less likely to reuse the adsorbents. After the chitosan composites crosslinked with epichlorohydrin, the hydrogen bonds between amino and hydroxyl group in chitosan were destroyed; hence the composites displayed a different structural pattern in the X-ray diffraction (XRD) image due to the destruction of the crystalline structure. Moreover, the concentration and contact time plots showed the presence of rapid and slow adsorption rate. Similar to their previous work, Wan Ngah, Ariff, and Hanafiah (2010) found that the experimental data correlated well with the pseudo-second order model and an adsorption capacity of 435.0 mg/g of Malachite Green was achieved (Wan Ngah, Ariff, Hashim, & Hanafiah, 2010).

2.5. Chitosan/oil palm ash composites

Hameed et al. (2008) prepared crosslinked chitosan/oil palm composite beads to remove Reactive Blue 19. The authors found that pH had a significant effect on the adsorption capacity of the chitosan composites. At lower pH, more protons were present and protonated the amino groups in chitosan, thus increasing the electrostatic attractions between the negatively charged dyes and the positively charged active sites. However, at pH > 10, the adsorption capacity decreased tremendously due to the decrease in the total number and the diameter of the pores in chitosan beads. This has resulted in difficulty in transferring dye molecules as crosslinking of beads took place. Hameed et al. (2008) studied four types of isotherms which are Langmuir, Freundlich, Temkin and Redlich–Peterson with the latter fitted the experimental data better than the other isotherms.

2.6. Chitosan/kaolin/γ-Fe_2O_3 composites

Kaolinite is a 1:1 aluminosilicate, consists of SiO_2 (42.14 mol%), Al_2O_3 (15.61 mol%) and H_2O (42.25 mol%) (Nandi, Goswami, & Purkait, 2009). Zhu et al. (2010) prepared a new chitosan bead which was blended with maghemite (γ-Fe_2O_3) and kaolin. From the SEM and tunneling electron microscope (TEM) images, it was found that there were many pores and pleats on the surface of the composites which provided active sites for dye entrapment. The composites exhibited good adsorption ability as it could adsorb up to 70% methyl orange at pH 6. The effect of competitive anions on the adsorption efficiency was studied, which involved Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-}. The results for the decolorization of dye are in the order: no addition > Cl^- > NO_3^- > SO_4^{2-} > CO_3^{2-} > PO_4^{3-}. Therefore, the addition of anions had caused the adsorption of methyl orange to decrease. This could be explained by the preference of PO_4^{3-} adsorption over methyl orange due to the higher negative charge of phosphate anion.

3. Heavy metals

Inefficient ways in managing heavy metal ions in wastewater may cause long-term risk to the ecosystem and humans. Harmful toxic heavy metals that are discharged by chemical industries include cadmium, mercury, lead, chromium, copper, nickel and zinc. Table 2 summarizes the adsorption capacities and the conditions of chitosan composites for various heavy metals removal from wastewater. Each chitosan composite will be discussed in the following section.

3.1. Chitosan/ceramic alumina composites

The importance of alumina as an adsorbent has been widely recognized (Ahmed et al., 2000; Khattak, Afzal, Saleem, Yasmeen, & Ahmad, 2000). Alumina is suitable to use as an adsorbent due to the amphoteric character of hydrous aluminum hydroxides. Their acid–base dissociation leads to the positive ($-OH_2^+$) or negative ($-O^-$) charges on the surface, depending on the pH (Márta, Etelka, Kinga, & Imre, 1998). Few works have been carried out on the application of chitosan/ceramic alumina composites as an adsorbent to remove anionic and cationic heavy metals such as As(III) (Veera, Krishnaiah, Jonathan, et al., 2008), As(V) (Veera, Krishnaiah, Jonathan, et al., 2008), Cr(VI) (Veera, Krishnaiah, Jonathan, & Edgar, 2003), Cu(II) (Veera, Krishnaiah, Ann, & Edgar, 2008) and Ni(II) (Veera, Krishnaiah, Ann, et al., 2008). Oxalic acid is used in the process of forming the composites instead of the acetic acid because oxalic acid is a dicarboxylate and functions as a bridge between alumina and chitosan. One carboxylate group can form a strong surface chelate via ester linkage with the alumina while the other one forms ionic bonds with amine group in chitosan (Dobson & Mc Quillan, 1999).

