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Review

Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review

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ABSTRACT

Chitosan based adsorbents have received a lot of attention for adsorption of dyes. Various modifications of this polysaccharide have been investigated to improve the adsorption properties as well as mechanical and physical characteristics of chitosan. This review paper discusses major research topics related to chitosan and its derivatives for application in the removal of dyes from water. Modification of chitosan changes the original properties of this material so that it can be more suitable for adsorption of different types of dye. Many chitosan derivatives have been obtained through chemical and physical modifications of raw chitosan that include cross-linking, grafting and impregnation of the chitosan backbone. Better understanding of these varieties and their affinity toward different types of dye can help future research to be properly oriented to address knowledge gaps in this area. This review provides better opportunity for researchers to better explore the potential of chitosan-derived adsorbents for removal of a great variety of dyes.

Contents

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1. Introduction and scope

Besides in the rapid growth of the world population, industrialization, unplanned urbanization, agricultural activities as well as the excessive use of chemicals have contributed to environmental pollution (Gupta, 2009). Inorganic and organic wastes produced by human activities have resulted in high volumes of contaminated water which threatens human health and other living organisms (Ceyhan & Baybas, 2001). Discharge of colored substances into water bodies not only can aesthetically cause issues but also it is harmful to biological organisms and ecology (Prasad & Santhi, 2012). Textile industries and other dyeing industries such as paper, printing, leather, food and plastic are major industrial wastewater sources. Generally, the volume of discharged wastewater from each step of a textile operation is approximately at a high rate of between 40 L/kg and 65 L/kg of the product (Mezohegyi, van der Zee, Font, Fortuny, & Fabregat, 2012). The presence of dyes in textile wastewater is an environmental problem due to their high visibility, resistance and toxic impact (Ali, Hameed, & Ahmed, 2009). Low concentration of dye in water is easily visible and can reduce photosynthetic activities in aquatic environments by preventing the penetration of light and oxygen (Crini, 2006). Given their synthetic origin and complex aromatic structures, dyes are non-biodegradable substances that remain stable under different conditions (Buthelezi, Olaniran, & Pillay, 2012). In addition, dyes have direct and indirect toxic effects on humans as they are associated with cancer, jaundice, tumors, skin irritation, allergies, heart defects and mutations (Alver & Metin, 2012; Hariharasuthan, Rao, & Bhaskaran, 2013).

Knowing the source, composition, and process of wastewater generation, it is necessary to select an appropriate treatment method for the removal of dye from wastewater and to improve the quality of treated wastewater discharged into the environment. Different treatment methods have been applied to remove trace amounts of pollutants from wastewaters. These techniques are such as ion exchange (Xing, Chen, & Wang, 2007), coagulation/flocculation (Chafi, Gourich, Essadki, Vial, & Fabregat, 2011), chemical precipitation (Kurniawan, Chan, Lo, & Babel, 2006), electrochemical reaction (García-Gabaldón, Pérez-Herranz, García-Antón, & Guinon, 2006), electro-dialysis (Mohammadi, Razmi, & Sadrzadeh, 2004), reverse osmosis and membrane filtration (Abdullah, Salamatinia, & Kamaruddin, 2009). However, each of these method exhibits several limitations such as high capital or operating costs, low efficiency and generation of excess sludge so that some of these methods are inappropriate for use by small-scale industries (Kobya, Demirbas, Senturk, & Ince, 2005). Adsorption is a method that is preferred over other options because it is rapid, convenient and inscrutable to toxic contaminants. It also has low initial costs, producing nontoxic by-products and rather simple in terms of design and operation of the treatment unit (Abbasi & Alikarami, 2012; Yadla, Sridevi, & Chandana Lakshmi, 2012).

Adsorption efficiency is affected by the nature and type of adsorbent. Both organic and inorganic materials could be used as adsorbents for dye removal. Researchers have focused on activated carbon (Guibal, McCarrick, & Tobin, 2003) and alumina (Iida, Kozuka, Tuziuti, & Yasui, 2004), zeolites (Alver & Metin, 2012), silica gel (Gaikwad & Misal, 2010), industrial by-products (Bhatnagar & Jain, 2005), agricultural solid wastes (Wang, Zhou, Jiang, & Sun, 2008), clays (Öztürk & Malkoc, 2014), peat (Fernandes, Almeida, Menezes, Debacher, & Sierra, 2007), bacterial biomass (Ratnamala & Brajesh, 2013) and polysaccharides (Saha et al., 2011). An ideal adsorbent for dye removal possesses the following properties: large surface area and high adsorption capacity, has suitable pore size and volume, easy accessibility, cost effectiveness, mechanical stability, compatibility, ease of regeneration, environmentally friendly, high selectivity to remove a wide range of dyes and does not require high processing procedures (Crini & Badot, 2008). Hence, researchers have recently focused on developing materials based on natural polymers such as chitosan to serve as alternative adsorbents with improved adsorption capacity and not compromising the low cost (Wan Ngah, Teong, & Hanafiah, 2011).

Chitosan is an abundantly available low-cost bio-polymer for dye removal that can be obtained from natural resources. As compared with other commercial adsorbents, it has received a lot of focus due to its specific properties such as cationicity, high adsorption capacity, macromolecular structure, abundance and low price (Muzzarelli et al., 2012). Different dyes have been reported to be effectively removed by chitosan or different modifications of this biopolymer. This highlights the necessity of a review to summarize the recent research findings in this area. The main objective of this study is to review the literature information on the use of chitosan and its derivatives for adsorption of different types of dye. Findings reported by other researchers are critically reviewed in order to reveal the efficacy of chitosan and its derivatives in dye removal application. This review compiles and presents relevant information in terms of the use of unmodified and modified chitosan as adsorbent so far. Furthermore, some of the results about adsorption performance of chitosan and its derivatives have been compared and discussed accordingly in this review paper. Also, some useful information about the most important features of adsorbents have been outlines. This review is mainly composed of four aspects. Initially, a highlight on chitosan properties is provided. After that, a structured review on the use of unmodified and modified chitosan for dye removal is presented. For the modified chitosans, a detailed review on different modification techniques such as beading, cross-linking, grafting and surface impregnation is provided. The third section of this review circulates around the environmental impacts and toxicity of chitosan modifications using different techniques. Finally the application of nano-chitosan in dye removal as a new approach in this area is discussed.

2. Chitosan

Chitosan is one of the world's most plentiful and low-cost biopolymers that possesses several properties as an ideal absorbent for removing pollutants from wastewater. Originally, chitin was boiled in potassium hydroxide to produce an acid-soluble product called chitosan (Kavitha, Keerthi, & Mani, 2011). Chitin, the second most abundant polysaccharide worldwide can be extracted from fungal species or from the exoskeleton of sea creatures such as crayfish, lobster, prawns, crab and shrimp (Gavhane, Gurav Atul, & Yadav Adhikrao, 2013; Muzzarelli, Ilari, Tarsi, Dubini, & Xia, 1994). Chitosan or poly-(1 → 4)-2-amino-2-deoxy-*b*-D-glucose is a biopolymer that can be chemically expressed as nontoxic, heterogeneous, linear, cationic and biodegradable polysaccharide with high molecular weight (Riva et al., 2011). Chitosan is produced from the alkaline de-acetylation of chitin (Jun et al., 2013; Li, Wang, Peng, & He, 2013; Li et al., 2013b; Rinaudo, 2006; Dotto & Pinto, 2011a). In this process, the acetyl groups of chitin are hydrolyzed and converted to free amine groups. This step determines the degree of de-acetylation (DD) or the ratio of de-acetylated to acetylated units. DD is influenced by temperature, time and the concentration of sodium hydroxide used in the de-acetylation (Abdulkarim, Isa, Abdulsalam, Muhammad, & Ameh, 2013; Hussain, Iman, & Maji, 2013). The degree of DD affects the adsorption capacity of the chitosan. High DD degree generally results from the presence of high amounts of amino groups and it can increase dye adsorption capacity of the chitosan by protonation (Piccin, Vieira, Gonçalves, Dotto, & Pinto, 2009). DD is commonly used to characterize chitosan alongside other properties such as molecular weight, crystallinity, and distribution of amine groups which

determine the physicochemical, biological and reaction of chitosan in the solution (Jana, Saha, Nayak, Sen, & Basu, 2013; Sorlier, Denuzière, Viton, & Domard, 2001). Previous studies reported that molecular weight affects the solubility (solubility decreases with increasing molecular weight), tensile strength (Park, Marsh, & Rhim, 2002), bacteriological properties (Cárdenas, Anaya, von Plessing, Rojas, & Sepúlveda, 2008), coagulant-flocculant performance of chitosan (Aranaz et al., 2009) and crystallinity (Jaworska, Sakurai, Gaudon, & Guibal, 2003). Meanwhile, crystallinity affects the adsorption capacity (Piron, Accominotti, & Domard, 1997) and accessibility of amine groups (Guibal, 2004). Chitosan is insoluble in water, alkaline solutions and organic solvents because of the hydrogen bonds between its molecules. However, it is soluble in acidic solutions due to the protonation of its amine groups (Aranaz et al., 2009; Hamdine, Heuzey, & Bégin, 2005). Based on the above properties, chitosan potentially has high affinity to adsorb pollutions such as heavy metals (Ren, Abbood, He, Peng, & Huang, 2013) and dyes (Peng et al., 2013) due to several functional groups available on this material. However, some drawbacks such as solubility in acid, low mechanical strength and low surface area limit the performance of this material in the adsorption process. This necessitated the modification of chitosan for dye removal by many researchers as elaborated in this review article.

