

Crosslinked Chitosan Materials for Adsorptive Removal of Dyes from Aqueous Solutions: A Brief Review

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Abstract

As a promising adsorbent, chitosan has been found to be extremely useful in its native form as well as in modified forms for the removal of variety of dyes from aqueous medium. Scientific workers have modified chitosan structurally by utilizing its -OH and -NH₂ functional moieties in numerous ways to obtain potential material with chemical and physical stabilities. Various modifications of chitosan involve crosslinking, grafting, impregnation and composite formation. Among various established routes of modifications, the most common way is its crosslinking to provide enhanced mechanical strength along with minimizing its solubility in acidic environment. In this paper, we review briefly only the crosslinked chitosan materials reported in last fifteen years by various researchers for adsorption of dyes as pollutants in order to provide clean and safe environment. Various materials formed through crosslinking, the dyes targeted for adsorption, various isotherms studies, kinetics studies and adsorption capacities of these materials have been discussed in details on case wise basis.

Keywords: Chitosan, crosslinked chitosan, adsorption, dyes, adsorption capacity.

Introduction

Bio-sorbents are considered to be ideal candidatures for effective removal of water toxicants since they have characteristic functional groups, large surface area with suitable porosity which leads to high adsorption capacities. The characteristics properties like ease of accessibility, cost effectiveness, mechanical stability and compatibility, its regeneration, non-toxicity towards environment, high selectivity to remove a wide range of water toxicants and simple processing procedures make these materials more attractive¹. In order to develop an effective bio-sorbent, researchers have focused on natural polymers such as cellulose, chitin

and chitosan to serve as potential adsorbents with magnificent adsorption capacity with minimal synthesis cost. Being abundantly available, chitosan is a low-cost bio-polymer that can be used for water treatment and can be obtained from natural resources. In comparison to majority of commercial adsorbents, chitosan has received attention due to its interesting properties like cationic nature in slightly acidic medium, macromolecular structure and low cost of synthesis.

When compared with cellulose and chitin, the chitosan has two major advantages. Firstly, it is soluble in acidic medium and can be recovered by adding base. This makes its purification and separation possible. Secondly, reactive $-NH_2$ functional group makes it possible to modify chitosan in various ways to achieve desired properties like mechanical and thermal stability and adsorption tendency towards targeted pollutant.

In general, chitosan is an acid-soluble de-acetylated product of chitin. Exoskeleton of sea creatures such as cray fish, lobster, prawn, crab and shrimp are the major sources of chitin which makes it one of the second most abundant polysaccharides worldwide after cellulose. This chitin on deacetylation with alkali leads to formation of chitosan. Chitosan is a linear, semi-crystalline polysaccharide composed of (1 \rightarrow 4)-2-acetamido-2-deoxy- β -D-glucan (N-acetyl D-glucosamine) and (1 \rightarrow 4)-2-amino-2-deoxy- β -D-glucan (D-glucosamine) units and can be chemically expressed as nontoxic, heterogeneous, linear, cationic and biodegradable polysaccharide with high molecular weight. Depending on the source of chitin, molecular weight of chitosan is typically ranging in between 300-1000 kDa. Although chitin is found naturally in large amounts through many sources, chitosan is only found in nature in limited quantities, such as in some fungi. To meet the industrial as well as research needs, chitosan is typically derived from chitin through chemical modification or enzymatic treatments leading to deacetylation (Fig. 1)^{2,3}.

The poor solubility and high molar mass of chitin restricts its applicability. On the other hand, presence of amino groups in chitosan increases its solubility in acidic solutions. Also, in near-neutral medium, the free $-NH_2$ group interact with cationic species including metal ions and cationic dyes making it highly useful customer in waste water treatment and purification. Protonation of amino groups of chitosan forms polycations for the formation of ionic complexes with series of anions like bio-macromolecules such as lipid, proteins and DNA along with some synthetic anionic species. In fact, chitosan remains as alone positively charged polysaccharide in nature⁴. In order to form stable covalent bonds during variety of

reactions such as etherification, esterification and reductive amination, chitosan involves both amino and hydroxyl groups. Chitosan has also proved its outstanding ability in biomedical field by acting as an antibacterial and antifungal agent, along with mucoadhesive, analgesic and hemostatic properties. Its biocompatibility can be considered due to biodegradation into nontoxic residues which is highly related to the molecular mass of chitosan and its degree of deacetylation. At least 50% of the free amine form can be observed after its deacetylation. But most commonly used chitosan has more than 80% degree of deacetylation that can be further increased by alkali treatment⁵.

Presence of amino and hydroxyl groups on chitosan are capable of forming a variety of interactions including amide and ester bonding as well as Schiff base formation. Schiff base is a weak base and insoluble in water and organic solvents, but usually soluble in acidic solutions. The most influencing properties such as mechanical strength, chemical stability, swelling, aqueous permeability, and solubility can be achieved through crosslinking of chitosan⁶.

In various adsorption applications, different crosslinkers modify chitosan by favoring bonding with the readily available amino and hydroxyl groups of chitosan. Crosslinking can be achieved through covalent bonding or through ionic bonding. Covalent bonding can be achieved either through $-NH_2$ group or $-OH$ group. The most frequently used crosslinker for $-NH_2$ group is glutaraldehyde while that for $-OH$ group is epichlorohydrin. Ionic crosslinking involves protonation of $-NH_2$ groups and interaction of multivalent anions like tripolyphosphate (TPP). The nature of bonding involving these three crosslinkers has been shown in Fig. 2. Use of epichlorohydrin as a crosslinker is of great significance because it preserves reactive $-NH_2$ group that is capable of coordinating with metal ions or can be further modified by impregnation with various organic moieties⁷. Indeed, crosslinking lowers the adsorption characteristics of chitosan, however it has been used to improve mechanical strength of chitosan. Improvement of metal binding capacity as a result of increase in hydrophobicity caused by partial destruction of crystallinity by homogeneous crosslinking of chitosan was observed as compared to heterogeneous crosslinking^{8,9}.

Dyes are a common class of pollutants released by most of the textile industries. Dyes can be classified in different ways as acid dyes, basic dyes, mordant dyes, direct dyes, vat dyes, reactive dyes, disperse dyes and sulphur dyes. Presence of textile dyes in wastewater discharged by these industries in aquatic environments such as valleys, rivers, sea, oceans and

lack of their biodegradability under normal ecological conditions, can destroy aquatic ecosystem. There are serious ecological consequences such as changing the nature of aquatic environments and reducing photosynthesis compared to aquatic flora. Aesthetic and health problems associated with such water is another aspect of concern. Such water can cause allergies, dermatitis, skin irritations, cancers and mutations in humans. Furthermore, 60 to 70% of azo dyes are toxic, carcinogenic and are refractory to conventional treatment processes because of their resistance to conventional physicochemical destruction and the absence of their biodegradability¹⁰.

Various methods used in textile effluent treatment have been depicted in Fig. 3. Among these, adsorption is the most preferred due to ease of operation, low cost involved and greener aspect associated with it. These methods can be broadly classified as- physical, chemical and biological. Among all these methods, the chemical methods include use of costly chemicals and also the unreacted chemicals may lead to contamination. Biological process using microorganisms and enzymes are superior, but are very slow and time consuming. Physical processes including reverse osmosis, filtration, coagulation/flocculation and adsorption are considered to be most practical methods and are widely used in water treatment. Among them, adsorption is considered to be most cost effective and useful for larger water bodies. Use of biosorbents make the adsorption process more eco-friendly. Regeneration and reusability of biosorbents gives another greener dimension to biosorption process.

Literature review

Among various methods of modifications of chitosan, only those involving crosslinking have been discussed in this paper. A comprehensive review of literature of last 15 years is presented below.

Adsorbent with a high adsorption capacity for anionic dyes was prepared by Chiou et al.¹¹ and co-workers in 2006. They studied adsorption behavior of MY (metanil yellow) and reactive dye (RB15, reactive blue 15) in aqueous solutions by crosslinked chitosan beads. The adsorption capacities were 1334 mg/g and 722 mg/g respective for these dyes at pH 4. The adsorption mechanism followed Langmuir model and fits well first order kinetics model with dynamic adsorption behavior. Adsorption capacity towards RB15 has been found to be one of the best ever reported in literature for this dye.