The oxalic acid can also form hydrogen bonds with $-OH$, $-CH_2OH$, or $-NH_2$ group in the biopolymer (Veera et al., 2003). The uptake of metal ions is due to various processes such as adsorption, ion exchange and chelation (Veera, Krishnaiah, Ann, et al., 2008; Veera, Krishnaiah, Jonathan, et al., 2008). Chelation occurs when the chitosan interacts with the metal ions through amino group. It involves two or more complexing groups. According to Veera, Krishnaiah, Ann, et al. (2008), the two amino groups that are involved in the chelation are from two glucosamine residues of the polymer chain. The lone pair of electrons on the amino group enables it to act as active sites for the metal ion adsorption. The chitosan composites adsorb oxoanions or chloro complex anions of metals in the sample solutions by ion-exchange mechanism.

3.2. Chitosan/perlite composites

Perlite is a glassy volcanic rock varying in color from gray to black. Different types of perlite and different origin of perlite will have different properties due to different compositions (Mathialagan & Viraraghavan, 2002). When perlite is heated to elevated temperatures (850–1100 °C), it will expand 4–35 times of its initial volume and is called 'expanded perlite' (Shameem, Tushar, Dabir, & Veera, 2008). In literatures, perlite has been used in the adsorption of dyes such as methyl violet (Mehmet & Mahir, 2003), methylene blue (Mehmet, Mahir, Aydin, & Yasemin, 2004) and radioactive substances like thorium (Talip, Eral, & Hiçsönmez, 2009), and p-chlorophenol (Koumanova & Peeva-Antova, 2002). Chitosan/perlite composites have been applied as an adsorbent to remove heavy metals such as cadmium (Shameem et al., 2006), chromium (Shameem et al., 2003), copper (Kalyani, Veera, Siva, &