2.1. Unmodified chitosan

Many researchers have investigated the adsorption performance of different forms of chitosan. The obtained chitosan from chitin; a solid material with high crystallinity called chitosan flakes, has been used by a few researchers as an adsorbent for dye removal from aqueous solutions. Adsorption ability of chitosan powder obtained from shrimp wastes to remove food dyes acid blue 9 and food yellow 3 from aqueous solution using a batch method has been investigated by Dotto and Pinto (2011a). The effect of the pH, contact time and stirring rate were elucidated and the obtained results showed that the adsorption capacity increased with time and pH decrease caused an increase in adsorption capacity. The optimal conditions were: pH 3, 150 rpm and 60 min for acid blue 9 and pH 3, 50 rpm and 60 min for food yellow 3. In these conditions, the adsorption capacities values were 210 mg/g and 295 mg/g for acid blue 9 and food yellow 3, respectively. Piccin et al. (2009) prepared chitosan from shrimp waste and used to eliminate food dyes (FD&C Red No. 40) from aqueous solutions in a batch system. Results showed that adsorption capacity was affected by chitosan particle size, deacetylation degree of chitosan and pH of the dye solution. Adsorption capacity increased with decreasing the pH and particle size while an increase in deacetylation degree led to an increase in the adsorption capacity. The maximum adsorption capacity was reported to be 529 mg/g at pH 6.6, temperature 35 °C, with particle sizes ranging between 0.10 ± 0.02 mm and a deacetylation degree of $84 \pm 3\%$. Elimination of Reactive Black 5 (RB-5) from an aqueous solution via chitosan flakes in a batch system has been investigated and the ability of chitosan flakes for regeneration and reuse by alkaline treatment after adsorption has been successfully exhibited (Saha et al., 2011). The results revealed that the adsorption capacity increased with decreasing the pH. The maximum adsorption capacity (39.5 mg/g) was reached at pH 5.0 while the minimum (12.5 mg/g) was observed at pH 9.0. Adsorption of RB-5 onto chitosan flakes was also investigated by Barron Zambrano, Szygula, Ruiz, Sastre, and Guibal (2010) in a continuous mode fixed-bed column system. Results showed that the initial dye concentration, superficial flow velocity, bed height and particle size significantly affected the adsorption process. Analysis of the breakthrough curves indicated that the adsorption was affected by mass transfer limitations, probably because of the intraparticle diffusion. Elution of the column with 0.01 mol/L NaOH allowed the chitosan to be regenerated and the dye to be recovered and concentrated. Several cycles of adsorption elution showed that the regenerated chitosan retained good adsorption efficiency. The removal of methyl orange dye from wastewater by chitosan flakes has been reported by Saha et al. (2010). Batch experiments showed that the adsorption was influenced by pH, dye concentration, and temperature. The highest adsorption capacities were 9.95 mg/g at pH 4.0 and 3.86 mg/g at pH 9.0. Mahmoodi, Salehi, Arami, and Bahrami (2011) used raw chitosan to eliminate anionic dyes, including Direct Red 23 (DR-23) and Acid Green 25 (AG-25) from wastewater in both single and binary systems from contaminated textile wastewater. In a single system, the maximum adsorption capacities of chitosan flakes were reported to 155 and 178 mg/g for the removal of DR-23 and AG-25, respectively.

The effect of stirring rate on the adsorption mechanism of Acid Blue 9and Food Yellow 3 onto chitosan powder has been investigated by Dotto and Pinto (2011b). Results suggested that the adsorption process was chemical in nature and occurs through internal and external mass transfer mechanisms. Increasing the stirring rate from 15 rpm to 400 rpm increased the adsorption capacity of chitosan powder for Acid Blue 9 and Food Yellow 3 by 50% and 60%, respectively. Stirring rate increased the film diffusivity while adsorption capacity increased with increasing intraparticle diffusivity. Batch adsorption tests using chitosan flakes with different DDs to remove Reactive Black M-2R (RBM) from wastewater has been conducted by Li and Ding (2011). In their experiments, the effects of different temperatures (25 to 50 °C), chitosan dosage, and DDs (55%, 66%, and 88%) on RBM removal were successfully elucidated. The sorption data suggested that the adsorption capacity decreased with increasing temperature. Chitosan with 66% DD demonstrated the highest sorption capacity (146 mg/g) within 1 h at 25 °C at a dye initial concentration of 19 mg/L. Iqbal et al. (2011) produced chitosan from the scales of both prawns and *Labeorohita* and studied their capacity to adsorb Acid Yellow 73 from water. The adsorption capacity of chitosan extracted from prawn scales was higher than that of chitosan extracted from *Labeorohita*. Their results also showed that the removal efficiency of Acid Yellow 73 was dependent on pH, initial dye concentration, surface area and pore volume of the adsorbent. The high adsorption capacity of chitosan under high initial dye concentration and low pH (3 to 4) was attributed to the positively charged polymer chain by protonation of amino groups, which promoted dye absorption on chitosan.

Ignat, Dulman, and Onofrei (2012) reported that the adsorption behavior of Reactive Red 3 (RR-3) and Direct Brown 95 on chitosan was influenced by chitosan structure, contact time, initial dye concentration, pH, addition of sodium chloride, and temperature. In this study, the chitosan flakes were ground and sieved to 0.10 mm to 0.15 mm and used in batch adsorption experiments. The highest adsorption values for RR-3 and DB-95 were reported to be 151.52 and 41.84 mg/g at 20 °C and 50 °C, respectively. It was observed that higher temperatures led to lower adsorption capacities. This could be due to the more activation of the dye molecules so that they were not allowed to keep on attaching on the surface of the adsorbent. A previous study by Hadi (2013) used chitosan flakes synthesized from fish shells as adsorbent to remove Methyl Orange (MO) from contaminated textile wastewater. The results of different studies showed that adsorption experiment was dependent on chitosan structure, surface area and pore volume of the adsorbent, contact time, temperature, adsorbent dosage, initial dye concentration, and pH. The highest removal percentage was reported to be 80.6% with an initial concentration of 50 mg/l of the dye solution for a duration of 140 min at pH 2. Acidic range of pH was found to result in better sorption capability. Table 1 summarizes the removal of different dyes from aqueous solutions by unmodified chitosan in the form of flake and powder. As could be observed in this table, the range of the flake size varied between 125 μm to 1.651 mm and

Table 1
Removal of different dyes from aqueous solutions by unmodified chitosan.

Chitosan	Particle size	Dye	Adsorption capacity (mg/g)	Temperature (°C)	pH	Reference
Flake	250–840 μm	Reactive red 222	380	30	6	Juang, Tseng, Wu, and
		Reactive yellow 145	179	30	6	Lee (1997)
		Reactive Blue 222	87	30	6	
Flake	16–30 mesh	Reactive red 222	494	30	–	Wu et al. (2000)
Flake	1.0–1.41 mm	Reactive red 222	339	30	–	Wu, Tseng, and Juang
		Reactive yellow 145	188	30	–	(2001)
Powder	125–710 μm	Reactive black 5	200	–	7	Guibal et al. (2003)
Flake	184–314 μm	Reactive yellow 84	500	–	5	Filipkowska (2006)
		Reactive red 11	450	–	5	
		Reactive black 5	650	–	5	
		Reactive black 8	387	–	5	
Flake	125–710 μm	Reactive black 5	1100	–	3	Guibal et al. (2005)
Powder	580 μm–1 mm	Reactive red 141	68	20	11	Sakkayawong,
			110	40	11	Thiravetyan, and
			156	60	11	Nakbanpote (2005)
Flake	125–250 μm	Reactive black 5	477	25	2.3	(Szygula et al., 2008)
Powder	–	Remazol yellow Gelb 3RS	417	25	2	Kyzas and Lazaridis
		Basic yellow	333	25	12	(2009)
Flake	125–500 μm	Reactive black 5	353	25	2	Barron Zambrano et al. (2010)
Flake	228 μm	Reactive black 5	62.92	33	5	Saha et al. (2011)
			19.91	33	9	
Flake	–	Reactive black M2R	146	25	–	Li and Ding (2011)
Flake	100–150 mesh	Reactive red 3	151.5	20	5	Ignat et al. (2012)
Flake	0.177–1.651 mm	Remazole black 13	96.0	60	6.7	Annadurai, Ling, and Lee (2008)
Flake	206 μm	Direct Scarlet B	37.18	47.5	8.5	Annadurai (2000)
Powder	125–710 μm	Direct blue 71	101	–	7	Guibal et al. (2003)
Flake	–	Direct red 23	155	25	2	Mahmoodi et al. (2011)
Flake	100–150 mesh	Direct blue 95	41.84	50	6	Ignat et al. (2012)
Powder	125–710 μm	Acid black 1	18	–	7	Guibal et al. (2003)
		Acid green 25	179	–	7	
		Acid violet 5	152	–	7	
		Acid yellow 25	179	–	7	
Flake	125–500 μm	Acid green 25	645.5	25	4	Wong et al. (2004)
		Acid orange 10	922.9	25	4	
		Acid orange 12	973.3	25	4	
		Acid red 18	693.2	25	4	
		Acid red 73	728.2	25	4	
Powder	355–500 μm	Acid orange 10	696.65	25	4	Cheung, Szeto, and
		Acid orange 12	931.85	25	4	McKay (2007)
		Acid red 18	670.97	25	4	
		Acid red 73	695.6	25	4	
Flakes	–	Acid yellow 73		25	4	Iqbal et al. (2011)
Flake	–	Acid green 25		25	2	Mahmoodi et al. (2011)
Powder	70 μm	Acid blue 9	256.0	25	3	Dotto and Pinto (2011a,b)
Powder	–	Acid blue 9	35	50	4	Sarkar, Banerjee, and Kundu (2012)
Flake	228 μm	Methyl orange	9.86	33	4	Saha et al. (2010)
Flake	0.177 mm	Methylene blue	30.0	60	9.5	Annadurai (2002)
Flake	–	Indigo carmine	403.9	25	–	Prado, Torres, Faria, and Dias (2004)
Powder	70 μm	Food Yellow 3	352.6	25	3	Dotto and Pinto (2011a,b)
Powder	125–710 μm	Mordant blue 29	37	–	7	Guibal et al. (2003)
		Mordant brown 33	91	–	7	
		Mordant orange 10	157	–	7	

mainly distributed closer to the smaller end of the range. It is noted in this table that the acidic dyes showed better affinity toward the chitosan adsorbent. This could be attributed to the positive charge of the chitosan polymer chain in acidic conditions due to protonation of amino groups. Guibal, Touraud, and Roussy (2005) achieved the highest adsorption capacity of 1100 mg/g of reactive black 5. The same researchers reported much lower results in the adsorption capacity (200 mg/g) for reactive black 5 at pH 7 (Guibal et al., 2003). Comparing their results with those of other researchers will lead to several conclusions. Saha et al. (2011) reported the lowest sorption capacity of 19.91 mg/g and 62.92 mg/g for the same dye at pH 9 and pH 5, respectively. Even though, this work was performed at lower pH as compared to the work reported by Guibal et al. (2003), the adsorption capacity was found to be lower. This could be attributed to the larger particle size of the flakes. Nevertheless, the enhancement of adsorption process in the acidic conditions was confirmed. Direct dyes and mordant dyes in general showed less affinity toward unmodified chitosan. It is also observed from the table that higher temperatures tend to cause lower sorption capacities as compared to the average of the capacities for all those dyes. However, unmodified chitosan showed good results for dye removal but low stability of this biopolymer has prompted many researchers to consider modifying this material. Next section discusses the abilities of modified chitosan for application in dye removal.