Meanwhile, the crosslinked chitosan/oil palm ash composite was applied as an excellent adsorbent for removal of reactive blue 19 dye from aqueous solution by Hasan et al¹². At pH 6, maximum adsorption was observed for crosslinked chitosan/oil palm ash composite beads. Various adsorption isotherms were studied such as Langmuir, Freundlich, Redlich–Peterson, and Temkin. Among these adsorption isotherms, Redlich–Peterson showed better correlation coefficient than the other models at all temperatures studied. The prepared adsorbent exhibited adsorption capacity of 423.5 mg/g at pH 6 and 30 °C. The pseudo-second order was better describing adsorption kinetics of dye upon crosslinked composite. Thermodynamic data indicate that dye adsorption onto synthesized composite was spontaneous in nature. Near-neutral conditions are the key features of this study that eliminates necessity of further neutralization of water after adsorption process.

Chitosan-EGDE (ethylene glycol di-glycidyl ether) beads were investigated by Kumari et al¹³, for the removal of acid red and blue dyes from aqueous solution. Crosslinking with EGDE enhances chemical resistance and mechanical strength of chitosan. Adsorption isotherm showed that Langmuir isotherm model was best fitting as compared to other models. The kinetics studies were carried out to find out order of reaction which followed pseudo-second order kinetics. Adsorption of acid dyes onto chitosan-based adsorbents was a physical adsorption confirmed by FT-IR spectral analysis. After successive examinations, the maximum adsorption capacity for acid red and blue dyes were found to be 59.52 mg/g and 142.86 mg/g at pH 2 and pH 4 respectively. The physical modification to obtain adsorbent in the form of beads make filtration easy after adsorption of dye.

Subsequently, efficiency of chitosan and crosslinked chitosan adsorbents was examined by Kumari et al¹⁴, using batch adsorption techniques for the removal of acid red and blue dyes from aqueous solution. Chitosan has been crosslinked with glutaraldehyde and sulphuric acid. The adsorption equilibrium data very well followed Langmuir isotherm, while the adsorption of both acid dyes best fits with pseudo-first order kinetics. Thermodynamic parameters were studied to find out enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°). It was observed that the adsorption process was spontaneous and exothermic. The additional advantage of these crosslinked chitosan–GLA and chitosan–H₂SO₄ adsorbents is that they can be regenerated and reused in multiple cycles.

A decade before, magnetically separable adsorbent, namely magnetic γ -Fe₂O₃ /crosslinked chitosan composites represented as MY-Fe₂O₃/CSCs were synthesized by Zhu et al¹⁵ using

process of micro-emulsion. The adsorbent has been employed for adsorption of methyl orange (MO) from aqueous solution. After successful characterization, it was observed that magnetic γ -Fe₂O₃ introduced well in MY-Fe₂O₃/CSCs which maintained magnetic properties in crosslinked composite. Additional dose of γ -Fe₂O₃ was given out to saturate magnetization of synthesized material. After adsorption of methyl orange by MY-Fe₂O₃/CSCs, composite was effectively separated from reaction solution by the application of external magnetic field. Adsorption kinetics of methyl orange on the adsorbent followed pseudo-second order kinetics model giving highest adsorption at pH 4.

Later on, adsorption studies of textile dyes EY-4G and S-Blue onto crosslinked chitosan poly(acrylamide) hydrogels has been carried out by Ekici et al¹⁶. The result of kinetics of CS-PAAM IPN hydrogels is in accordance with second order model. It was observed that interpenetrating polymeric network structure affects network parameters of PAAM hydrogels. The best fitted adsorption isotherm was Langmuir. The maximum adsorption capacities were in between 18.90 mg/g to 63.20 mg/g. From thermodynamic equilibrium, it was clear that the nature of adsorption phenomenon was endothermic. This study shows that in powder, film, or bead form synthesized hydrogel have greater adsorption potential.

Guo et al¹⁷ studied adsorption properties of Reactive dye on crosslinked chitosan beads for various parameters such as concentration of adsorbent, pH, initial dye concentration and temperature of adsorbate. The adsorption modeling was carried out to analyze equilibrium data at different temperatures. Freundlich isotherm was found to fit well. Crosslinked chitosan showed adsorption capacity of 19.613 mg/g to remove reactive dye and proved great adsorption capability even after repeated cycles. In this material, crosslinking leading to formation of spherical beads giving mechanical stability to adsorbent that remains in solid form even in strongly acidic conditions.

The nanoparticles of templated crosslinked chitosan have been investigated by Chen et al¹⁸ using ECH-RB5 and ECH-3R through imprinting process for adsorptive removal of Remazol Black 5 (RB5) and Remazol Brilliant Orange 3R (3R) dyes. The results match with the second order kinetics and Langmuir adsorption models. Dubinin-Radushkevich model revealed that adsorption process may be physisorption. The maximum adsorption capacities were found to be 5572 mg/g and 5392 mg/g for Remazol Black 5 and Remazol brilliant Orange 3R respectively at pH 3, that are much higher as compared to most of the reported

materials. The most interesting aspect of this material is its enormously high adsorption capacity towards both of these dyes.

Another study on adsorption of methyl orange (MO) from aqueous solutions on protonated crosslinked chitosan was investigated by Huang et al¹⁹. There was a negligible effect of pH on adsorption of methyl orange. Langmuir model was fitted perfectly well and the maximum monolayer adsorption capacities obtained from Langmuir model was 130.9 mg/g. The adsorption kinetics followed pseudo-second order model. This study is an example of ionic crosslinking process adopted for simple modification of chitosan.

The removal of Direct Red 80 (DR80), Reactive Yellow 25 (RY25) and Acid Blue 25 (AB25) dyes by chitosan-based beads has been investigated by Luk et al²⁰. Glutaraldehyde crosslinked chitosan beads achieved complete removal of the three dyes within one hour. It was observed that adsorption with crosslinked beads at pH 5 promotes removal of RY25 and AB25 by at least two folds more than that by non-crosslinked chitosan beads. The adsorption capacity towards RY25 and AB25 are 368.3 mg/g and 443.3 mg/g respectively. DR80 adsorption is achieved at more acidic condition at 610.5 mg/g. Adsorption isotherm fitted Langmuir model and pseudo-second order equation agreed very well with kinetics data. This material has a potential of multi-toxicant removal and these studies could be very well extrapolated to simultaneous removal of organic dyes from a single solution.

Bulut and Karaer²¹ reported crosslinked chitosan/bentonite composite for the removal of Methylene blue from aqueous solution. From the observation of kinetics and thermodynamic parameters of adsorption process, it was confirmed to be an endothermic spontaneous adsorption process. Equilibrium experiments fitted well with Langmuir isotherm model and the maximum monolayer adsorption capacity for MB was 95.24 mg/g at 298K. Kinetics studies estimated that the process was rapid and followed second order kinetics. The maximum uptake was achieved in more basic aqueous environment.

Glutaraldehyde crosslinked magnetic chitosan nanoparticles (GMCNs) have been examined for adsorption of FD&C Blue 1 and D&C Yellow 5 dyes from aqueous solutions, by Zhou et al²². Results indicated that GMCNs not only exhibited excellent food dyes adsorption, but also showed low cytotoxicity. From study, it was observed that the adsorption capacity of GMCNs for food dyes were affected by initial pH values, initial dye concentrations and temperatures. Adsorption followed pseudo-second order reaction, and equilibrium

experiments were well fitted Langmuir isotherm. GMNCs displayed maximum capacity of adsorption at pH 3.0 at 298K. Spontaneous and exothermic nature of adsorption was demonstrated through thermodynamic studies. Experimental observations indicated that GMNCs can be regenerated and reused through dye desorption in alkaline solution. Magnetization of the material has made separation of composite extremely easy and rapid after adsorption of dye.