Table 2
Adsorption capacities and experimental conditions of chitosan composites for various heavy metal removal from wastewater.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	pH	Temperature (°C)	Kinetic model	Isotherm	Reference
Chitosan/cotton fibers (via Schiff base bond)	Hg(II)	104.31	5.0	35	Pseudo first order	Langmuir, Freundlich	Qu, Sun, Fang, et al. (2009)
Chitosan/cotton fibers (via C–N single bond)	Hg(II)	96.28	5.0	25	Pseudo second order	Langmuir, Freundlich	Qu, Sun, Fang, et al. (2009)
Chitosan/cotton fibers (via Schiff base bond)	Cu(II)	24.78	6.5	25	–	Langmuir, Freundlich	Zhang et al. (2008)
Chitosan/cotton fibers (via Schiff base bond)	Ni(II)	7.63	6.5	25	–	Langmuir, Freundlich	Zhang et al. (2008)
Chitosan/cotton fibers (via Schiff base bond)	Pb(II)	101.53	6.5	25	–	Freundlich	Zhang et al. (2008)
Chitosan/cotton fibers (via Schiff base bond)	Cd(II)	15.74	6.5	25	–	Langmuir, Freundlich	Zhang et al. (2008)
Chitosan/cotton fibers (via Schiff base bond)	Au(III)	76.82	3.0	25	Pseudo second order	Langmuir, non linear Langmuir, Redlich–Peterson	Qu, Sun, Wang, et al. (2009)
Chitosan/cotton fibers (via C–N single bond)	Au(III)	88.64	3.0	25	Pseudo second order	Langmuir, non linear Langmuir, Redlich–Peterson	Qu, Sun, Wang, et al. (2009)
Magnetic chitosan	Cr(VI)	69.40	4.0	–	–	Langmuir	Huang et al. (2009)
Chitosan/magnetite	Pb(II)	63.33	6.0	–	–	Langmuir	Tran et al. (2010)
Chitosan/magnetite	Ni(II)	52.55	6.0	–	–	Langmuir	Tran et al. (2010)
Chitosan/cellulose	Cu(II)	26.50	–	25	–	Langmuir	Sun et al. (2009)
Chitosan/cellulose	Zn(II)	19.81	–	25	–	Langmuir	Sun et al. (2009)
Chitosan/cellulose	Cr(VI)	13.05	–	25	–	Langmuir	Sun et al. (2009)
Chitosan/cellulose	Ni(II)	13.21	–	25	–	Langmuir	Sun et al. (2009)
Chitosan/cellulose	Pb(II)	26.31	–	25	–	Langmuir	Sun et al. (2009)
Chitosan/perlite	Cu(II)	196.07	5.0	–	–	Langmuir	Kalyani et al. (2005)
Chitosan/perlite	Ni(II)	114.94	5.0	–	–	Langmuir	Kalyani et al. (2005)
Chitosan/perlite	Cd(II)	178.6	6.0	25	–	–	Shameem et al. (2006)
Chitosan/perlite	Cr(VI)	153.8	4.0	25	–	Langmuir	Shameem et al. (2003)
Chitosan/perlite	Cu(II)	104.0	4.5	25		Langmuir	Shameem et al. (2008)
Chitosan/ceramic alumina	As(III)	56.50	4.0	25	–	Langmuir, Freundlich, Redlich–Peterson	Veera, Krishnaiah, Jonathan, et al. (2008)
Chitosan/ceramic alumina	As(V)	96.46	4.0	25	–	Langmuir, Freundlich, Redlich–Peterson	Veera, Krishnaiah, Jonathan, et al. (2008)
Chitosan/ceramic alumina	Cu(II)	86.20	4.0	25	–	Langmuir, Freundlich, Redlich–Peterson	Veera, Krishnaiah, Ann, et al. (2008)
Chitosan/ceramic alumina	Ni(II)	78.10	4.0	25	–	Langmuir, Freundlich, Redlich–Peterson	Veera, Krishnaiah, Ann, et al. (2008)
Chitosan/ceramic alumina	Cr(VI)	153.8	4.0	25	–	Freundlich	Veera et al. (2003)
Chitosan/montmorillonite	Cr(VI)	41.67	4.0	25	Pseudo second order	–	Fan et al. (2006)
Chitosan/alginate	Cu(II)	67.66	4.5	–	Pseudo second order	Langmuir	Wan Ngah and Fatinathan (2008)
Chitosan/calcium alginate	Ni(II)	222.2	5.0	–	Pseudo second order	Langmuir	Vijaya et al. (2008)
Chitosan/silica	Ni(II)	254.3	5.0	–	Pseudo second order	Langmuir	Vijaya et al. (2008)
Chitosan/PVC	Cu(II)	87.9	4.0	–	Second order	Langmuir	Srinivasa et al. (2009)
Chitosan/PVC	Ni(II)	120.5	5.0	–	Second order	Langmuir	Srinivasa et al. (2009)
Chitosan/PVA	Cd(II)	142.9	6.0	50	Pseudo second order	Langmuir	Kumar et al. (2009)
Chitosan/PVA	Cu(II)	47.85	6.0	–	Second order	Langmuir	Wan Ngah et al. (2004)
Chitosan/sand	Cu(II)	10.87	4.2	–	–	Langmuir	Wan et al. (2007)
Chitosan/sand	Cu(II)	8.18	–	–	Pseudo second order	Langmuir	Wan, Kan, Buenda, and Maria (2010)
Chitosan/sand	Pb(II)	12.32	–	–	Pseudo second order	Langmuir	Wan et al. (2010)
Chitosan/clinoptilolite	Cu(II)	574.49	5.0	–	Pseudo second order	Langmuir	Dragan, Dinu, and Timpu (2010)
Chitosan/clinoptilolite	Cu(II)	719.39	5.0	25	Pseudo second order	Langmuir	Dinu and Dragan (2010)
Chitosan/clinoptilolite	Co(II)	467.90	5.0	25	Pseudo second order	Langmuir	Dinu and Dragan (2010)
Chitosan/clinoptilolite	Ni(II)	247.03	5.0	25	Pseudo second order	Langmuir	Dinu and Dragan (2010)
Chitosan/nano-hydroxyapatite	Fe(III)	6.75	–	–	–	–	Kousalya, Muniyappan, and Sairam (2010)
Poly(methacrylic acid) grafted-chitosan/bentonite	Th(IV)	110.5	5.0	30	Pseudo second order	Langmuir	Thayyath et al. (2010)

Krishnaiah, 2009; Shameem et al., 2008) and nickel (Kalyani et al., 2009).