2.2. Modified chitosan

Raw chitosan could be physically modified via conversion to a conditioned form on the consideration of the favorable properties and applications of the derivatives. They are used in different forms including powder, flakes, and gel (beads, membranes, film, etc.) (Miretzky & Cirelli, 2009). Although chitosan shows great potential, it suffers from drawbacks such as inadequate mechanical

properties (Chatterjee, Lee, Lee, & Woo, 2009b), low acid stability, low solubility in acidic solutions (Zhou, Liu, & Liu, 2009), low porosity, low thermal resistance (Crini & Badot, 2008) and low surface area (Setthamongkol & Salaenoi, 2012; Alhwaige, Agag, Ishida, & Qutubuddin, 2013). Therefore, modification is an effective solution to produce a product with the desired properties to overcome the limitations of chitosan. Modification of chitosan is easier than that of other polysaccharides because of its reactive functional groups including amino and hydroxyl groups (Rinaudo, 2006). The mechanical properties and adsorption capacity of chitosan can be enhanced by physical and chemical modifications (Raghunadh Acharyulu, Gomathi, & Sudha, 2013). Conversion of raw chitosan flakes into beads has been reported to be an essential way to improve the adsorption capability by enhancing the porosity and surface area. This conversion has been performed by dropping acid-dissolved chitosan into an alkali solutions such as NaOH or methanol-NaOH, followed by drying (Zhou, Liu, Liu, & Huang, 2010). Chitosan membrane and film can be made by casting the chitosan solution mixed with alkali into a flat surface to evaporate the solvent (Mello, Bedendo, Nome, Fiedler, & Laranjeira, 2006). In general, physical modification expands chitosan polymer chains, thereby increasing access to internal sorption sites and enhancing the diffusion mechanisms and crystalline state of the polymer to be reduced (Azlan, Wansaime, & Lai Ken, 2009).

The use of unmodified chitosan in industry subjects to drawbacks of low mechanical strength and vulnerability in acidic media. Hence, researchers used chemical modification to achieve the desirable properties and applications of chitosan (Osifo et al., 2008). Chemical modification does not change the basic structure of chitosan, but brings new derivatives with improved properties for special applications in various areas (Mourya & Inamdar, 2008). Such modification improves the adsorption properties and increases the mechanical strength and chemical stability of chitosan in acidic media (Guibal, 2004; Salmah, Faisal, & Kamarudin, 2011). It also decreases the biochemical and microbiological degradation of chitosan (Wan Ngah, Kamari, & Koay, 2004). In chemical modification, reactions occupy functional groups, mainly amino groups, in which aldehydic functions react with the amino groups (Rinaudo, 2006). Cross-linking, impregnation, and grafting are methods used for chemical modification of chitosan. The use of chitosan in relatively low pH medium is not feasible because it leads to the dissolution of chitosan. Thus, one way to overcome this drawback is by inducing cross-linking of chitosan to reduce its dissolution in acidic media (Chan, Husseinsyah, & Sam, 2013). A cross-linking agent (a molecule with a minimum of two reactive functional groups) links chitosan chains using covalent bonding. It enhances the mechanical strength and chemical resistance of chitosan against chemicals such as alkali, and acids (Mohamed & Fahmy, 2012). Generally, cross-linking may decrease the adsorption capacity because the cross-link agent's will bind with functional groups such as amino groups, rendering them unavailable (Guibal, 2004). However, cross-linking can also enhance the adsorption capacity by the reactive functional groups in the cross-linking agent structure as well (Miretzky & Cirelli, 2009). Different monomers can also be grafted and functionalized by covalently bonded to the functional groups (hydroxyl or amine) of chitosan (Jayakumar, Prabaharan, Reis, & Mano, 2005). Grafting improves the potential of chitosan for different applications such as adsorption by increasing the density of functional groups (Zhou et al., 2010).

2.3. Chitosan beads, membrane and films

In general, physical parameters including crystallinity, porosity, and particle size are the major factors affecting the adsorption capacity of chitosan. Their high crystallinity, low hydrophilicity, low surface area, non-porosity, resistance to mass transfer and low adsorption capacity limit the applications of chitosan flakes. Chitosan flakes do not behave ideally in columns. It is because they are highly crystalline and hydrophobic which increase their resistance to mass transfer rate, column clogging and high pressure drops, resulting in high operation costs (Guibal, 2004). Low surface area and non-porosity also decrease the adsorption capacity and rate because of poor access to interior adsorption sites (Crini & Badot, 2008). The amino groups in chitosan flakes are not active/available or at least accessible. The hydrogen bonds linked between the monomer units of the same chain (intramolecular bonds) or between the monomer units of different chains (intermolecular bonds) decrease their reactivity. In dye adsorption on flakes, large dye molecules cannot easily penetrate the porous network with steric hindrance increased along with the progressive saturation of the sorbent. Therefore, the use of chitosan in dissolved-state increases the accessibility to reactive sites (improved process kinetics) and/or increase their availability. The breaking of hydrogen bonds between amino groups and between hydroxyl groups (inter-chain or intra-chain bonds) during polymer dissolving makes them much more available for interacting with dyes. This phenomenon may explain the highly efficient use of the amino groups of chitosan used in dissolved-state for dye removal (Guibal et al., 2005). Furthermore, the beads can be simply separated from the treated solution for reuse. Other comparative studies found that the adsorption capacity of chitosan flakes is lower than that of chitosan beads.

Chitosan flakes are usually subjected to physical modification by converting them into gel beads to increase porosity, expand chitosan polymer chains, increase surface area, decrease crystallinity and improve access to internal sorption sites, all of which lead to enhanced adsorption capacity (Miretzky & Cirelli, 2009). Wu, Tseng, and Juang (2000) compared the adsorption capacity of chitosan flakes and beads from 3 different sources as adsorbents for removing Reactive Red 222 (RR 222) dye from wastewater at 30 °C. They found that the adsorption rate of chitosan beads was higher than that of chitosan flakes because of the higher surface area of the beads. Chitosans derived from shrimp, crab and lobster were used both as flakes and beads. The maximum levels of eliminated dye for chitosan flakes from shrimp source and beads from crab source were 494 mg/g and 1106 mg/g, respectively. However, in general it was reported by the same researchers that beads from different source showed higher capacities than chitosan flakes by a factor of 2.0–3.8. Hence, chitosan beads are preferred over chitosan flakes as suitable adsorbents for the removal of dyes from aqueous solutions. A year later, the same researchers immobilized chitosan beads with tyrosinase to prepare highly swollen beads. The swollen beads showed much higher sorption capacity of 1653 mg/g at 40% faster rate than chitosan flakes. The adsorption capacities and other parameters of chitosan beads without use of cross-linkers or extra functionalizing for the removal of different dyes from aqueous solutions are summarized in Table 2. From this table, the effect of pH is clearly observed. Lower pH values tend to cause higher adsorption capacities. This confirms the fact that the preparation of beads from chitosan does not significantly change the structure of the chitosan. The higher adsorption capacities as mentioned earlier could be attributed to higher surface area as the chemical structure does not experience any changes. In comparison, reactive dyes showed higher capacities varying between 201.90 mg/g and 1106 mg/g. Only in a study by Ong and Seou (2013) a lower sorption capacity was observed which could be attributed to the high pH value employed in that study. Removal of acid dyes ranged from 130 to 357.14 mg/g on a basis of adsorption capacity. This shows lower capacity range for acid dyes as compared to reactive dyes. Congo red adsorption capacity averaged at 173.88 mg/g. Chatterjee, Chatterjee, Chatterjee, & Guha (2007) reported that the

Table 2
Removal of different dyes from aqueous solutions by modified chitosan.

Chitosan	Dye	Adsorption capacity (mg/g)	Temperature (°C)	pH	Reference
Bead	Eosin Y	79	30	8	Chatterjee, Chatterjee, Chatterjee, Das, and Guha (2005)
Bead	Acid red 37	357.14	27–47	6	Kamari et al. (2009)
	Acid blue 25	178.57	27–47	4	
Bead	Acid red 37	130	–	6	Azlan et al. (2009)
	Acid blue 25	250	–	4	
Bead	Orange-G	95	–	4	Konaganti et al. (2010)
Bead	Eosin Y	170.65	25	5	(Huang et al., 2011)
Bead	Reactive red 222	1106	30	–	Wu et al. (2000)
Bead-immobilized with	Reactive red 222	1653	30	–	Wu et al. (2001)
tyrosinase	Reactive yellow 145	885	30	–	
Bead	Reactive red 189	1189	30	6	Chiou and Li (2002)
Bead	Reactive red 189	950	30	6	Chiou and Li (2003)
Bead	Reactive yellow 84	690	–	3	Filipkowska (2006)
	Reactive red 11	480	–	3	
	Reactive black 5	480	–	3	
	Reactive black 8	487	–	3	
Bead	Reactive red	648	25	2	Kyzas et al. (2011)
	Reactive yellow	430	25	2	
	Reactive violet	398	25	2	
Bead	Reactive black 5	201.90	30	4	(Chatterjee et al., 2011c)
Bead	Reactive black 5	4.83	25	7	(Ong & Seou, 2013)
Bead	Reactive yellow	334	25	2	Kyzas and Lazaridis (2009)
Bead	Congo red	93	30	6	(Chatterjee et al., 2007)
Bead	Congo red	178.32	–	5	(Chatterjee, Lee, & Woo, 2009c)
Bead	Congo red	223.25		4	(Chatterjee, Lee, Lee, & Woo, 2009a)
Bead	Congo red	200.0	30	5	(Chatterjee et al., 2010)
Bead	Congo red	174.83	–	4	(Chatterjee et al., 2011a)
Bead	Remacryl red TGL	204.22	25	–	Lazaridis, Kyzas, Vassiliou, and Bikiaris (2007)
Bead	Metyl green	93.55	30	8	Bekçi et al. (2008)
	Metyl green	74.83	40	8	
	Metyl green	82.17	50	8	
Bead	Basic yellow	134	25	12	Kyzas and Lazaridis (2009)
Bead	Methylene blue	99.01	30	9	Chatterjee et al. (2011b)
Film	Acid red 18	194.6	25	7	Dotto et al. (2013)
	FD&C blue no. 2	154.8	25	7	
Film	Tartrazine	413.8	25	2	Rêgo et al. (2013)
Amaranth	278.3	25	2		Esquerdo et al. (2014)
Scaffold	FD&C yellow 6	788	25	6	Mirmohseni et al.
	FD&C yellow 5	1078	25	6	(2012)
	Food red 2	1552	25	6	
	FD&C blue 2	3032	25	6	
	FD&C red 40	3316	25	6	
Fiber	Reactive blue 19	454.5	25	3.5	

lowest capacity for Congo red was 93 mg/g. The low value was attributed to higher pH value used in that study.