Magnetic chitosan nanocomposites (MCNCs) were synthesized by Kadam et al²³ using reduction precipitation technique with glutaraldehyde as a crosslinker. These supermagnetic MCNCs exhibited magnetic saturation of 17.5 emu/g. and showed 90.60% adsorption of Acid Red 2. Experimental data showed that high adsorption of dye on MCNCs was resulted from presence of free amino and hydroxyl groups. It was observed that the optimum pH and adsorbent concentration were 3 and 1.0 g/L, respectively. Adsorption isotherm best fitted according to Redlich-Peterson models. This isotherm model has a linear dependence on concentration in numerator and an exponential function in denomination which altogether represent adsorption equilibrium over a wide range of concentration of adsorbate which is applicable in either homogenous or heterogeneous systems because of its versatility.

Liu and co-workers²⁴ reported adsorption of anionic azo dye by crosslinked chitosan/bentonite composite. They synthesized crosslinked chitosan (CCS)/bentonite (BT) composite by the intercalation of chitosan in bentonite and crosslinking reaction between chitosan and glutaraldehyde. Crosslinked chitosan/bentonite composite adsorbed Amido Black 10B at pH 2 to a greater extent. Maximum adsorption capacity of CCS/BT composite was 323.6 mg/g at 293 K and pH 2 and best fitted with Langmuir adsorption isotherm. Thermodynamic and kinetics parameters study showed that adsorption of Amido Black 10B by CCS/BT composite was spontaneous and endothermic in nature and followed a pseudo-second order kinetics model. The only limitation of this process was very low working pH that makes post-adsorption process necessary to eliminate excess acidity imparted to solution.

Xuemei et al²⁵ synthesized crosslinked chitosan hybrid membranes with oxidized starch and silica couple agent (CS/OSR/Silica) had been employed for removals of two direct dyes (Blue 71 and Red 31). With the help of crosslinking, they achieved enhanced thermal stability and swelling property of CS/OSR/Silica hybrid membrane. The adsorption capacity of CS/OSR/Silica membrane was higher at pH 9.82 for two direct dyes at a fixed membrane dosage and dye concentration. Adsorption of dyes onto CS/OSR/Silica membranes follow

pseudo-second order model and experimental equilibrium data fitted well Freundlich isotherm model. The adsorption capacities on CS/OSR/Silica membranes are 67.2 mg/g and 94.4 mg/g respectively for Blue 71 and Red 31 respectively²⁵. It is one of the very few materials that act as good adsorbents in alkaline pH range.

Another example of decorated chitosan with Fe₃O₄ nanoparticles followed by crosslinking with Graphene oxide to prepare Fe₃O₄ supported chitosan-graphene oxide composite (Fe₃O₄@-GO) was synthesized by Gul et al²⁶. and co-workers for the removal of Methyl violet and Alizarin yellow R dyes. Adsorption kinetics best fitted with pseudo-second order model. Langmuir and Freundlich isotherm were applied to understand the interaction of dye with adsorbent. Adsorption of Methyl violet and Alizarin yellow R dyes onto Fe₃O₄@-GO best fitted with Langmuir isotherm and maximum adsorption was achieved at pH 10 and 6 respectively for Methyl violet and Alizarin yellow R. The enhanced surface area due to mesoporous nature of graphene-magnetite composite has led to enhancement in adsorption capacity.

Hydrothermal treatment of NaOH was carried out by Khanday et al²⁷ to obtain crosslinked beads of activated oil palm ash zeolite/chitosan (Z-AC/C) composite using activated oil palm ash followed by beading with chitosan. Batch adsorption of methylene blue (MB) and acid blue 29 (AB29) were studied to find out effect of dye concentration, temperature and pH. Adsorption of both dyes on Z-AC/C was better described by Pseudo-second order kinetics and Freundlich isotherm model. The maximum adsorption was found to be 151.51 mg/g for MB and 212.76 mg/g for AB29 at pH 11 and 3 respectively. As working pH are two extreme values, it has not been possible to study simultaneous removal of both the dyes.

In line with the adsorption of methylene blue (MB) and reactive orange 16 (RO 16), crosslinked chitosan/sepiolite composite was employed by Marrakchi et al²⁸ where sepiolite clay and chitosan were crosslinked using epichlorohydrin. Adsorption studies were carried out for MB and RO16 adsorption onto Crosslinked chitosan/sepiolite composite. It was observed that Methylene blue gives highest adsorption at pH 9 while for Reactive orange 16 maximum adsorption was achieved at pH 3 and their adsorption capacities were found to be 40.986 mg/g and 190.965 mg/g respectively. Various adsorption isotherms were examined such as Freundlich, Langmuir, and Temkin. From adsorption data for both the dyes it was noticed that Freundlich was best fitted model. For both the dyes pseudo-second order kinetics were found to describe adsorption process better than pseudo-first order kinetics.

A novel graphene oxide-based adsorbent (FCGO) from fly ash crosslinked with chitosan and graphene oxide was synthesized by Guanghong et al²⁹. It was used for effective removal of anionic and cationic dyes, namely, Acidic Red GR (ARG) and Cationic 5GN (CRX), respectively. The effect of pH upon adsorption was carried out. It was noticed that percentage removal of anionic dye by FCGO decreases with increasing initial pH in acidic Red X-solutions but is not affected at pH higher than 6 while initial pH minimally influences percentage removal of cationic dye. After adsorption of both anionic and cationic dyes by graphene oxide-based adsorbent, final pH becomes close to neutral in acidic medium because of protonation effect. The adsorption kinetics of ARG and CRX follow pseudo-second order kinetics model. Adsorption process fits well with Redlich-Peterson model. The maximum adsorption capacities are 38.87 and 64.50 mg · g⁻¹ for ARG and CRX, respectively. From thermodynamic data, it was noticed that adsorption is a spontaneous and endothermic process.

Jawad et al³⁰ and co-worker fabricated immobilized crosslinked chitosan-epichlorohydrine thin film (CLCETF) onto glass plate for adsorption of reactive orange 16 (RO16) dye using direct casting technique. Batch adsorption studies were carried out taking contact time, initial dye concentration and pH. From adsorption isotherm it was noticed that adsorption of reactive dye onto CLCETF followed Langmuir model. The adsorption capacity of CLECTF for RO16 was 356.50 mg/g at 27 ± 2°C. The kinetics parameters demonstrated that the process closely followed pseudo-second order model. From the results, it was clear that immobilized CLECTF can be used as a potential candidate for the treatment of reactive dye without using filtration process.

Crosslinked chitosan(C)/marble powder (M) composites were prepared by Deniz et al³¹ from marble powder and chitosan and crosslinked using glutaraldehyde. Adsorption behavior of chitosan/marble powder composite for Dimozol Blue was evaluated. Adsorption behavior of Dimozol Blue onto the chitosan/marble powder composites was carried out to evaluate adsorption kinetics and equilibrium isotherms from aqueous solution. Dimozol Blue dye adsorption on Crosslinked chitosan(C)/marble powder (M) composites was described well by pseudo-second order and Freundlich isotherm models. Study shows maximum adsorption capacity of chitosan/marble powder composites for removing Dimozol Blue to be 234.5 mg/g at pH. The thermodynamic studies revealed that Adsorption process is spontaneous and exothermic and adsorption is physical adsorption was revealed from thermodynamic

equilibrium experiment. The marble powder that gets waste after cutting of marble stones was successfully utilized to enhance the adsorption capacity of chitosan towards Dimazol Blue.

Potential of novel crosslinked chitosan for removal of Congo red dye from an aqueous phase was studied by Zahir et al³². Adsorption of dye onto Diammonium tartrate modified Chitosan (DMC) and Urea Diammonium tartrate modified Chitosan (UDMC) examined at different conditions like effect of adsorbent dose, contact time, initial solution pH and temperature. Sips Isotherm model was followed strictly according to adsorption isotherm studies and maximum dye uptake was 1597 mg/g for Diammonium tartrate modified Chitosan (DMC) while 1447 mg/g for Urea Diammonium tartrate modified Chitosan (UDMC). Pseudo second order kinetics model was best fitted. From value of ΔH° and ΔG° , it is suggested that the process of adsorption is feasible and endothermic nature of Congo red adsorption over both adsorbents. Incorporation of nitrogen containing moieties into chitosan matrix was found to have a positive impact on adsorption efficiency.