There was a slight difference between the procedures found in literatures (Shameem et al., 2003, 2006, 2008; Veera, Kalyani, Siva, & Krishnaiah, 2009). Perlite powder was soaked in oxalic acid in order to remove any acid soluble constituents and to introduce acidic groups onto perlite surface that may enhance the adherence of chitosan to perlite (Shameem et al., 2008). Washing and drying of perlite powder helped to maintain a proper ratio of acid to chitosan in the mixture during bead forming process (Shameem et al., 2008).

Shameem et al. (2006) found that pure perlite and chitosan did not adsorb any cadmium at $pH < 4$. The composites showed two distinct regions in the pH curve. At pH between 2 and 4.5, mainly $-NH_2$ groups in chitosan acted as active sites but at $pH > 4.5$, –OH groups became the active sites for cadmium adsorption. The authors also studied the interference effects of anions during cadmium adsorption. All the three anions (chlorides, nitrates and sulfates) did not show any significant effects on the adsorption, but EDTA showed a rapid reduction in adsorption capacity of cadmium which indicated that EDTA chelated with cadmium better than the composites do and proved that it was a stronger agent. EDTA was used in desorption studies based on its strong chelating properties and it was found that almost 98% of the adsorbed Cd(II) ions were recovered in the first cycle.

Kalyani et al. (2009) studied the competitive adsorption of Cu(II), Co(II) and Ni(II) from their binary and tertiary aqueous solutions using chitosan/perlite composites. They carried out the experiment at pH 5.0 because chitosan undergoes dissolution at $pH < 3$. pH above 5.0 is not favorable due to the formation of copper hydroxide. Based on their EDXRF and Fourier transform infrared (FTIR) spectra, amine and hydroxyl groups were the main active sites for copper ions. Copper was more strongly attracted to the sorbent when compared with the other two metal ions. The order of affinity based on adsorption capacity was Cu(II) > Co(II) > Ni(II) in binary as well as in ternary solutions. Adsorption of each single ion was reduced by the presence of other ion, which competed for some of the same active sites of the adsorbent (Kalyani et al., 2009).

3.3. Chitosan/magnetite composites

Magnetite is one of the main iron corrosion products under a reducing environment, which is the condition expected to prevail in a deep geological high level radioactive waste repository (Miquel et al., 2007). Different studies have been carried out to study the magnetite adsorption capacity for the sorption of some radionuclides (Martínez, Giménez, Pable, Rovira, & Duro, 2006). Among the magnetic nano-sized materials, iron oxides play a major role in many areas of chemistry, physics and materials science. Magnetic iron oxides such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) can be modified to achieve a better magnetic properties, lower toxicity and lower price. There are few literatures found on the preparation of chitosan/magnetite composites for the removal of heavy metals in wastewater (Huang, Zhang, Jeffrey, & Tim, 2009; Liu, Hu, Fang, Zhang, & Zhang, 2009; Tran, Tran, & Nguyen, 2010). Tran et al. (2010) reported that hydrogel (2-acrylamido-2-methyl-1-propansulfonic acid, AMPS) cross-linked with chitosan matrix and magnetic particles were more attractive for the removal of pollutants. On the other hand, Huang et al. (2009) prepared crosslinked chitosan–magnetite composites by using epichlorohydrin as the crosslinking agent. Huang et al. (2009) found that modification by cross-linking did not always reduce adsorption capacity. Meanwhile, Liu et al. (2009) investigated the removal efficiency of Pb(II), Cu(II) and Cd(II) from water and found that there was a decrease in magnetic saturation due to the increased mass of glutaraldehyde and chitosan on the surface of the magnetic nanoparticles. This magnetic property has strong magnetic response and can be separated easily from the solution with the help of external magnetic force. Ultrasound radiation was employed to disperse magnetic chitosan composites so that the magnetic chitosan composites and Pb(II) could interact efficiently and at a much faster rate.

3.4. Chitosan/cotton fiber composites

Cotton, a natural cellulosic fiber, possesses many useful characteristics such as comfort, soft, good absorbency, color retention and good strength. Cellulose is a polymer consisting of anhydroglucose units connected with 1,4 oxygen bridges in the beta position. Hydroxyl groups in cellulose allow hydrogen bonding between two adjacent polymer chains. Cotton swells in high humidity environment and in concentrated solutions of certain acids, salts and bases. The diameter of the cotton fibers is about 20 mm while the length is about 18 mm (Sorapong, Peter, Ruangsri, & Surasak, 2004). Natural cellulose fibers are negatively charged due to the presence of carboxyl and hydroxyl-groups. These groups are covered by non-cellulose compounds present in the primary wall of the natural fiber in the raw material (Stana-Kleinschek & Ribitsch, 1998).