As noted in Table 2, Bekçi, Özveri, Seki, and Yurdakoç (2008) investigated the adsorption ability of chitosan beads to remove cationic dye Malachite Green (MG) from aqueous solution using a batch method. The effect of temperature and solution pH was studied. The results showed that chitosan beads could be suitable adsorbents at high pH (8 and above) for cationic dye adsorption. The maximum adsorption capacities were 93.55 mg/g at 303 K, 74.83 mg/g at 313 K, and 82.17 mg/g at 323 K during the adsorption process performed at pH 8 for 300 min. From the findings in Tables 1 and 2, it is expected that by decreasing the pH, better adsorption capacities could be observed. Phung, Ong, and Keng (2013) identified the adsorption ability of chitosan beads to remove RB 5 from aqueous solution in a batch system under different reaction conditions. Experimental data revealed that the maximum adsorption capacity was 8.14 mg/g (more than 99% removal) under the following optimum conditions: pH 4, agitation rate, 200 rpm, sorbent dosage, 1.0 g, contact time, 300 min and initial dye concentration, 25 mg/L. Elimination of RB 5 from wastewater using chitosan beads in a batch system has been studied by Ong and Seou (2013). In this study, the maximum adsorption percentage for RB5 uptake was 96.2% under the following optimum sorption conditions: contact time 182.5 min, initial concentration 60 mg/L, pH 7 and agitation rate 200 rpm. Despite high adsorption affinity of chitosan with different beads, one of the serious drawbacks of the use of chitosan as adsorbent for dye adsorption is its easy solubility in some acidic media (pH <5.5). This results in formation of chitosan gels which can eventually lead to loses in the adsorption capacity. Cross-linking is a chemical modification method that makes chitosan insoluble in acidic media. The cross-linked chitosan maintains constant reactivity in a wide pH range and is characterized by high mechanical resistance (Filipkowska, 2012). In addition, converting chitosan flakes into membrane and film is an alternative way to prepare adsorbents from chitosan presenting fibrous structure, good mechanical properties and higher surface areas (Dotto, Moura, Cadaval, & Pinto, 2013). Chitosan in the form of membrane and films have been reported by a few researchers as an adsorbent for dye removal from aqueous solutions. However, matured understanding is yet to be achieved.

Rêgo, Cadaval, Dotto, and Pinto (2013) identified the elimination of azo dyes (tartrazine and amaranth) from aqueous solutions via chitosan film. Results showed that chitosan films could be suitable adsorbents at a pH of 2 and a chitosan film concentration of 100 mg/L for azo dyes adsorption. The maximum adsorption capacities for the tartrazine and amaranth were 413.8 and 278.3 mg/g, respectively. It was concluded that its adsorption capability was due to the electrostatic interactions between protonated amino

groups of chitosan film (NH_3^+) and sulfonated groups (SO_3^-) of the azo dyes. The desorption study revealed that after two cycles of adsorption and desorption by NaOH (0.50 mol/L) adsorbents retained their promising adsorption abilities. Adsorption ability of chitosan films to remove food dyes (acid red 18 and FD&C blue no. 2) from aqueous solution using a batch method was investigated by Dotto et al. (2013). The effect of temperature was studied and results showed that chitosan films could be suitable adsorbents at 298 K. From the thermodynamic data, it was found that the adsorption of food dyes onto chitosan films is a spontaneous, favorable and exothermic process. The maximum adsorption capacities were 194.6 mg/g and 154.8 mg/g for the acid red 18 and FD&C blue no. 2, respectively. The chitosan films maintained its structure and were easily separated from the liquid phase after the adsorption process.

Esquerdo, Cadaval, Dotto, and Pinto (2014) studied the possibility of chitosan scaffold as an able adsorbent of FD&C blue 2, FD&C red 40, FD&C yellow 5, FD&C yellow 6 and Food red 2 (food dyes) from aqueous solution. The equilibrium and thermodynamic studies showed that chitosan scaffold can be used as a appropriate adsorbent for adsorption of food dyes. It was due to its suitable structural characteristics for adsorption purposes, with high values of pore size, porosity and specific surface area as well as electrostatic interactions occurred between chitosan scaffold and dyes. In this work, the adsorption capacity was favored by a decrease in temperature and the maximum values were attained at 298 K. In their experiment, it was found that the adsorption capacity of the adsorbates followed the following order: FD&C red 40 > FD&C blue 2 > Food red 2 > FD&C yellow 5 > FD&C yellow 6. The experimental equilibrium data fitted the two-step Langmuir model satisfactorily and the total adsorption capacities ranged from 788 to 3316 mg/g. Chitosan hollow fibers with high mechanical strength have been prepared via a dry-wet spinning technique and applied as an effective adsorbent for reactive blue 19 (RB19) (Mirmohseni, Dorraji, Figoli, & Tasselli, 2012). Results showed that initial pH was the most effective parameter. The adsorption capacity value of reactive blue 19 on chitosan hollow fibers was 454.5 mg/g. The adsorption was well described by pseudo-second-order kinetics and Freundlich equation.

2.3.1. Cross-linking

From a practical viewpoint, chitosan shows high adsorption capacities to eliminate dyes in neutral solutions. The pH effect may be an important factor in the dye-binding capacity of chitosan as the amino groups in chitosan are easier to cationize at low pH and they strongly adsorb the dye anions by electrostatic attraction. Mostly acetic acid is often used as stimulators in the dying process, in which the dye solution pH is normally adjusted from 3 to 4. However, chitosan forms gel below pH 5.5 and cannot be evaluated. The dissolution tendency of chitosan in the acid effluent can severely limit the use of chitosan as an adsorbent for dye removal (Chiou & Li, 2002). To overcome this behavior, chitosan can be modified by cross-linking the polymer chains to prevent swelling as well as to improve the mechanical resistance, reinforcement of the chemical stability of chitosan in acidic solutions. It also improved stability to a drastic pH, all of these features are important to act as an effective adsorbent (Chatterjee et al., 2009b; Dal Pozzo et al., 2000; Muzzarelli, 2011; Muzzarelli, Weckx, Filippini, & Sigon, 1989). In cross-linking reaction, some chemical agents are used as cross-linkers. The molecules have at least two reactive functional groups that allow the formation of bridges by introducing covalent bonding between polymer chains and amino groups (Crini & Badot, 2008). Cross-linking occurs when a reagent (cross-linker) introduces intermolecular bridges and/or cross-links between polysaccharide macromolecules. Cross-linking significantly reduces segment mobility in polymers. By creating new inter-chain linkages, a series of interconnected chains appear and this is followed by the formation of a three dimensional network (Shweta & Sonia, 2013). To date, the most common cross-linkers used for modifying chitosan for dye adsorption are such as glutaraldehyde (GLA) (Mirzaei, Ramazani, Shafiee, Danaei, 2013), epichlorohydrin (ECH) (Jing, Liu, Yu, Xia, & Yin, 2013), ethylene glycol diglycidyl ether (EDGE) (Hsien et al., 2013) and tripolyphosphate (TPP) (Mengatto, Ferreyra, Rubiolo, Rintoul, & Luna, 2013). These chemicals are commonly known as ionic cross-linkers.

2.3.1.1. Epichlorohydrin cross-linker. Epichlorohydrin (chloromethyloxirane, C_3H_5ClO) (ECH) is an abundant chemical intermediate that is applied in many fields. ECH is a relatively small size organic molecule which consists of a highly reactive three-membered oxirane ring and oxygen and chlorine heteroatoms (Stranges et al., 2011). ECH is commonly referred by many researchers as a suitable cross-linking agent to obtain more stable and stronger chitosan to be used as adsorbents (Kyaw, Wint, & Naing, 2011). Compared with other cross linkers, the chitosan modified with ECH shows higher adsorption capacities. This is due to the fact that since ECH mostly binds with–OH group, the availability of major adsorption sites (amine groups) is not compromised. These sites are not eliminated during the cross linking process of chitosan while other cross linkers interact with the amine groups (Chiou & Li, 2003). Li et al. (2013a,b) prepared the ECH cross-linked chitosan under alkaline conditions for Congo red removal from wastewater. It was observed that the adsorption capacity of the cross-linked chitosan adsorbents for Congo red was higher than that of unmodified chitosan. Chiou and Li (2002) investigated the adsorption of a reactive dye i.e. Reactive Red 189 (RR 189) from aqueous solutions on ECH cross-linked chitosan beads in a batch system. The obtained maximum adsorption capacities were 1936, 1686, and 1642 mg/g for small, medium, and large particle sizes, respectively at pH 3.0, 30 °C and 0.2 cross-linking ratio. Results showed that both the initial dye concentration and the solution pH significantly affected the adsorption capacity, but the temperature and the cross-linking ratio were relatively minor factors. An increase in initial dye concentration resulted in the increase in the adsorption capacity and the same also increased with decreasing pH. Chiou, Kuo, and Li (2003) examined the elimination of a reactive dye i.e. Reactive Red 222 (RR 222) from aqueous solution using ECH cross-linked chitosan beads. The maximum adsorption capacity was 2252 mg/g at 30 °C with a pH of 3.0.