Apart from usual adsorbent, antimicrobial terephthaloyl thiourea crosslinked chitosan (TTCCH) hydrogels was investigated by El-Harby et al³³ for Congo red dye removal from its aqueous solution. Hydrogel was synthesized by reacting chitosan with terephthaloyl diisothiocyanate crosslinker. To achieve best adsorption capacity of hydrogel, its structure, dye adsorption parameters were studied. The parameters includes initial concentration of the dye solution, temperature and time of exposure to dye. The investigation of adsorption kinetics and isotherms informed that the process of adsorption of Congo red dye onto TTCCH was better fitted by pseudo-second order equation and Langmuir equation, respectively. Adsorption of Congo red dye achieved maximum sorption capacity of 44.248 mg/g. which confirmed the process of uptake of Congo red dye on adsorbent is a chemisorption process. Examination of thermodynamic data showed that adsorption reaction was endothermic and spontaneous in nature.

Foam membrane based crosslinked chitosan was discussed by Hu-Cheng et al³⁴, to remove some colored dyes. Polyurethane foam membrane filled with humic acid-chitosan crosslinked gels (HA-CS-PUF) was synthesized for dye removal by soaking foams into humic acid-chitosan (HA-CS) crosslinked gels and hot-pressing them into membranes. HA-CS-PUF was characterized for structural morphology by SEM, thermal stability was studied by DTA and membrane was characterized for X-ray photoelectron spectroscopy. These studies revealed

that humic acid and chitosan crosslinked through ionic bonding. Different charged dyes were examined for membrane properties. For that purpose, three dyes were selected including positively charged methylene blue (MB), neutrally charged rhodamine B (RB) and negatively charged methyl orange (MO). Adsorption experiment were carried out to tests their maximum adsorption capacities, kinetics parameters and thermodynamics. Study revealed that adsorption process was better fitted with Pseudo-second order and Freundlich model. Maximum adsorption capacities were found to be 10.31 mg/g, 8.26 mg/g and 5.29 mg/g for MB, RB and MO respectively. The highest adsorption of methylene blue, rhodamine B and methyl orange was achieved at pH 10, pH 4 and pH 4 respectively.

New material for adsorption of textile dye Direct orange 2GL was introduced by Dilarri et al³⁵, and group. They proposed immobilized *Saccharomyces cerevisiae* in crosslinked chitosan beads to analyze kinetics, isotherm and thermodynamics for adsorptive removal of textile dye. Adsorption studies were carried out according to pH, it was found that Maximum adsorption of Direct orange 2GL dye onto *saccharomyces cerevisiae* immobilized crosslinked chitosan was achieved at pH 8. Study revealed that Freundlich isotherm was the best fitted model and adsorption process followed Pseudo second order kinetics. The process was spontaneous and endothermic in nature observed according to thermodynamic data.

The example of β -chitosan crosslinked with nitrogen containing polyamine base eg. triethylenetetramine, (BCCT) demonstrated by Chih-Wei et al³⁶ for adsorption and removal of Reactive Blue 221 (RB221) dye. Results indicated that, with increasing temperature from 303 to 333 K, adsorption rates of adsorbent BCCT for RB221 dye changed from 1.48×10^6 mg/g.min to 1.52×10^{13} mg/g.min. Adsorption of dye at all temperatures followed Elovich model. These results confirmed that crosslinking leads to incorporation of amine groups, thereby promoting ability of BCCT to adsorb dyes under strongly acidic conditions. Adsorption process revealed that Langmuir isotherm was best fitted with maximum adsorption capacity of 625.0 mg/g.

Carboxymethylated and partially crosslinked chitosan (NaCS-GL) was employed as an effective adsorbent, for removal Of Methylene Blue from aqueous solution, by Doshi et al³⁷. Carboxylate groups protonates amino groups on surface of NaCS-GL. Initial rate of adsorption of MB onto NaCS-GL controlled by chemical reaction later it governs by intraparticle diffusion. Kinetics study revealed that the process was following pseudo-second order kinetics. Adsorption isotherms best fitted with Sips isotherm and maximum adsorption

capacity was 365.77 mg/g. The Sips model is a hybrid model combining both Langmuir and Freundlich models. Sips model can describe the homogeneous or heterogeneous systems. Spontaneous and exothermic nature of adsorption of methylene on NaCS-GL was revealed by thermodynamic parameters. The highest adsorption of Methylene blue onto partially carboxymethylated and partially crosslinked chitosan was achieved at pH 5.6.

Sulphate crosslinked chitosan (SCC) for removal of Congo red (a benzidine-based anionic diazo dye) was studied by Jeyaseelan and co-workers³⁸. Adsorption studies carried out considering pH, contact time, adsorbent dosage, and concentration of adsorbent. Maximum adsorption capacity obtained at pH 3.0 was 91.8 mg/g at which percentage recovery was about 90% and followed Freundlich adsorption isotherm. The process of capture of congo red dye by SCC followed pseudo-second order kinetics. Thermodynamic equilibrium study noticed that process of adsorption is spontaneous and exothermic in nature. Regeneration of SSC was done with NaOH after repeated cycles.

Polymeric hydrogel (N-maleyl chitosan crosslinked P(AA- co-VPA))synthesized from acrylic acid (AA), vinylphosphonic acid (VPA) and N-maleyl chitosan was studied for the adsorptive removal of crystal violet (CV) and methylene blue (MB) dyes from aqueous solutions. In this study, Nakhjir et al³⁹ examined Langmuir, Freundlich, Temkin and Redlich-Peterson isotherm models. Experimental data was well described by Redlich-Peterson isotherm model. The adsorption kinetics followed pseudo-second order model. Hydrogel polymer showed adsorption capacity of for removal of CV and MB in 50 ppm dye solutions was 64.56 mg/g and 66.89 mg/g, respectively. Data obtained from thermodynamic studies dictated adsorption process was endothermic and spontaneous. In addition to that adsorbent was regenerated after four fold of adsorption-desorption cycle.

Antimicrobial agent, trimellitic anhydride isothiocyanate-crosslinked chitosan hydrogels has been investigated by Mohamed et al⁴⁰. This new adsorbent was applied to Congo red (CR) dye removal from its aqueous solution. Being polycationic hydrogel, the adsorption capacity of this material has been highly influenced for CR dye. Study revealed that the uptake of congo red dye onto trimellitic anhydride isothiocyanate-crosslinked chitosan hydrogels increased significantly with increasing temperature, with decreasing solution pH and with an increase in their contents of crosslinking. The process of adsorption fitted well to pseudo-second order kinetics model and confirmed to Langmuir model. The maximum adsorption capacity of hydrogel was found to be 63.05 mg g⁻¹ with removal efficiency of 96.59%. The

process is remarkably controlled by chemisorption phenomenon and it was endothermic in nature according to thermodynamic observation. Its an excellent combination of adsorbent formed with antimicrobial activity leading to removal of chemical as well as biological pollution.

One of established groups of Jawad et al⁴¹ reported an inorganic–organic hybrid nanocomposite bioadsorbent for removal of reactive red 120 (RR120) dye from aqueous environment using hybrid crosslinked chitosan-epichlorohydrin/TiO₂ nanocomposite (CTS-ECH/TNC). Adsorption of reactive dye was carried on synthesized adsorbent, maximum adsorption capacity of CTS-ECH/TNC for RR120 dye was recorded to be 210 mg/g at 303 K. From kinetics and adsorption modelling experiments, it was recommended that, the process well illustrated by pseudo-second order (PSO) kinetics and Langmuir isotherm model. Thermodynamic parameters study confirmed spontaneous and endothermic in nature of adsorption RR120 dye on CTS-ECH/TNC. On the basis of characterization and adsorption studies, the uptake of dye on the synthesized nanocomposite was governed by interactions such as electrostatic attraction, n- π stacking, and H-bonding which proves CTS-ECH/TNC as potential adsorbent for removal of RR120 dye as model of reactive azo dyes from aqueous environment.