Chitosan/cotton fiber composites had been prepared to remove Au(III) (Qu, Sun, Wang, et al., 2009), Pb(II), Ni(II), Cd(II), Cu(II) (Zhang et al., 2008) and Hg(II) (Qu, Sun, Fang, et al., 2009). In the preparation of the composite beads, cotton fiber was treated with sodium periodate before being added into the chitosan solution. Oxidation of carbohydrates by periodate ion (glycon cleavage) was for a long time a classical method used for structure determination of complex carbohydrates. In later years, it seems more or less abandoned as novel or more sophisticated methods have been developed (Kåre, Antje, & Bjørn, 2010). Periodates have been used to introduce dialdehydes into polysaccharides or glycoproteins (Kåre et al., 2010). Periodate–Schiff base, the reaction between the Schiff reagent and aldehydes formed by periodate oxidation, was used in the staining method for carbohydrates (Kåre et al., 2010; Silvia et al., 2004). Ethylene glycol was added into the solution after the cotton fiber was treated with sodium periodate to terminate the reaction (Zhang et al., 2008). Based on kinetic studies, Zhang et al. (2008) found that the rate controlling step for Pb^{2+}, Ni^{2+} and Cd^{2+} was liquid film diffusion. For Cu^{2+}, the rate controlling step was particle diffusion and it was found the adsorption rate was much slower compared to Pb^{2+}, Ni^{2+} and Cd^{2+}. This was due to the interaction rate of Cu^{2+} with coordination atom was much faster than the other metal ions. As a result, a copper complex matrix rapidly formed around the resin particle, which retarded the diffusion of metal ions into the interior part of resin particle. There was no significant difference in adsorption capacity between composite with Schiff base bond and C–N single bond (Qu, Sun, Fang, et al., 2009; Qu, Sun, Wang, et al., 2009).

3.5. Chitosan/sand composites

Sand can be modified to adsorb heavy metals and dyes in wastewater. Wan, Kan, Lin, Buenda, and Wu (2007) have reported on the application of chitosan immobilized on sand in the adsorption of Cu(II). Hatice, Parfait, Erdogan, and Sage (2006) showed that by coating clay particles with chitosan, the net surface charge of the clay has shifted from negative to positive and the pH_{PZC} has increased from 2.8 to 5.8. Chitosan/sand composites have shown better adsorption capacity than any of its component used alone. This is due to the three dimensional structure of the adsorbent used. Amine groups in chitosan provide active sites for the formation of complexes with metallic ions, which are stabilized by coordination. As the amount of acetyl groups in the structure increases, the maximum adsorption capacity of heavy metals decreases (Wan et al., 2007). Isotherm data best fitted the Langmuir isotherm with maximum adsorption capacity of 10.87 mg/g.

3.6. Chitosan/cellulose composites

Cellulose, the most abundant and renewable biopolymer in nature is also one of the promising raw materials available for the preparation of various functional materials with better cost efficiency (Benoît, Aji, & Kristiina, 2009; Rosa et al., 2010; Saito & Isogai, 2005; Zugenmaier, 2001). Cellulose is a polydisperse linear homopolymer consisting of regio-enantioselective β-1,4 glycosidic linked D-glucose units. The polymer contains three reactive hydroxyl groups at C-2, C-3 and C-6 atoms which are accessible to the typical conversion of primary and secondary alcoholic –OH groups. Vicinal secondary hydroxyl groups may undergo typical glycol reactions (Heinze & Liebert, 2001). Three hydroxyl groups in each β-D-glucopyranose units are able to interact with one another forming intra and intermolecular hydrogen bonds and form various types of supra-molecular semicrystalline structures (Oh et al., 2005). The crystallinity and also hydrogen bonding patterns have a strong influence on the whole chemical behavior of cellulose.