Hanh et al. (2007) produced chitosan beads from crustacean shells and reported that chemical cross-linking was necessary to improve the chemical resistance and mechanical strength of chitosan beads. They applied ECH cross-linked chitosan beads to study the adsorption of azo dye AB 92 from aqueous solution. Kim, Park, and Cho (2012) used strongly pH-dependent chitosan beads cross-linked with ECH to adsorb RB 5 from wastewater. Results indicated that the process was strongly pH and temperature dependent. The maximum adsorption capacity of RB 5 onto the cross-linked chitosan beads was 2043 mg/g at pH 3.0 and 35 °C. The surface area and average pore diameter of the cross-linked chitosan beads were 315 m^2/g and 70.9 Å, respectively.

2.3.1.2. Glutaraldehyde cross-linker. Glutaraldehyde (GLA) molecule (HCO-$(CH_2)_3$-CHO) is also relatively small, containing two aldehyde groups separated by a flexible chain of three methylene bridges. The reaction of chitosan with glutaraldehyde using an acidic catalyst results in formation of a cross-linked chitosan membrane (Uragami, Matsuda, Okuno, & Miyata, 1994). Guibal et al. (2003) assessed the ability of GLA in cross-linking chitosan in powder form to remove a number of anionic dyes from wastewater. The sorption was dependent on the solution pH and the type of dye. Low pH solution led to the protonation of chitosan

amino groups which caused the sorption of sulfonic acid groups of anionic dye. In this experiment, equilibrium was reached after 12 h and maximum adsorption capacity was in the range of 109.91 mg/g to 750.58 mg/g. Cestari, Vieira, dos Santos, Mota, & de Almeida (2004) studied the influence of the chemical structures of dyes and the temperature on the adsorption process using cross-linked chitosan beads. Chitosan beads cross-linked by GLA were synthesized and used as adsorbent to remove Reactive Yellow, Reactive Blue and Reactive Red dyes from aqueous solutions at pH 2.0. The study found that the chemical structures of the dyes, the temperatures and the contact times strongly influenced the adsorption amount and changes in adsorption mechanisms. In this work, adsorption of yellow dye increased from approximately 3 mg/g to 9 mg/g at 25 °C to 50 °C. However, adsorption of the blue dye decreased from approximately 10 mg/g to 2 mg/g at 25 °C to 50 °C. The adsorption of the red dye decreased from 3 mg/g to 1.5 mg/g at 25 °C to 35 °C and increased from approximately 3.5 mg/g to 7.5 mg/g at 45 °C to 50 °C.

The adsorption of methyl orange (MO) on GLA cross-linked chitosan beads has been studied by Morais, de Almeida, Pereira, and Fonseca (2008). In this work, equilibrium studies showed that chitosan could be used as an adsorbent to treat effluents from the textile industry, especially for negatively charged dyes such as MO because of its cationic polyelectrolyte nature. Dye adsorption increased as the pH was increased from 2 to 2.5, and initial dye concentration in the continuous phase was increased. Kamari, Ngah, Chong, and Cheah (2009) employed GLA and sulfuric acid as cross-linking reagents and used batch adsorption techniques to study the possibility of chitosan and cross-linked chitosan beads as adsorbents for Acid Blue 25 (AB 25) and Acid Red 37 (AR 37) from aqueous solution. The adsorption capacity of chitosan beads was better compared to that of chitosan–GLA and chitosan —H_2SO_4 beads for both AR 37 and AB 25 dyes. This advantage was attributed to the decline in the number of major adsorption sites (—NH^{3+}) on chitosan as a result of cross-linking reaction with GLA and sulfuric acid. Although chitosan-GLA and chitosan —H_2SO_4 beads showed lower adsorption capacity, they have greater chemical stability to allow their use in both acidic and basic media and continuous stages of adsorption and desorption. Feng, Zhang, Wang, and Huang (2011) carried out the adsorption of CR on GLA cross-linked chitosan films from aqueous solutions in a batch system. Results indicated that cross-linked chitosan film could successfully remove 96% of the dye.

2.3.1.3. Ethylene glycol diglycidyl ether cross-linker. Ethylene glycol diglycidyl ether (EDGE) is a compound having two epoxide functional groups (cyclical ethers constituted by a three-embered ring) located at both ends of the molecule. EDGE is significantly more reactive as compared to other ethers due to the high energy associated to the considerable strains that exist in the three-membered ring (Nagura, Yokota, Ikeura, Gotoh, & Ohkoshi, 2002). Azlan et al. (2009) examined the capabilities of chitosan and cross-linked chitosan beads to remove Acid red 37 (AR 37) and Acid blue 25(AB 25) from aqueous solution. Chitosan beads were cross-linked with EDGE to enhance its chemical resistance and mechanical strength. The adsorption capacities of chitosan for both acid dyes(AR 37 and AB 25) were comparatively higher than those of chitosan-EDGE because cross-linking using EDGE reduced the major adsorption sites of —NH^{3+} on chitosan. The desorption study revealed that after three cycles of adsorption and desorption by NaOH and HCl, both adsorbents retained their promising adsorption abilities. Results also showed that chitosan and cross-linked chitosan beads are favorable adsorbents and can be employed as low-cost alternatives to remove acid dyes in wastewater.

2.3.1.4. Tripolyphosphate as an ionic cross-linker. Tripolyphosphate (TPP) is a poly anion and can interact with cationic chitosan by electrostatic forces (Shu & Zhu, 2000). The ionic interactions between the positively charged amino groups and negatively charged counterion i.e. tripolyphosphate were used for modification of chitosan beads. The anionic counterion i.e. TPP can form either intermolecular or intramolecular linkages. This is responsible for the successful formation of the beads (Bhumkar & Pokharkar, 2006; Crini & Badot, 2008). In acidic TPP solutions, the presence of both H^+ and multivalent tripolyphosphate ions in the solution is confirmed. Free amine group on the chitosan molecule will be protonated upon the contact between chitosan and acidic TPP solution. Subsequently, the protonated amine groups on different or same chitosan molecules could be cross-linked by negative charged multivalent TPP ions (Liu, Bai, & Nan, 2004). Chiou and Li (2003) used cross-linked chitosan beads to remove RR 189 dye from wastewater in a batch system. In the experiments, several chemical cross-linking reagents were used to stabilize chitosan in acid solutions, including ECH, GA and EDGE and then cross-linked the beads again with TPP. Results showed that chitosan beads cross-linked with ionic TPP where found to be more rigid but ECH chitosan beads presented higher adsorption capacity. The adsorption capacity increased largely with a decrease in the solution pH or with increasing initial dye concentration. In this set of experiments, the maximum adsorption capacity was more than 1800 mg/g at pH 3.0 and 30 °C. The desorption data showed that the removal rate of RR 189 dye from the cross-linked chitosan beads was 63% in a NaOH solution at pH 10.0 and 30 °C. The desorbed chitosan beads can be reused to adsorb the dye and to reach the same capacity as that before desorption. Hu, Zhang, Chan, and Szeto (2006) also employed chitosan in nanoparticle form (particle size = 180 nm; DD = 74%) cross-linked by sodium TPP as an adsorbent to adsorb an acid dye i.e. Acid Green 27 (AG27) from aqueous solution. The nanoparticles were obtained by freezing the emulsion at 4 °C and then thawed in the atmosphere. The values were significantly higher than those of micron-sized chitosan. Kyaw et al. (2011) studied the adsorption behavior of cross-linked chitosan beads to remove both anionic and cationic dyes using TPP and ECH as cross-linker agents and CR or Direct Red 28 (anionic dyes) and MB or Basic Blue 9 (cationic dye) as adsorbates. The adsorption capacity increased largely with decreasing pH of the dye solution. Anionic dye removal of 87.2% by ECH beads and 81.9% by TPP beads were achieved with an optimal dosage of 3.5 g at the optimum pH of 4 in 60 min contact time. At this pH, the highest percentage of dye removal of cationic dye was approximately 49% for ECH beads and 42% for TPP beads. The rate constants increased with increasing temperature.

2.3.1.5. Other cross-linkers. Shimizu, Taga, and Yamaoka (2003) synthesized cross-linked chitosan with a higher fatty di-acid diglycidyl (7-ethyloctadecane di-acid diglycidyl) as the cross-linking agent and analyzed the adsorption abilities of the resulting polymers evaluated in typical acid dyes. At higher dye concentrations, the adsorption abilities of the cross-linked chitosan toward hydrophilic Acid Orange 7 (AO-7) and Acid Red 1 (AR-1) increased with decreasing degree of substitution. However, at lower dye concentrations, the cross-linked chitosan with the lowest degree of substitution exhibited the lowest adsorption capability. The extent of adsorption for such hydrophilic acid dyes decreased significantly as the pH of the solution increased. By contrast, Acid Red 138 (AR 138), which contains a dodecyl group in the chemical structure, was adsorbed to a considerable extent even at higher pH values, suggesting hydrophobic interaction between the alkyl group in the dye molecule and the hydrophobic cross-linker. Fahmy, Mohamed, Abo-Shosha, and Ibrahim (2004) used dimethyloldihydroxy ethylene urea to cross-link the chitosan and remove Optical Red RSGR (direct dye), Ergalon Rubine RL (acid dye), and Brilliant Red M5BR-2 (reactive dye) from aqueous solutions. It was found that the higher

percentage of dye removal of cross-linked adsorbent was due to the higher amino content of the cross-linked sample. Moreover, the percentage of dye removal followed the order of hydrolyzed reactive > direct > acid. The percentage of dye removal increased significantly by decreasing the pH and increasing the time of process.

The adsorption capacities and other parameters of chemically cross-linked chitosan for the removal of different dyes from aqueous solutions are tabulated in Table 3. At a glance, it could be observed that all the cross-linked chitosan adsorptions occurred in acidic range. This confirmed the stability of this material even at very low pH values of 1.5. Nevertheless, the results revealed that very low pH values led to significant drop in the sorption capacity. This could be attributed to excess release of H^+ ions in the solution, limiting the ion exchange to happen effectively due to a competition between hydrogen ions and the dye ions. Based on the results from this table, the most effective pH is within the range of 3 to 4.