Same group of researchers came up with an alternative for adsorptive removal of reactive red 120 (RR120) dye from an aqueous solution⁴². Tunable Schiff's base-crosslinked chitosan-glutaraldehyde (CS-GLA/TNA) was selected for studies. Batch adsorption experiment carried out considering parameters, such as adsorbent dosage (0.01–1.2 g/mL), RR120 dye concentration (30–400 mg/L), solution pH (3–12), and contact time (0–400 min). Different adsorptions modelling along with kinetics of the process were examined and results suggested that the process was well described by Freundlich model and pseudo-second order kinetics model. Maximum adsorption capacity of CS-GLA/TNC for RR120 dye was 103.1 mg/g at 30°C at pH 3 which was the combined effect of various interactions, such as electrostatic attraction, n- π stacking, and H-bonding.

Chitosan crosslinked graphene oxide/carboxymethyl cellulose aerogel globules CS-GO/CMC was administrated toward methylene blue (MB) removal by Hyang et al⁴³. The results showed that CS-GO/CMC composite aerogel had extremely high adsorption capacity reported so far in literature was 3190 mg/g. Various parameter such as adsorption isotherms, kinetics and thermodynamics were investigated. Data recommended that adsorption of

methylene blue onto CS-GO/CMC followed Langmuir adsorption model, pseudo-second order model and adsorption was a spontaneous and endothermic process.

To remove two structurally different reactive orange 16 (RO-16) and methyl orange (MO) dyes Jawad and co-workers⁴⁴ used crosslinked chitosan with glyoxal (Chi-Gly) and deposited onto glass plate to be a superior adsorbent film using non-conventional adsorption system without filtration process. Further, various adsorption isotherms were investigated, among all those adsorption isotherm of RO-16 and MO by Chi-Gly film were best described by Langmuir isotherm, with maximum adsorption capacities of 1554.3 mg/g and 1451.9 mg/g, respectively. Kinetics modelling data revealed that pseudo- first order kinetics model best fitted. Thermodynamic study informed that adsorption process was spontaneous and exothermic in nature at Chi-Gly at pH ~3. The highest values of uptake of RO-16 and MO by Chi-Gly film involved various interactions such as electrostatic attractions, dipole–dipole hydrogen bonding interactions, Yoshida H-bonding and n- π stacking.

Lyu et al⁴⁵ functionalized chitosan with ionic liquid to obtain ionic liquid functionalized crosslinked chitosan (IL-CCS) for removing sunset yellow FCF (SY) from aqueous solutions. Adsorption studies were carried out considering parameters such as initial pH, adsorbent dose and contact time. Investigation showed that there was negligible effect of pH on adsorption capacity of IL-CCS for SY. Maximum uptake of IL- CCS for SY observed was 300.28 mg/g, In addition, results of adsorption isotherm, kinetics and thermodynamics showed that adsorption process could fit with Langmuir model, pseudo- second order model, separately. The exothermic nature of reaction was revealed through thermodynamic parameters.

Graphene oxide/lignosulfonate aerogel (GLCA) crosslinked by chitosan without using any toxic chemicals was investigated by Mingfang et al⁴⁶ to test adsorption performance of GLCA to methylene blue (MB) considering factors such as pH, dosage, contacting time, temperature and initial concentration. The results showed that synthesized GLCA uptake MB dye potentially remove 99% MB dye from its 100 ppm dye solution. Calculated capacity of MB dye onto GLCA was 1023.9mg/g, which was highest ever than any other reported value for GO/polymer composites and activated carbon in literature. Thermodynamic data noticed that adsorption of MB on GLCA was spontaneous and endothermic in nature. The adsorptive removal of MB onto GLCA may consider various interactions such as electrostatic attraction, π - π interaction and hydrogen bond between GLCA and MB. In addition to that, adsorbent could be regenerated by washing with HCl solution and ethanol for number of cycles.

Another example of crosslinked chitosan-glyoxal/TiO₂ nanocomposite (CCG/TNC) by loading different ratios of TiO₂ nanoparticles into polymeric matrix of crosslinked chitosan-glyoxal (CCG) have been used for removal of methyl orange (MO) from waste water. Results obtained by Mohammed et al⁴⁷ showed that adsorption of MO on CCG/TNC described by pseudo-first order kinetic. The process was in agreement with Langmuir isotherm model with maximum adsorption capacity of 416.1 mg/g at pH 4. Mechanism of adsorption involved various interactions such as electrostatic attractions, n- π stacking interactions, dipole-dipole hydrogen bonding interactions, and Yoshida H-bonding.

Methylenebisacrylamide (MBA) and acrylic acid (AA), chitosan/polyacrylic acid/bentonite composites (CCS/PAA/BNTs) was synthesized and used for adsorption of malachite green (MG) by Yildirim et al⁴⁸. Experimental data gave good agreement with Langmuir model and followed pseudo-second order kinetics. The highest adsorption capacity calculated was found as 384.62 mg/g for MG adsorption at 318 K at pH 6. MG adsorption was endothermic, caused spontaneous reaction and increased entropy between 298-318 K described by thermodynamic studies. Study revealed that adsorption reactions of MG was physisorption ($\Delta H < 80 \text{ kJ mol}^{-1}$).

Jawad et al⁴⁹ reported blending of coalesced Chitosan (CS) with activated charcoal (AC), followed by crosslinking reaction with epichlorohydrin (ECH) was studied to remove thionine (TH) a model cationic dye, from aqueous solution. Batch adsorption studies of CS-ECH/AC was carried out considering various parameters such as initial concentration, adsorbent dose, time etc. The experimental studies showed good agreement with Freundlich isotherm. The maximum adsorption capacity of CS-ECH/AC for TH dye adsorption was 60.9 mg/g at 303 K. The kinetics followed pseudo-second order model. The values calculated for enthalpy and entropy indicated a spontaneous and exothermic nature of adsorption process. The study proved from characterizations that adsorption mechanism included mostly electrostatic attractions, H- bonding interactions, and π - π interactions. CS-ECH/AC found to be compatible composite for the removal of cationic dyes from wastewater.

Mohammed et al⁵⁰ physically modified Chitosan (CS) with fly ash (FA) powder and then chemical crosslinking reaction with tripolyphosphate (TPP) to produce a crosslinked FA composite (CSTPP/FA) was examined as adsorbent for removal of reactive orange 120 (RR120) dye. Adsorption studies noticed that the highest removal (88.8 %) of RR120 dye was achieved by CS-TPP/FA at pH 4. The adsorption equilibrium provide good agreement

with Freundlich model and maximum adsorption capacity of CS-TPP/FA for RR120 dye was found to be 165.8 mg/g at 45 °C. Kinetics uptake was well described by Pseudo second order. Thermodynamic studies concluded that adsorption process was spontaneous and exothermic in nature. CSTPP/FA concluded as an ideal composite adsorbent for removal of textile dyes from aqueous environment on the basis of adsorption parameter study.

Crosslinked Chitosan/ β -Cyclodextrin beads have been utilized by Kekes and Tzia⁵¹ to study the adsorption of Indigo Carmine. Adsorption studies were carried out considering various parameters such as dye's initial concentration, pH and temperature, and high concentrations of adsorbent. At lower concentration of dye, it was observed that adsorbent removes Indigo Carmine at faster rate at pH 4. On the basis of adsorption study, equilibrium adsorption data were described well for Langmuir model and maximum adsorption capacity was 1000.0 mg/g. Adsorption of Indigo Carmine was found to follow pseudo-second order. The data obtained from thermodynamic study such as negative values of ΔG° , ΔH° and ΔS° dictated adsorption process is exothermic, spontaneous and favorable at low temperatures.