A further consequence of the supra-molecule structure is the insolubility of macromolecule in water as well as in common organic liquids. This has stimulated the search for solvents appropriate for homogenous phase reactions which still use unconventional synthesis paths (Heinze & Liebert, 2001). Cellulosic fibers generally have very few functional groups that are capable of anchoring metals. As a result, many attempts have been made to utilize cellulose as a metal scavenger through some derivatizations (Leandro, Osvaldo, Rossimiriam, & Laurent, 2008). Modification of cellulose can be achieved through esterifications (Low, Lee, & Mak, 2004; Marchetti, Clement, Loubinoux, & Gerardin, 2000), halogenations (Aoki, Fukushima, Kurukata, Sakamoto, & Furuhata, 1999), oxidation (Camy, Montanari, Vignon, & Condores, 2009) and etherification (Navarro, Sumi, Fuji, & Matsumura, 1996). Another method of modification of cellulose is by grafting in which the side chain grafts are covalently attached to the main chain of a polymer backbone to form a branched copolymer. David, Thomas, & Colin (2008) pointed out three kinds of grafting in their review paper which are photografting, high energy radiation grafting and chemical initiation grafting.

There are some literatures which reported on the use of cellulose immobilized on chitosan to form chitosan–cellulose composite beads. Li and Bai (2005) and Sun, Peng, Jing, Chen, and Li (2009) prepared the composite beads using almost similar method. Sun et al. (2009) used 1-butyl-3-methylimidazolium instead of acetic acid as the solvent for dissolution purpose. Ionic liquids (ILs) have recently received much attention as the green solvents and are very promising replacements for the traditional volatile organic solvents due to their characteristics such as non-volatility, non-flammability, thermal stability and ease of recycling (Hameed & Guo, 2009; Ueki & Watanabe, 2008; Zhang et al., 2006). 1-Butyl-3-methylimidazolium has a melting point of 70 °C and is very hygroscopic and has a high viscosity compared to other ILs (Tina, Jürgen, Claudia, & Ulrich, 2008). However, this solvent is very potent to cellulose. 1-Butyl-3-methylimidazolium solutions with cellulose concentrations up to 25 wt% can easily be produced by microwave heating. The specificity and superior efficiency of microwave heating over regular heating by radiation or convection allows for quick and energy efficient cellulose dissolution (Swatloski, Spear, Holbrey, & Rogers, 2002). Sun et al. (2009) reported that the adsorption capacity of dried chitosan biosorbent was nearly three times higher than that of freeze-dried chitosan composites, indicating the better stability of freeze-dried chitosan/cellulose composites. Li and Bai (2005) reported that the crosslinking reaction improved the acid resistance of the composite beads and provided the evidence that some of the amine groups in chitosan were consumed or shielded by the crosslinking reactions, as indicated in zeta potential studies.

3.7. Chitosan/montmorillonite composites

Polymer/montmorillonite nanocomposites have improved properties such as excellent mechanical properties, thermal stability, gas barrier, and flame retardation in comparison to conventional composites (Zhao, Wang, Zhao, Zhu, & Du, 2010). The isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer have resulted in a negatively charged surface on montmorillonite. With these structural characteristics, montmorillonite has excellent sorption properties and possesses available sorption sites within its interlayer space (Luckham & Rossi, 1999; Wu et al., 2009) as well as large surface area and more narrow channels inside (Bradbury & Baeyens, 2002; Staunton & Levacic, 1999; Vejsada, Hradil, & Randa, 2005). Fan, Zhu, Xu, and Yan (2006) produced chitosan coated montmorillonite for the removal of Cr(VI). The preparation of the composite beads is similar to Wang and Wang's (2007) work, except for the temperature and the pH used in the preparation are slightly different. Like other composites, the pH of the solution affects the adsorption capacity because chromium will form different kinds of anions at different pH values of the solution. Their kinetic results best fitted the pseudo second order model, indicating that the rate determining step involved chemisorption (Fan et al., 2006).