As shown in Table 3, ECH as a cross-linker resulted in the highest sorption capacities as compared to other cross-linkers. The adsorption capacities were between 722 mg/g and 2498 mg/g for reactive dyes and acid dyes. The uptake of Acid dyes and reactive dyes by using ECH cross-linker did not show significant difference. ECH was also reported to be used as a cross-linker for Direct Red 81 (DR-81) and the adsorption capacity was reported to be 238 mg/g which was relatively lower than those of reactive dyes and acid dyes. GLA as a cross-linker for chitosan has also been widely researched for different types of dye removal and the adsorption capacities are significantly lower than that of ECH. This is attributed to the fact that GLA uses the–NH_2 groups of the chitosan for the binding to happen (Macquarrie & Bacheva, 2008) while the ECH generally targets the —OH groups of chitosan for the linking purpose. Amino groups in general show better affinity for adsorption purpose as compared to hydroxyl group leading to higher adsorption capacities (Chiou & Li, 2003).

In general, cross-linking improves the mechanical resistance and reinforces the chemical stability of chitosan in acidic solutions, modifies hydrophobicity, and stabilizes the chitosan at drastic pH. However, cross-linking also decreases the number of free and available amino groups in the chitosan backbone, and hence, the possible ligand density and polymer reactivity. Cross-linking also decreases the accessibility to internal sites of the material leading to loss in flexibility of the polymer chains. Therefore, cross-linking may cause a significant decrease in dye uptake efficiency and adsorption capacities, especially in chemical reactions involving amine groups. It is because the amino groups of the polymers are much more active than the hydroxyl groups and can be more easily attacked by cross-linkers. Consequently, these functional groups are no longer available for complex formation and dye adsorption capacity decreases. To minimize this effect, efforts are made to maintain the degree of cross-linking as low as possible, followed by further chemical modifications such as grafting or functionalizing to improve the selectivity and the capacities.

2.3.2. Grafting

Grafting reactions to improve and enhance the dye adsorption characteristics of chitosan has received a particular focus. The modifications can amend both physical and mechanical properties of the chitosan polymer. These modifications can control the diffusion properties of the chitosan and decrease the sensitivity of adsorption to environmental conditions as well (Crini & Badot, 2008). Chitosan has two types of reactive groups where grafting occurs, namely amino and hydroxyl groups. Many different functional groups have been grafted onto chitosan by covalent bonding of a molecule onto the chitosan backbone. Even though the grafting of chitosan modifies its properties, it does not compromise the interesting characteristics of this biopolymer such as muco-adhesivity, biocompatibility and biodegradability. With the objective of expanding chitosan applications, many researchers have studied the graft copolymerization of chitosan with focusing on preparing polysaccharide-based advanced materials with unique bioactivities (Alves & Mano, 2008; Jayakumar et al., 2005). Graft copolymerization of synthetic polymers onto chitosan can enhance the desired properties of the chitosan and subsequently widen the field of the potential applications of them. Recently, ammonium persulfate (APS), potassium persulfate (PPS), ceric ammonium nitrate (CAN), thiocarbonation-potassium bromate (TCPB), potassium diperiodatocuprate (III) (PDC), 2,2′-azobisisobutyronitrile (AIBN) and ferrous ammonium sulfate (FAS) have been used to initiate grafting copolymerization. Moreover, it is reported that γ-irradiation and enzymes could initiate that graft copolymerization as well. The characteristics of the resulting graft copolymers are mostly dependent on the properties of the side chains, including molecular structure, length, and number (Jayakumar et al., 2005). The following discusses the worls of scholars using different functional groups for grafting chitosan for the purpose of dye removal.

2.3.2.1. Chitosan grafted amino group. Kyzas, Kostoglou, Vassiliou, and Lazaridis (2011) investigated the removal of reactive dyes Remazol Red 3BS (RR), Remazol Blue RN (RB), and Remazol Yellow Gelb 3RS (RY) from real industrial dyeing effluents originating directly from the dyeing bath of a Greek industry on cross-linked chitosan beads as adsorbents. In this study, cross-linking reagents (GLA and ECH) and grafting reagents (acrylamideand poly(ethyleneimine)) were used to modify the chitosan beads. Results showed that the addition of amido and imino groups on the chitosan backbone through grafting reactions increased the adsorption capacity of adsorbents, whereas the cross-linking method develops their capability for reuse for at least 10 cycles without significant capacity loss (5%). Chitosan derivatives present maximum adsorption behavior at pH 2. The adsorption capacity still remained considerably high at the original pH of 10 of the effluent. The adsorption capacity followed the order chitosan-grafted-poly(ethyleneimine) > chitosan-grafted-acrylamide > chitosan. This was attributed to the higher basicity (electro positivity) of imino groups (chitosan-grafted-poly(ethyleneimine) versus amide groups (chitosan-grafted-acrylamide). Thus, more positively charged groups had the chance to occur on poly(ethyleneimine)-grafted derivative as compared to that of amido-grafted, rendering a stronger electrostatic interaction between chitosan and dye molecules.

Huang, Bin, Bu, Jiang, and Zeng (2011) grafted ethylenediamine (EDA) on chitosan to create an adsorbent to remove dye from aqueous solution, which showed interesting sorption properties toward anionic dye eosin Y because of the high zeta potential contributing to a great amount of amino groups introduced in the mixture. Based on the excellent adsorption performance of EDA-chitosan, it can be used as a low-cost and efficient adsorbent to remove anionic dye (acid dye) from wastewater by introducing more amino groups. The maximum adsorption capacity of EDA-chitosan adsorbent was 294.12 mg/g at 25 °C, which was much higher than that of chitosan (170.65 mg/g).

The effect of polyethyleneimine(PEI) grafted chitosan beads on the adsorption capacity for Reactive Black 5 has been studied by Chatterjee, Chatterjee, and Woo (2011c). The adsorption capacity in PEI-chitosan was found to increase with the increase in the amount of PEI during the grafting process. This was attributed to the increase in available binding (aminated) sites by increasing PEI amount during grafting. The maximum adsorption capacity value of PEI-chitosan (709.27 mg/g) was higher than that of chitosan (201.90 mg/g) to indicate that the adsorption

Table 3
Removal of different dyes from aqueous solutions by cross-linked chitosan.

Chitosan	Cross-linking Reagent	Dye	Adsorption capacity (mg/g)	Temperature (°C)	pH	Reference
Bead (2.3–2.5 mm)	ECH	Reactive red 189	1936	30	3	Chiou and Li (2002)
Bead (2.5–2.7 mm)	ECH	Reactive red 189	1686	30	3	
Bead (3.5–3.8 mm)	ECH	Reactive red 189	1642	30	3	
Bead	ECH	Reactive red 222	2252	30	3	Chiou et al. (2003)
Bead	ECH	Reactive blue 2	2498	30	3	Chiou, Ho, and Li
	ECH	Reactive red 2	2422	30	3	(2004)
	ECH	Reactive yellow 86	1911	30	3	
	ECH	Reactive yellow 2	2436	30	4	
Bead	ECH	Reactive blue 15	722	30	4	Chiou and Chuang (2006)
Bead	ECH	Reactive black 5	2043	35	3	Kim et al. (2012)
Powder	GLA	Reactive black 5	109	–	4	Guibal et al. (2003)
	GLA	Reactive black 5	198	–	4	
Bead	GLA	Reactive yellow	9	50	2	Cestari et al. (2004)
	GLA	Reactive blue	10	25	2	
	GLA	Reactive red	7.5	50	2	
Flake	GLA	Reactive Orange 16	1060	25	4	Rosa, Laranjeira, Riela, and Fávere (2008)
Bead	ECH	Acid Orange 12	1954	30	3	Chiou et al. (2004)
		Acid red14	1940			
		Acid Orange 7	1940		4	
Bead	ECH	Metanil yellow	1334	30	4	Chiou and Chuang (2006)
Bead	ECH	Acid blue 92	1262.6	25	4	(Hanh et al., 2007)
Powder	GLA	Acid black 1	37	–	4	Guibal et al. (2003)
	GLA	Acid green 25	138	–	4	
	GLA	Acid violet 5	140	–	4	
	GLA	Acid yellow 25	124	–	4	
	GLA	Acid black 1	76	–	1.5	
	GLA	Acid green 25	166	–	1.5	
	GLA	Acid violet 5	194	–	1.5	
	GLA	Acid yellow 25	144	–	1.5	
Bead	GLA	Acid red 37	166.67	–	6	Kamari et al. (2009)
	GLA	Acid blue 25	127.06	–	4	
Bead	GLA	Methyl orange	7	22	5	Morais et al. (2008)
Bead	EGDE	Acid red 1	50	40	5	Azlan et al. (2009)
Bead	EGDE	Acid blue 25	150	–	4	Azlan et al. (2009)
Fiber	Denacol EX841	Acid Orange 2	1200–1700	–	4	Yoshida, Okamoto, and Kataoka (1993)
Bead	ECH	Direct red 81	238	30	4	Chiou et al. (2004)
Powder	GLA	Direct blue 71	14	–	4	Guibal et al. (2003)
Film	GLA	Congo red	24.18	25	–	Feng et al. (2011)
Bead	GLA	Methylene blue	101.4	25	6	Xing, Sun, and Li
	GLA	Methyl green	33.7	25	4	(2009b)
Powder	GLA	Indigo carmine	0.613	35	4	Cestari, Vieira, Tavares, and Bruns (2008)
Powder	GLA	Mordant blue 29	48	–	4	Guibal et al. (2003)
	GLA	Mordant brown 33	130	–	4	
	GLA	Mordant orange 10	103	–	4	
	GLA	Mordant blue 29	114	–	1.5	

performance of chitosan could be enhanced significantly through PEI grafting.