Chanajaree and co-workers⁵² examined removal of two dye species i.e. Malachite Green (MG) and Indigo Carmine (IND) using Glutaraldehyde crosslinked chitosan (CSglu), by computational and experimental methods. Freeze dry method was applied to obtain CSglu beads. It is found from adsorption study that the CSglu beads can remove MG much better than IND. The maximum adsorption capacity was found to be 714.29mg/g for Malachite Green and 303.03mg/g for indigo carmine at pH 6. Adsorption kinetics study described well by pseudo-second order kinetics model for both complexes. Thermodynamic study has been carried out to find out values of ΔH and ΔG . The results suggested that adsorption processes of MG-CSglu are spontaneous and endothermic due to negative value of ΔG and positive value of ΔH , while IND-CSglu is non-spontaneous and exothermic.

Crosslinked oxalic acid/chitosan hydrogel (ChOxb) for adsorption of azo-dyes (Reactive Red 195 RR195) from wastewater was reported by John et al⁵³. Batch adsorption performance showed a maximum percentage of removal of 90.6%, at pH 4. The maximum adsorption capacity at pH 4 was 110.7 mg/g. Among various adsorption isotherm studied, results gives good agreement with Redlich-Peterson adsorption isotherm and best fitted with pseudo-second order kinetics. Thermodynamic data suggested that adsorption process is endothermic and spontaneous.

Epichlorohydrin crosslinked chitosan/carbon–clay (CSCC) bio-hybrid was studied as an adsorbent by Marrakchi et al⁵⁴ for adsorption of cationic methylene blue (MB) and anionic azo acid blue 29 (AB 29). Batch adsorption of MB and AB 29 on CSCC was carried out considering initial dye concentration, initial pH (3–11), and contact time and adsorption temperature. Results of dyes adsorption onto CSCC described well to pseudo-second order model. The isotherms analysis demonstrated that Freundlich isotherm followed adsorption data, and maximum adsorption capacity was found to be 95.31(mg/g) for MB and 167.35 (mg/g) for AB29.

Potential sorbent for exclusion of Reactive Blue 9(RB 9) dye, nano chitosan, crosslinked with activated carbon obtained from fish scales have been employed by Sundararaman et al⁵⁵. Among different isotherms applied Freundlich isotherm proved to be successful and multilayered adsorption was achieved at pH 6.25 with maximum adsorption capacity was revealed to be 31.25 mg/g. Thermodynamic and kinetics data proved the evidence of involved second order kinetics and adsorption of process of Reactive Blue 9(RB 9) dye on nanocomposite owing to occurrence of spontaneous, exothermic and feasible process.

Various pollutants including bacteria, proteins, fluoride, dyes, and pharmaceuticals have been proposed to be removed by crosslinked chitosan/nitrogen doped-graphene quantum dot nanocomposites (CS/NGQD) synthesized via glutaraldehyde as crosslinker by a research group of Amari⁵⁶. Interestingly, it was demonstrated that the synthesized CS/NGQD showed great uptake of dyes. Adsorption studies revealed that CS/NGQD significantly removes dyes as- 82% for Azo blue, 84% for methylene blue and 94% for orange G. Along with that, study noticed after reusability of adsorbent, the nanocomposite remains efficient for removal of pollutants from water after 5 number of repeated cycles.

For effective simultaneous removal of dyes and metals, Usman et al⁵⁷ reported a new adsorbent Nitrilotriacetic acid β -Cyclodextrin-Chitosan (NTA- β -CD-CS) was employed. In process of adsorption, the β -CD cavities play an important role for the uptake of Methylene blue (MB) by host/guest contacts while rest of the functionalities were able to capture metal ions and Methyl orange (MO). Maximum adsorption capacities calculated of NTA- β -CD-CS adsorbent toward MB and MO were 162.6, and 132.5 mg/g, at pH 6 and 3 respectively. Among all adsorption models studied, Sips model was appropriate to define adsorption system and mechanism and worked constantly even after four cycles.

Graphene oxide (GO) crosslinked nanocomposites hydrogels (NCH) of chitosan (CS) and carboxymethyl cellulose (CMC) was synthesized and its application for the removal of cationic and anionic dyes contaminated waste water was explored by Mittal and Alhassan⁵⁸. From the adsorption studies, it was revealed that about 99% dye was adsorbed from the dye solution of MB dye with CS/CMC-NCH at pH 7, whereas, for MO about 88% dye was adsorbed with CS/CMC-NCH at pH 3. Kinetics data explained the adsorption process of both dyes follows pseudo-second order and Langmuir models with the maximum adsorption capacities of 655.98 mg/g for MB and 404.52 mg/g for MO. From the values of change in enthalpy and change in entropy it was suggested that the process of uptake of methyl orange as well as methylene blue onto CS/CMC-NCH was spontaneous and exothermic in nature.

Recently, ultrasound wave-induced synthesis of crosslinked chitosan hydrogels (CAAT) using terephthalaldehyde as crosslinking agent was reported by Garg et al⁵⁹. The adsorption performance for the removal of congo red dye on CAAT revealed that the adsorption of congo red dye on CAAT best fitted the Redlich-peterson isotherm. Kinetics of adsorption strictly follows pseudo-second order model. CAAT hydrogel shown its potential up to six adsorption-desorption cycles after its desorption studies.

We have reported glutaraldehyde crosslinked chitosan-alginate material including the Twizzer-like aniline pendants to enhance the adsorption efficiency towards brilliant green, methyl orange and patent blue V dyes. All the three dyes followed Freundlich model with pseudo-second order kinetics. Adsorption capacities of 235.82, 198.09 and 117.34 mg/g were observed for the three dyes respectively at pH 8, 6 and 3 respectively⁶⁰.

A most recent work of our own research group⁶¹ reports chitosan-activated charcoal composite with tripolyphosphate as a crosslinker for the removal of remazol brilliant blue R dye with excellent adsorption capacity of 540.3 mg/g in accordance with Langmuir isotherm model. More than 95% of the dye was removed from 200 mg/L solution of the dye within 60 minutes. The process was observed to be endothermic and entropy-driven in nature. This material is probably the best in terms of adsorption capacity as well as the rate of adsorption. Tripolyphosphate crosslinker was found to impart thermal as well as mechanical stability to the composite.

Conclusion

Immense developments and studies have been done on chitosan with focus of evaluating and marketing chitosan as an alternative adsorbent for activated carbon. Major goal behind chitosan to be emerging as adsorbent is that it has to be abundant at lower cost, non-toxic to the nature, its processing should be easier and must remove the dyes effectively from the waste water. The results indicated that chitosan provides greater class of agreement with majority of essential criteria's because of its advantageous nature such as cheaper in cost, maximum adsorption capacity and selectivity, its versatile nature, non-toxicity to environment, compatibility and biodegradability. It is noticed that modified chitosan is found to be potential adsorbents for the removal of dyes from effluents. Functional characteristics along with surface morphology and adsorption application of chitosan significantly influenced by chemical and physical processing. Study revealed that dissolution of chitosan required acidic medium and modified with various crosslinkers (such as glutaraldehyde, epichlorohydrin, tripolyphosphate etc). To improve surface characteristics of chitosan in adsorption applications it could be modified with some common solid adsorbents such as activated carbon, clay and magnetized materials. Although crosslinking is commonly utilized for improving the chemical and mechanical stabilities of chitosan but often decreases adsorption capacity of chitosan/modified-chitosan for the uptake of dyes from the waste water. In this review we noticed that glutaraldehyde and epichlorohydrin are the most commonly used crosslinkers used for the modification of chitosan. Adsorption isotherm modelling revealed that in most of the cases Langmuir isotherm fitted best and the kinetics were well explained by pseudo-second order kinetics. On the basis of properties of chitosan and from the results obtained, we can evaluate chitosan to be a very prominent adsorbent for wastewater treatment. Still, chitosan-based research has scope of improvement, and believed that chitosan and its crosslinked derivatives can largely be employed commercially and its use should not be limited to the laboratory. A comparative account of various crosslinked chitosan materials used for the removal of dyes has been summarized in Table 1.