3.8. Chitosan/polyvinyl alcohol (PVA) composites

Poly(vinyl alcohol) (PVA), is a highly hydrophilic, nontoxic, biocompatible polymer with excellent mechanical strength, thermal stability, and pH stability (Brian, Thuy, Manh, & Xie, 2009; Li, Liu, & Xu, 2000; Ma, Su, Sun, Wang, & Jiang, 2007). It can be used for the creation of hydrophilic surfaces desirable for biological needs. This is due to the highly polar nature of PVA which minimizes fouling in such applications. In contrast, non-polar surfaces encourage the adsorption of water contaminants because of hydrophobic interactions, which include natural organic compounds such as humic and fulvic acids (Carroll, Booker, & Meier-Haack, 2002; Ma et al., 2007). In the past, PVA were widely utilized for the hydrophilic modification of nonporous surfaces (Kozlov, Quarmyne, Chen, & McCarthy, 2003; Serizawa, Kamimura, Kawanishi, & Akashi, 2002). However, limited research work was done on porous surface because of the difficulties in manipulating the modification process (Gholap, Badiger, & Gopinath, 2005). It is crucial to develop the technique to modify the porous surfaces of PVA since porous surfaces play an important role in bio-process (Ma et al., 2007). PVA has been used to immobilize chitosan to form chitosan/PVA composites (Kumar, Bijay, & Vinod, 2009; Wan Ngah, Kamari, & Koay, 2004). This type of composite has been used to remove Cu(II) (Wan Ngah et al., 2004) and Cd(II) (Kumar et al., 2009) from wastewater. The methods for the preparation of the composite beads are slightly different. In Kumar et al. (2009) work, the system temperature was raised to 90 °C in order to distill out some part of the water as an azeotropic mixture. Tween 80 was used in the preparation process as a non-ionic surfactant. It acted as an emulsifier during the preparation of droplets suspension (Avranas, Malasidou, & Mandrazidou, 1998; Malgorzata, Jeroen, Jason, & Steve, 2007). Desorption studies were carried out with more than 60% recovery, suggesting that the adsorbent was recyclable (Kumar et al., 2009; Wan Ngah et al., 2004). Cu(II) kinetic data fitted well the pseudo second order model.

3.9. Chitosan/polyvinyl chloride (PVC) composites

Poly vinyl chloride (PVC) has high surface area, good physical and chemical stabilities especially in concentrated acidic, basic media and organic solvents for a period of time. Furthermore, the surface of PVC can be modified by sorbent to obtain reversible and efficient enrichment of metal ions (Farzaneh, Mehrorang, Ardeshir, Morteza, & Shanaz, 2009). PVC-coated analytical reagent has some advantages as it does not swell or strain, has a good mechanical strength and manages to undergo heat treatment. Sodium dodecyl sulfate coated PVC has been used to remove heavy metals (Farzaneh et al., 2009). Another biosorbent was developed by coating chitosan onto PVC beads (Srinivasa, Vijaya, Veera, & Krishnaiah, 2009). The composite beads were used to adsorb copper and nickel ions from aqueous solution. Similar to other composite beads, the pH of the solution has to be taken into consideration since complexation of the metal ions occurred at higher pH (Srinivasa et al., 2009). The maximum adsorption capacities of chitosan/PVC composites were 87.9 and 120.5 mg/g for copper and nickel, respectively. The isotherm data were best described by Langmuir model (Srinivasa et al., 2009).

3.10. *Chitosan/calcium alginate composites*

Alginate is a water-soluble linear polysaccharide extracted from brown seaweed. It contains alternating blocks of 1–4 linked α-L-guluronic and β-D-mannuronic acid residues (Gombotz & Wee, 1998; Meera & Emilia, 2006). Currently the use of alginate hydrogels in biotechnology and pharmaceutical industry is widespread due to the unique properties they possess such as high biocompatibility and biodegradability (George & Nikolaos, 2006). The physical and chemical properties of alginates such as porosity and degradability can be easily modified in mild conditions (Gombotz & Wee, 1998). Vijaya, Srinivasa, Veera, & Krishnaiah (2008) and Wan Ngah and Fatinathan (2008) used alginate to form their composite beads. The methods of preparation are different in the sense that Vijaya et al. (2008) converted sodium alginate into water insoluble calcium alginate beads using calcium chloride solution. Wan Ngah and Fatinathan (2008) however immobilized the alginate on chitosan to form the composite beads. The adsorption capacity between the two methods could not be compared because the composite beads were used to adsorb different heavy metals. Based on desorption studies, the composite beads showed moderate performance since it recovered only 43% of heavy metal (Wan Ngah & Fatinathan, 2008). Further studies on desorption have to be done so that the composite beads can be recyclable and commercially applicable.