2.3.2.2. Chitosan grafted carboxyl group. Xing, Sun, and Li (2009a) grafted pyromellitic dianhydride (PMDA) on GLA cross-linked chitosan to enhance its cationic dye adsorption from printing and dyeing wastewater. This study indicated that the grafting of PMDA on the surface of chitosan microspheres is very effective for removing cationic dyes in aqueous solution. The adsorption capacities for Methylene Blue (MB) and Neutral Red (NR) dyes were enhanced significantly because of the presence of a large number of carboxyl groups. The maximum adsorption capacities were reported to be 935 and 909 mg/g for MB and NR, respectively.

Özkahraman, Bal, Acar, and Güçlü (2011) conducted a graft copolymerization of itaconic acid (IA) and crotonic acid (CA) onto ECH cross-linked chitosan beads using ammonium persulfate as initiator to remove a cationic dye (Brilliant Green) from aqueous solutions. In this study, the adsorption capacities were determined as 108 and 135 mg/g for chitosan-CA and chitosan-IA, respectively. The reason for this increase was the higher amount of carboxyl group on chitosan-IA.

2.3.2.3. Chitosan grafted sulfur group. Crini et al. (2008) studied the chemical grafting of sulfonate groups onto chitosan as a method to improve its ability in removing basic dyes, in particular Basic Blue 3 (BB 3), from aqueous solutions. Modified chitosan was prepared by using 4-formyl-1,3-benzene sodium disulfonate. Results of adsorption experiments showed that the process was rapid and that modified chitosan exhibited relatively high sorption capacities toward BB 3 attributed to the presence of sulfonate groups. The maximum adsorption capacity was reported to be 166.5 mg/g. The result clearly verified that these groups contributed to the sorption mechanism through electrostatic interactions between SO^{3-} groups of the sorbent and the cationic sites of BB 3.

2.3.2.4. Chitosan grafted alkyl group. Konaganti, Kota, Patil, and Madras (2010) grafted several poly(alkyl methacrylate), such as poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), and poly(hexyl methacrylate) (PHMA) on chitosan, and used them successfully to adsorb various sulfonated anionic dyes (Orange-G, CR, Remazol Brill Blue R (RBBR), and Methyl Blue). In this experiment, it was found that the adsorption capacity of the adsorbates followed the following order: RBBR >MB > CR > OG. In addition, the adsorption

capacity followed the order Ch-PMMA > Ch-PEMA > Ch-PBMA > Ch-PHMA > chitosan, with the adsorption equilibrium capacity of Ch-PMMA 4.5 times that of chitosan. The observed order in the adsorption was attributed to the increase in steric hindrance, distortion of geometry and decrease in inductive effect, in conjunction with the increase in the number of carbon atoms of alkyl group substituent.

Singha, Sharmaa, Tripathi, and Sanghi (2009) proved that chitosan grafted with poly(methylmethacrylate) remained water insoluble even under highly acidic conditions and was a much better adsorbent than chitosan in removing anionic azo dyes (Procion Yellow MX, Remazol Brilliant Violet, and Reactive Blue H5G) from synthetic dye solutions as well as from real textile wastewater over a wide pH range of 4–10. The maximum adsorption capacities of modified chitosan for yellow, violet, and blue dyes were 250, 357, and 178 mg/g, respectively at pH 7. However, at pH 4, the maximum adsorption capacities increased to 263, 384, and 204 mg/g, respectively. This again confirmed the better sorption abilities in acidic range especially at pH values around 4.

The adsorption capacities and other parameters of various chitosan derivatives synthesized by grafting/functionalizing for the removal of different dyes from aqueous solutions are tabulated in Table 4. Based on this table, a wider range of pH has been elaborated in the grafted chitosan adsorption as compared to the results from Tables 1–3. However, it is still noted that lower pH values tend to have better sorption capacities as compared to basic and neutral pH ranges. The best results have been reported by Kyzas et al. (2011) for amide and imine grafted chitosan. The adsorption capacities using these functional groups ranged from 294.12 mg/g for removal of Eosin Y using ethylenediamine at pH 5 (Huang et al., 2011) to 1412 mg/g for removal of reactive red using poly ethyleneimine at pH 2 as reported by (Kyzas et al., 2011). Polyacrylic acid and polyacrylamide were also reported for uptake of Basic Yellow and Remacryl Red TGL, showing uptakes of 309.82 to 563 mg/g. This is more than 50% smaller than the values reported by other amide and imine groups. The lower intake could be attributed the higher pH values used in this study. Comparing the results of basic removal with the results from Table 2 on the same dye, significant increment in the uptake of Basic yellow even in highly basic conditions was noted. This confirms the high potential of grafting effect in the adsorption of dyes. Itaconic acid and crotonic acid were also reported as grafting agents for chitosan modification for removal of Basic green. Nonetheless, the results are not satisfactory as compared to other grafting agents.

2.3.3. Surface impregnation

Surfactant impregnation of chitosan is also a method to improve its adsorption capacity. Surfactants such as SDS, cetyltrimethyl ammonium bromide (CTAB) or triton X-100 (TX-100) were used to increase the adsorption capacity of chitosan. They could link with chitosan through electrostatic interactions, giving rise to supra-molecular aggregates called surfactant chitosan complexes (Onesippe & Lagerge, 2008). Using surfactants can enhance electrostatic interactions because they formed a chemical bond with chitosan using the hydrophilic groups of surfactants and chitosan. Hydrophobic interactions can also occur between the chitosan backbone and the hydrophobic part of the surfactant that will enhance the adsorption capacity of chitosan. These strong interactions render a strong attachment between the surfactant and the chitosan leadsing a slower release of surfactant from the beads during the adsorption process (Chatterjee, Chatterjee, & Woo, 2010).

Chatterjee et al. (2010) synthesized a type of chitosan beads generated by SDS. The sorbent exhibited higher mechanical strength and acid stability than chitosan beads. The effect of variation of SDS concentration during gelation on the adsorption capacity of chitosan bead/SDS for CR as a model anionic dye showed that sorbent formed by 4 g/L SDS gelation had the highest adsorption capacity. The maximum adsorption capacity of sorbent (208.3 mg/g) was slightly higher than that of the chitosan beads (200.0 mg/g). Chatterjee, Chatterjee, Lim, & Woo (2011b) also used a surfactant to improve the adsorption capacity of a cationic dye, MB in aqueous solution on chitosan beads. Since chitosan has a polycationic nature, the adsorption capacity of cationic substrate is low because of the charge repulsions between the chitosan and the MB. Therefore, an anionic surfactant, SDS, was grafted on chitosan to introduce anionic charged groups on the bead surface. The adsorption capacity of chitosan bead/SDS decreased significantly with increasing SDS concentration during gelation. This decrease was a result of the increase in the density of chitosan bead/SDS membrane materials. The MB adsorption of chitosan bead and chitosan bead/SDS increased with increasing values for the initial pH of the solution. Data from both chitosan bead and chitosan bead/SDS showed that the maximum adsorption capacity of chitosan bead/SDS (226.24 mg/g) was higher than that of chitosan bead (99.01 mg/g). Chatterjee, Chatterjee, Lim, and Woo (2011a) investigated the effect of CTAB and TX-100 impregnation into chitosan hydro gel beads formed by SDS gelation on the adsorption of CR from aqueous solutions. CTAB impregnation was found to be more effective than TX-100 impregnation, indicating that electrostatic interactions between CTAB and CR enhanced the adsorption process. Chitosan bead/SDS/CTAB exhibited less sensitivity to initial pH change than non-impregnated chitosan bead and chitosan bead/SDS/TX-100. Results indicated that the maximum adsorption capacity value of chitosan bead/SDS/CTAB (271.74 mg/g) was higher than that of chitosan bead/SDS/TX-100 (242.72 mg/g) or CSB without surfactant impregnation (174.83 mg/g).

3. Environmental and toxicity consideration of chitosan modification

Studies have proven that modifications on chitosan in terms of cross-linking, grafting and surface impregnation are essential to maximize the adsorption capabilities of chitosan on dyes. At the same time, they are also important to ensure that the structure of chitosan remain intact even at very low pH condition. Modified chitosan adsorbents are environmentally friendly alternatives to commercial activated carbon. The main drawback of the modifying agents is that they are considered to be toxic and might bring negative effects to the environment. Even if the presence of free unreacted agents in gels is unlikely, since the materials are purified before use, the toxicity of the adsorbents should still be evaluated. Therefore, in this section, the toxicities of these modification agents are discussed.

One of the widely used cross-linkers is ECH. Many toxicology researches have been conducted on ECH. It was found that high concentration ECH led to CNS depression and respiratory tract irritation (Gage, 1959). Several tests showed that exposure to 30 ppm of ECH on laboratory rats resulted in severe kidney damage (Laskin et al., 1980). As such, it was suggested that within a threshold limit of 5.3 ppm of ECH per daily exposure is safe (Lawrence, Malik, Turner, & Autian, 1972). At very high concentrations, GLA poses a big threat to the aqua ecosystem (Jolibois, Guerbet, & Vassal, 2002). According to Sano, Krueger, and Landrum (2005) long-term exposure to GLA with concentration at least 2.5 ppm will reduce the reproduction rate of fishes to as high as 97%.

Unlike ECH and GLA, TPP cross-linker is significantly less toxic than ECH and GLA. Basically, TPP is non-toxic to human as it does not irritate skin and eyes upon exposure, as well as does not affect the digestion system. It is also not mutagenic and not genotoxic. Even at a high concentrations (100 ppm) of TPP, there is no observable toxicity effect on the aqua ecosystem and TPP is considered an

Table 4
Removal of different dyes from aqueous solutions by chitosan synthesized by grafting.