An important aspect of chitosan-based adsorbents is its potential of regeneration and reusability. Almost all the studies mentioned in this review have shown that the crosslinked chitosan materials could be very effectively used in multiple adsorption-desorption cycles. The number of cycles reported in literature range from 3 to 15. This shows the cost-effectiveness of these materials as compared to other treatment technologies like chemical and biological processes where the recovery of treatment material is not feasible.

Figures :

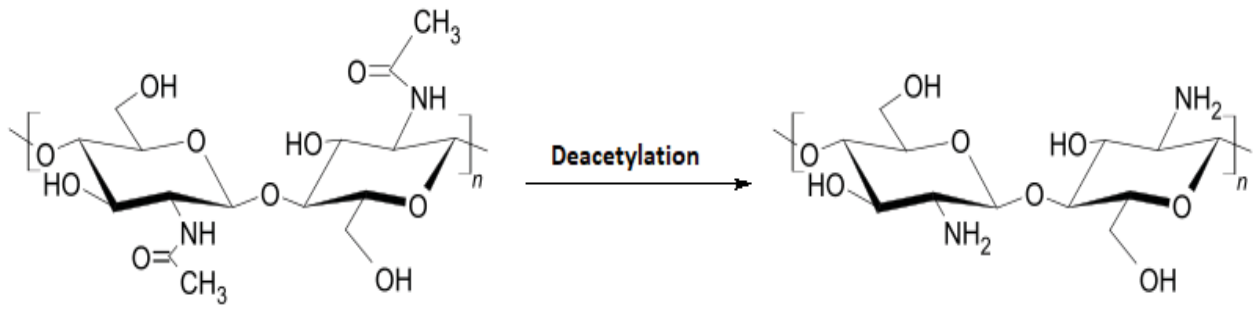


Fig. 1: Synthesis of chitosan from chitin

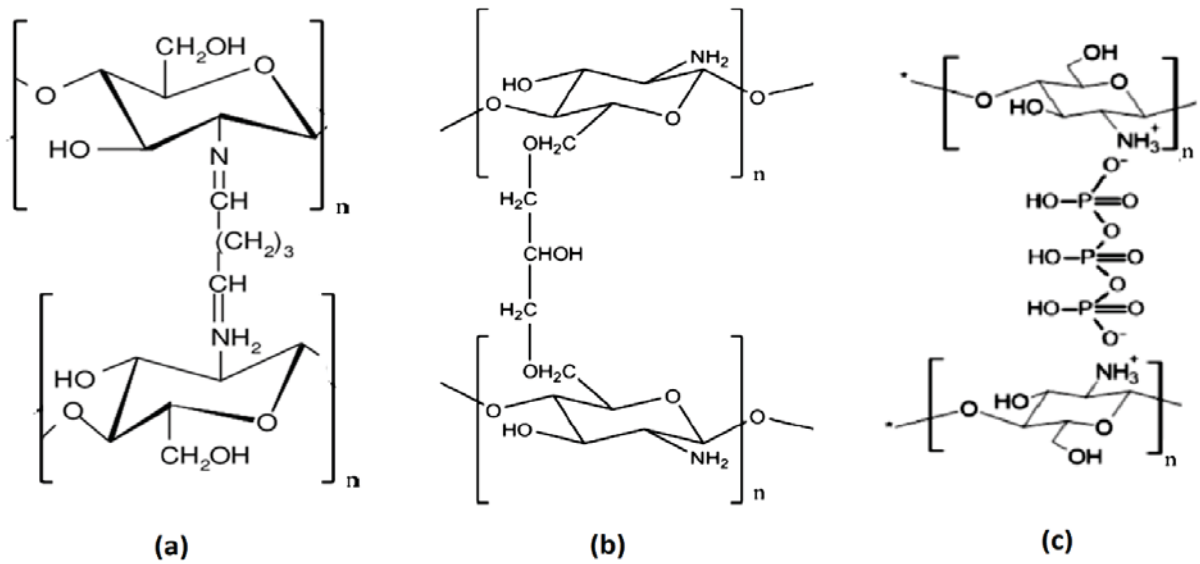


Fig. 2: Crosslinking of chitosan using (a) glutaraldehyde (b) epichlorohydrin (c) tripolyphosphate

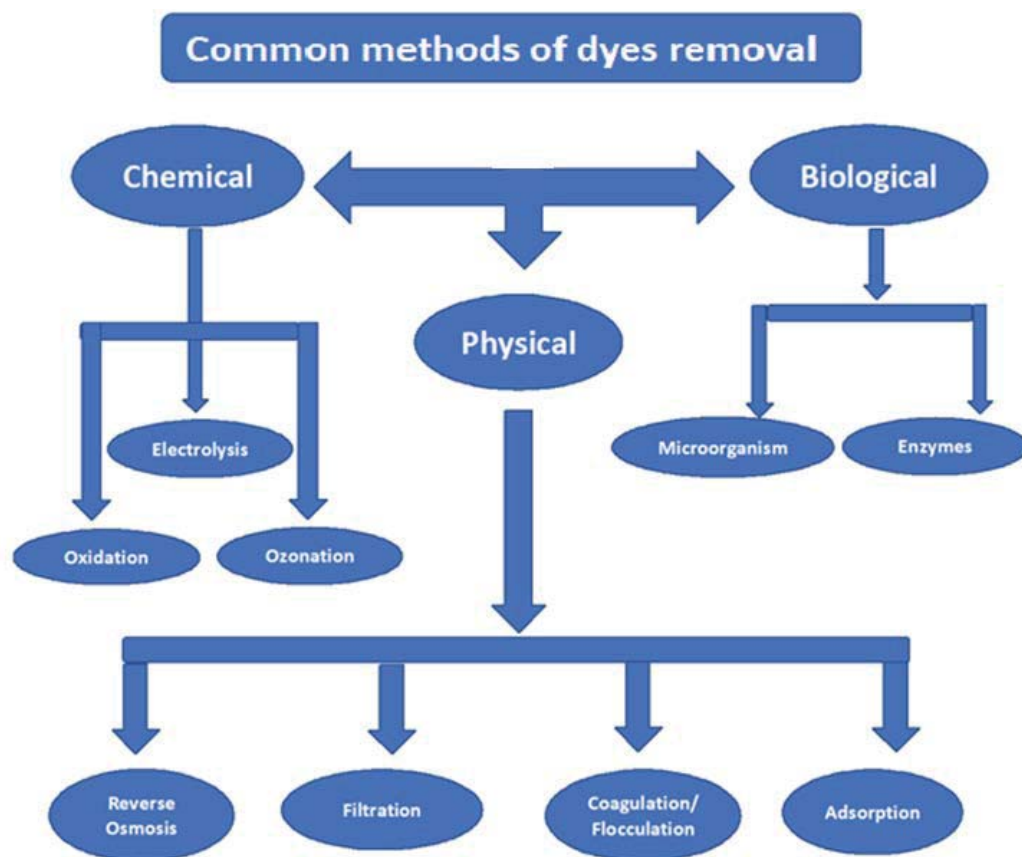


Fig. 3: Methods for removal of dyes from water bodies

Table:

Table 1: Crosslinked chitosan reports for adsorption of dyes

Sr. no	Adsorbent	Adsorbate	Adsorption Capacity (mg/g)	pH	Kinetics	Isotherm	Ref
1	Sodium tripolyphosphate crosslinked chitosan beads	i) Metanil yellow	1334	4	PFO	Langmuir	11
		ii) Reactive Blue 15	722	4	PFO	Langmuir	
2	Crosslinked chitosan/oil palm ash composite	Reactive Blue 9	423.5	6	PSO	Redlich-Peterson	12
3	Ethylene glycol diglycidyl ether crosslinked chitosan	i) Acid Red 37	59.52	2	PSO	Langmuir	13
		ii) Acid Blue 25	142.86	4	PSO	Langmuir	
4	i)sulphuric acid	i) Acid blue 25	102.53	6	PSO	Langmuir	14

	crosslinked chitosan beads	ii) Acid Red 37	139.28	4	PSO	Langmuir	
	ii) Glutaraldehyde crosslinked chitosan beads	i) Acid blue 25	127.06 166.67	6 4	PSO PSO	Langmuir Langmuir	
5	Magnetically separable γ -Fe ₂ O ₃ /crosslinked chitosan	Methyl Orange	-	4	PSO	-	15
6	Crosslinked chitosan poly (acrylamide)	i) EY-4GL ii) S Blue	63.20 18.90	-	PSO	Langmuir	16
7	Crosslinked chitosan beads	Reactive dye	19.613	-	-	Freundlich	17
8	Template crosslinked chitosan nanoparticles (epichlorohydrin)	i) Remazol Black 5 ii) Remazol brilliant orange 3R	5572 5392	3 3	PSO PSO	Langmuir Langmuir	18
9	Protonated crosslinked chitosan	Methyl orange	130.9	6.7	PSO	Langmuir	19
10	Glutaraldehyde crosslinked chitosan	i) Direct Red 80 ii) Reactive Yellow 25 iii) Acid Blue 25	610.5 368.3 443.3	2 5.5 5.5	PSO PSO PSO	Langmuir Langmuir Langmuir	20
11	Crosslinked chitosan/bentonite composite	Methylene Blue	95.24	11	PSO	Langmuir	21
12	Glutaraldehyde crosslinked magnetic chitosan nanoparticles	i) FD&C Blue 1 ii) D&C Yellow 5	475.61 292.07	3	PSO	Langmuir	22
13	Glutaraldehyde crosslinked magnetic chitosan	Acid Red 2	90.06	3	-----	Redlich-Peterson	23

	nano composite						
14	Crosslinked chitosan/Bentonite composite	Amido Black 10B	323.6	2	PSO	Langmuir	24
15	Oxidized starch crosslinked chitosan/silica hybrid membrane	i)Blue 71 ii) Red 31	67.2 94.4	9.8 9.8	PSO PSO	Freundlich Freundlich	25
16	Magnetic chitosan crosslinked with graphene oxide	i) Methyl Violet ii) Alizarin yellow R	- -	10 6	PSO PSO	Langmuir Langmuir	26
17	Crosslinked beads of activated oil palm ash zeolite/chitosan	i)Methylene Blue ii) Acid Blue 29	151.51 212 .76	11 3	PSO PSO	Freundlich Freundlich	27
18	Crosslinked Chitosan/sepiolite composite	i)Methylene Blue ii) Reactive orange 16	40.986 190.965	9 3	PSO PSO	Freundlich Freundlich	28
19	Fly ash crosslinked chitosan/graphene oxide composite	i)Acid Red GR ii) Cationic Red X-5GN	38.87 64.50	3 6	PSO PSO	Redlich-Peterson	29
20	Crosslinked chitosan epichlorohydrine thin film	Reactive orange 16	356.50	3	PSO	Langmuir	30
21	Crosslinked chitosan/Marble powder composite	Dimozol Blue	234.5	5	PSO	Freundlich	31
22	i)Diammonium tartarate crosslinked chitosan ii) Urea diammonium tartarate crosslinked	Congo Red	1597 1447	4 5	PSO PSO	Sips	32

	chitosan						
23	Antimicrobial terephthaloyl thiourea crosslinked chitosan	Congo Red	44.248	---	PSO	Langmuir	33
24	Polyurethane foam membrane filled with humic acid-chitosan crosslinked gels	i)Methylene Blue ii)Rhodamine B iii) Methyl orange	10.31 8.26 5.29	10 4 4	PSO	Freundlich Freundlich Freundlich	34
25	Saccharomyces cerevisiae immobilized crosslinked chitosan beads	Direct orange 2GL	-----	8	PSO	Freundlich	35
26	β Chitosan crosslinked with triethylenetetramine	Reactive Blue 221	625.00	2	Elovich	Langmuir	36
27	Partially carboxymethylated and partially crosslinked chitosan	Methylene blue	365.77	5.6	PSO	sips	37
28	Sulphate crosslinked chitosan	Congo Red	91.8	3	PSO	Freundlich	38
29	N-maleyl chitosan crosslinked-acrylic acid and vinyl phosphonic acid	i)Crystal Violet ii) Methylene Blue	64.56 66.89	7 7	PSO PSO	Redlich-peterson	39
30	Novel antimicrobial trimellitic anhydride isothiocyanate crosslinked chitosan hydrogels	Congo Red	60.05	4	PSO	Langmuir	40

31	Crosslinked chitosan epichlorohydrin/TiO ₂ nanocomposite	Reactive red 120	210	3	PSO	Langmuir	41
32	Tunable Schiff's base crosslinked chitosan-glutaraldehyde	Reactive Red 120	103.1	3	PSO	Freundlich	42
33	Chitosan crosslinked graphene oxide/carboxymethyl cellulose aerogel globules	Methylene Blue	3190	----	PSO	Langmuir	43
34	Crosslinked chitosan glyoxal	i) Reactive orange 16 ii) Methyl orange	1554.3 1451.9	3 3	PFO PFO	Langmuir Langmuir	44
35	Ionic liquid functionalized crosslinked chitosan	Sunset yellow FCF	300.28	No effect	PSO	Langmuir	45
36	Chitosan crosslinked graphene oxide/lignosulfonate composite aerogel	Methylene Blue	1023.9	7	PSO	Langmuir	46
37	Crosslinked chitosan-glyoxal/TiO ₂ nanocomposite	Methyl orange	416.1	4	PFO	Langmuir	47
38	Crosslinked chitosan/polyacrylic acid/bentonite composite	Malachite Green	384.62	6	PSO	Langmuir	48
39	Mesoporous crosslinked chitosan-epichlorohydrin/activated charcoal	Thionine cationic dye	60.9	7	PSO	Freundlich	49

	composite						
40	Crosslinked chitosan tripolyphosphate, fly ash composite	Reactive orange 120	165.8	4	PSO	Freundlich	50
41	Chitosan/ β cyclodextrin crosslinked beads	Indigo carmine	1000	3	PSO	Langmuir	51
42	Glutaraldehyde crosslinked chitosan	i) Malachite Green ii) Indigo Carmine	714.29 303.03	6 6	PSO PSO	Langmuir Freundlich	52
43	Crosslinked chitosan / oxalic acid	Reactive Red 195	110.7	4	Elovich	Redlich-peterson	53
44	Epichlorohydrin crosslinked chitosan / Carbon clay	i) Methylene Blue ii) Azo Acid blue 29	96.08 132.04	11 5	PSO PSO	Freundlich Freundlich	54
45	Nano Chitosan crosslinked with fish scales based activated carbon	Reactive Blue 9	31.25	6.5	PSO	Freundlich	55
46	Crosslinked chitosan/nitrogen doped-graphene quantum dot nanocomposites	i) Azo Blue ii) Methylene Blue iii) Orange G	82% 84% 94%	-	-	-	56
47	Crosslinked Nitrilotriacetic acid β -cyclodextrin chitosan beads	i) Methylene Blue ii) Methyl Orange	162.6 132.5	6 3	PSO PSO	Langmuir Langmuir	57
48	Graphene oxide crosslinked hydrogel nanocomposites of chitosan/carboxymethyl cellulose	i) Methylene Blue ii) Methyl Orange	655.98 404.52	7 3	PSO PSO	Langmuir Langmuir	58
49	Terephthalaldehyde crosslinked	Congo Red	-----	--	PSO	Redlich-Peterson	59

	chitosan						
50	Glutaraldehyde-cross-linked chitosan–alginate	i) Brilliant Green ii) Methyl Orange iii) Patent Blue V	235.82 198.09 117.34	8 6 3	PSO PSO PSO	Freundlich	60
51	Tripolyphosphate crosslinked chitosan-activated charcoal composite	Remazol brilliant blue R	530.4	6	PSO	Langmuir	61

(PFO = Pseudo First Order , PSO = Pseudo Second Order)

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