3.11. *Chitosan/bentonite composites*

Most adsorption studies of heavy metals were conducted in an aqueous condition. However, Zhang et al. (2009) introduced an experiment on the removal of mercury vapor (Hg^0) by chitosan/bentonite composites. It was reported that chitosan/bentonite composites had a much lower surface area compared to bentonite. This could possibly be due to the blockage of micropores in bentonite after chemical modification. This resulted in a decrease in the amount of Hg^0 removed. In contrast, Yang and Chen (2007) found that chitosan/bentonite composites were a good adsorbent for removing mercury ions from wastewater. Therefore, based on the above findings it can be concluded that the mechanisms of Hg^0 in the gas phase are completely different from that of mercury ions in aqueous condition. However, the detailed mechanisms of Hg^0 removal by chitosan/bentonite composites were not identified.

4. Future perspectives

The adsorption of heavy metals and dyes by chitosan composites had been compiled and reviewed in this paper. From the literatures, adsorption of heavy metals and dyes using chitosan composites is expected to have improved performance in the future. However, the comparison between the composites is just a guideline. It is almost impossible to make a comparison between composites due to the different materials used during the formation of the chitosan composites. Different experimental conditions, scarcity of information provided and the inconsistencies in data presentation have also added to the difficulty in making the comparison. Here, we would like to highlight some points which might help future research. The cost factor should be taken into consideration as low production cost with high removal efficiencies are much preferred. It is one of the key issues to determine whether the selection of the adsorbent is appropriate to be implemented in large scale. Chitosan composites, one of the chitosan-based materials are economically feasible because they are easy to prepare and involve inexpensive chemical reagents.

Regeneration studies need to be performed in detail as it will enhance the economic feasibility. Based on the literatures, not many regeneration studies had been reported. The regeneration studies will determine the reusability of the chitosan composite which contributes to the effectiveness of the composite as an adsorbent. Regeneration could be done using several techniques but solvent extraction is the most common way found in literatures. EDTA, hydrochloric acid, nitric acid, sodium chloride solution, and sodium hydroxide solution are the common solvents found in literatures for regeneration studies. Mechanism that is involved in the process is not well defined. Not many literatures discussed about the mechanism involved in the process. Assumptions were made based on the kinetic studies. Isotherm models were also insufficient to explain the mechanisms that were involved. The use of scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) analysis, electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) are highly recommended. Different techniques can provide various kinds of information on the composites. Therefore, combining different techniques will give a better picture in exploring the adsorption mechanism.

Research should not only limit to lab scale batch studies. Unlike laboratory solutions, industrial effluents contain various pollutants. There is a need to investigate the simultaneous removal of many co-existing pollutants. It is more preferable to develop a multipurpose adsorbent which can remove different kinds of pollutants. Although multi-purpose adsorbent tends to make the characterization of the adsorbent more complicated, it represents a more realistic approach to the design. Thus, a novel reactor system should be designed and their operation conditions should be optimized for large scale use. In laboratory, column study is highly recommended as a better approach to the design. To date, not many studies have been done on the adsorption on dyes compared to heavy metals. Furthermore, there are no systematic or comparative studies taking into account the physicochemical properties of the different kinds of pollutant dyes. A more detailed study appears to be necessary to show how the chemical structure of a dye affects not only its adsorption capacities, but also the understanding of the adsorption phenomena involved for that dye. Thus, more investigation should be focused on studying the influence of the chemical structure of dyes on the adsorption capacity (Crini & Badot, 2008).

5. Conclusion

This review paper indicates that adsorption using chitosan composites is becoming a promising alternative to replace conventional adsorbents in removing dyes and heavy metal ions. Although chitosan itself can dissolve in acidic medium, the use of cross-linking agent such as glutaraldehyde or with some modification process like coating, the dissolution properties of chitosan can be improved, allowing chitosan composites to work well in acidic condition. The adsorption mechanism of chitosan composites to adsorbate is indeed unique as it is dependent on its cationic nature. Amino groups of chitosan composites can undergo protonation (forming protonated amine) which can adsorb metal ions or dye molecules through various types of interaction mechanisms such as electrostatic attractions and chelation. Since there are a variety of chitosan based adsorbents (raw chitosan, chitosan derivatives, chitosan composites, etc.), arguments on which type of adsorbent is better in adsorption is still going on. There is no definite answer to this argument since each of the adsorbents has its own advantages and disadvantages. Comparison between adsorbents is almost impossible to make since the parameters and the adsorbate used are different. This field of research has a great room for improvement in the hope that chitosan composites can be applied commercially instead of only at laboratory scale.

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