Chitosan	Modification Reagent	Dye	Adsorption capacity (mg/g)	Temperature (°C)	pH	Reference
Flake	4-Formyl-1,3-benzene sodium disulfonate	Basic blue 3	166.5	25	3	Crini et al. (2008)
Bead	Pyromelliticdianhydride	Methylene blue	935	–	5	Xing et al. (2009a)
		Neutral red	909	–	5	
Bead	Poly(acrylic acid)	Remacryl red TGL	510.74	25	–	Lazaridis et al. (2007)
	Poly(acrylamide)	Remacryl red TGL	309.82	25	–	
Bead	Poly(acrylic acid)	Basic yellow	563	25	12	Kyzas and Lazaridis (2009)
	Poly(acrylamide)	Basic yellow	363	25	12	
Powder	Poly(acrylic acid)	Basic yellow	595	25	12	
	Poly(acrylamide)	Basic yellow	528	25	12	
Bead	Poly(methacrylic acid)	Methylene blue	1000	25	6	Xing et al. (2009b)
		Methyl green	523.6	25	4	
Bead	Polymethyl methacrylate	Procion yellow MX	250	–	7	Singha et al. (2009)
		Remazol Brilliant violet	357	–	7	
		Reactive blue H5G	178	–	7	
		Procion yellow MX	263	–	5	
		Remazol Brilliant violet	384	–	5	
		Reactive blue H5G	204	–	5	
Bead	Acrylamide	Reactive red	1185	25	2	Kyzas et al. (2011)
		Reactive yellow	1160	25	2	
		Reactive blue	1125	25	2	
	Polyethylene imine	Reactive red	1412	25	2	
		Reactive yellow	1392	25	2	
		Reactive blue	1329	25	2	
Bead	Poly(acrylic acid)	Reactive yellow	456	25	2	Kyzas and Lazaridis (2009)
	Poly(acrylamide)	Reactive yellow	1058	25	2	
Powder	Poly(acrylic acid)	Reactive yellow	527	25	2	
	Poly(acrylamide)	Reactive yellow	1211	25	2	
Bead	Polymethyl methacrylate	Orange-G	435	–	3–6	Konaganti et al. (2010)
	Polyethyl methacrylate	Orange-G	360	–	3–6	
	Polybutyl methacrylate	Orange-G	290	–	3–6	
	Polyhexyl methacrylate	Orange-G	265	–	3–6	
Bead	Pthylenediamine	Eosin Y	294.12	25	5	(Huang et al., 2011)
Bead	Pthylenediamine	Acid orange 7	1215.61	25	4	Zhou, Jin, Liu, Liang, and Shang (2011), Zhou, Shang, and Liu (2012a)
	Ethylenediamine	Acid orange 10	1017.83	25	3	
Powder	Polyamidoamine	Acid blue 9	1265	50	4	
Bead	Itaconic acid	Basic green	135	Room temperature	–	Chatterjee et al. (2011b)
	Crotonic acid	Basic green	108	Room temperature	–	

environmentally friendly cross-linker (Anonymous, 2003). However, it has the least reports being published on TPP compared to GLA and ECH. Thus, more research should be carried out using TPP as cross-linker for the adsorption of dyes. As for EDGE, there are no reported data on the threshold toxicity limit of EDGE concentration. However, upon long term exposure to EDGE, respiratory and kidney system might be affected.

While most of the grafting agents used are generally low to moderate in toxicity, Pyromelliticdianhydride is especially highly toxic, and like any hydride compound, it causes haemorrhage and severe kidney problems (Kaplan et al., 1993). Many medical reports discussed long term exposure of pyromelliticdianhydride and it was found that mutagenic effect on human is possible (Viktorova, Khustnutdinova, Lobanov, & Rafikov, 1994). Thus, the threshold limit of pyromelliticdianhydride is set to be 0.00112 ppm (Sokolov, Filonov, Amvrosev, & Drobenia, 1996). Even though, after grafting the toxicity of this agent might be eliminated; the possibility of presence of non-reacted agents must not be rules out.

Numerous researches have been done to analyze the toxicities of CTAB and SDS surfactants. It was found that 0.032 wt.% of CTAB in drinking water is sufficient to prevent proper nutrition being distributed in the rat's body (Isomaa, Reuter, & Djupsund, 1976). According to Dehghan-Noudeh, Housaindokht, & Bazzaz (2005), exposure to 20 ppm of CTAB and 50 ppm of SDS is sufficient to rupture erythrocytes which is an important part of the haemoglobin blood cell of human. There is no toxicity data available for TX-100 surfactant.

In summary, despite the toxicities of certain modification agents, they are still widely used for modification of chitosan to be used as an adsorbent. As cross-linkers are used, the stability of chitosan in low pH medium is ensured, but the adsorption capacities might be compromised. Due to toxicity of the modification agents, researchers begin to find other alternative methods to solve this issue. One of the most effective methods is the application of nano-chitosan. With the synthesis of nano-chitosan, the specific surface area of nano-chitosan is increased significantly, and consequently might increase the adsorption capacities of most dyes.

4. Nano-chitosan

Nano-chitosan is a natural material with excellent physico-chemical properties, making it a superior environmentally friendly material, and it possesses bioactivity which is not harmful to human being. Compared to traditional micro-sized supports used in separation process, nano-sized adsorbents possess better performance that can be attributed to their high specific surface area, small size, absence of internal diffusion resistance and quantum size effect that could lead to exhibition of higher adsorption capacities. Nano-chitosan could be prepared through different techniques such as using coagulation or precipitation, covalent cross-linking, ionic cross-linking and emulsion droplet coalescence methods (Huang, Sheu, & Chao, 2009). Chitosan nanoparticles could also be prepared by the interaction of oppositely charged macromolecules. The most common method to synthesis nano-chitosan is through the addition of TPP into chitosan solution (Calvo, Remunan-Lopez, Vila-Jato, & Alonso, 1997). As TPP is nontoxic, multivalent and is able to form gels through ionic interactions and the nano-chitosan produced through this technique is considered environmentally friendly. The

interaction is controlled by pH of the solution which can tune the charge density of TPP and chitosan (Zhao et al., 2011). Note that TPP is one of the ionic cross-linkers that might decrease the adsorption capacity due to the decrease in amino and hydroxyl groups as compared to other cross-linkers such as ECH. However, the large surface area of nano-chitosan itself will make up for the decrease in amino and hydroxyl group. Thus, the overall adsorption capacities for most dyes are still much higher than chitosan powder or chitosan beads. Moreover, TPP cross-linker is one of the least toxic cross-linkers, and thus, nano-chitosan is still considered as a green adsorbent.

Enhancing the adsorption capacities of acid dyes (Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Orange 73 and Acid Red 18) by chitosan nano-particles have been studied by Cheung, Szeto, and McKay (2009). Under the same conditions and same types of dyes, the adsorption capacities of these dyes were compared with the work of Wong, Szeto, Cheung, and McKay (2004), using flake-based chitosan as adsorbent. It was clearly seen that nano-chitosan provided a significant improvement in terms of adsorption capacities. It was remarked that the adsorption capacity of Acid Green 25 increased more than 3 times. An optimum chitosan-TPP ratio is also important to ensure a more homogenous nano-chitosan is produced. If the concentration of chitosan is significantly higher, a clear solution occurs, indicating the nano-chitosan is not formed due to lack of TPP (Momenzadeh, Tehrani-Bagha, Khosravi, Gharanjig, & Holmberg, 2011). Vice-versa, occurrence of aggregation, indicates that non-homogenous adsorbent is formed. Adsorption of an azo reactive dye, C.I. Reactive Red 120 (RR120), from aqueous solution on chitosan and on a chitosan nanodispersion was studied by Momenzadeh et al. (2011). It was found that an optimum ratio of chitosan to TPP is 3:1, whereby opalescent suspension is observed and 80% removal of Reactive Red 120 was achieved.

5. Conclusions and future perspectives

Throughout the years, intensive developments and researches have been done on chitosan with a major goal of commercializing chitosan into an alternative adsorbent to activated carbon. At the same time, the adsorbent has to be cost effective, available, environmentally friendly, and does not require high processing. Most importantly, it must be effective in removing dyes. It is evident that chitosan could fulfil most of these requirements because of their specific characteristics such as low cost, high adsorption capability and selectivity, versatility, environmentally friendly and biodegradability. However, employing chitosan in the form of flake or powder as adsorbents has drawbacks. Chitosan (flakes or powder) has low adsorption capacity because of its crystallized structure. As a result, adsorption merely occurs on the amorphous region of the crystals to consequently limit the adsorption capacity. This problem is solved by making chitosan into beads. The crystallinity is therefore reduced and as a consequence, the adsorption capacity increases. Still, extra problem arises as chitosan beads have high dissolution tendency in acidic solutions.

Thus, the beads must be stabilized chemically by cross-linking to reinforce the chemical stability of the chitosan in acidic solutions and improve mechanical resistance. By contrast, cross-linking decreases the number of free and available amino groups on the chitosan backbone. This lead to a decrease in the accessibility to internal sites and subsequently leads to a loss in flexibility of the polymer chains as well as a decrease in the adsorption capacity. In addition, the amine groups of chitosan do not have good selectivity for the adsorption of different dyes. Therefore, to minimize this effect, efforts have to be made to maintain the degree of cross-linking as low as possible. It is followed by further chemical modifications such as grafting functional groups onto the polymer backbone to improve the selectivity and capacities. Graft copolymerization of chitosan introduces the desired properties and enlarges the field of potential applications of chitosan depending on the type of side chain. Adsorption capacities could also be improved using surface impregnation.

Cross-linked chitosan beads and graft copolymerized chitosan as well as surface impregnation represent good alternatives to replace commercial adsorbents. There are also other factors to be considered. Most of the major cross-linkers, surfactants and certain grafting agents are highly toxic and are very harmful to the environment and health especially on possible long term exposure should commercialization become reality. Because of the structure of chitosan, cross-linkers could not be avoided and should be minimized. Alternatively, a much safer cross-linker such as TPP should also be more investigated. Recently, with nano-chitosan and TPP, lack of adsorption sites due to TPP cross-linkers could be made up by its large surface area and thus able to adsorb dyes with significantly larger adsorption capacities.

The development of chitosan adsorbent from chitosan flake into nano-chitosan has made the goal of commercialization much closer to reality. Only a handful of dyes adsorption using nano-chitosan have been studied and thus more studies should be done with many other different dyes or organic pollutants. Developing a multipurpose adsorbent that can remove different kinds of pollutants from polluted industrial effluents is preferable. Investigating more complex adsorbents capable of treating industrial wastewater is necessary. Regeneration studies also need to be performed in detail to enhance the economic feasibility of adsorbents. Based on the literature, few regeneration studies have been reported. Regeneration studies will determine the reusability of chitosan derivatives and will contribute to the effectiveness of the derivatives as an adsorbent.

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