

## Chitosan Based Adsorbent: A Remedy to Handle Industrial Waste Water

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### ABSTRACT

A healthy environment is chief requirement of modern society and to make the surroundings to live, especially firstly needed water must be pollution free. Adsorption is one of the best wastewaters treatment process. Keeping in view, we have reviewed the utility of chitosan as an adsorbent for the removal of dyes and metals from aqueous solution, which is a non toxic, biocompatible, positively charged, biodegradable natural polymer and obtained by alkaline deacetylation of chitin. To introduce desired characteristics and broaden the scope of the potential applications of chitosan as an adsorbent, physical and chemical modifications have been carried out and obtained various chitosan based materials. Our review article produced an evidence that chitosan based beads, have outstanding adsorption efficiencies for metals and dyes and can be auspicious substitute for conventional adsorbents for removing pollutants.

**Keywords:** chitosan, beads, crosslinking, adsorption, dyes etc.

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### I. INTRODUCTION

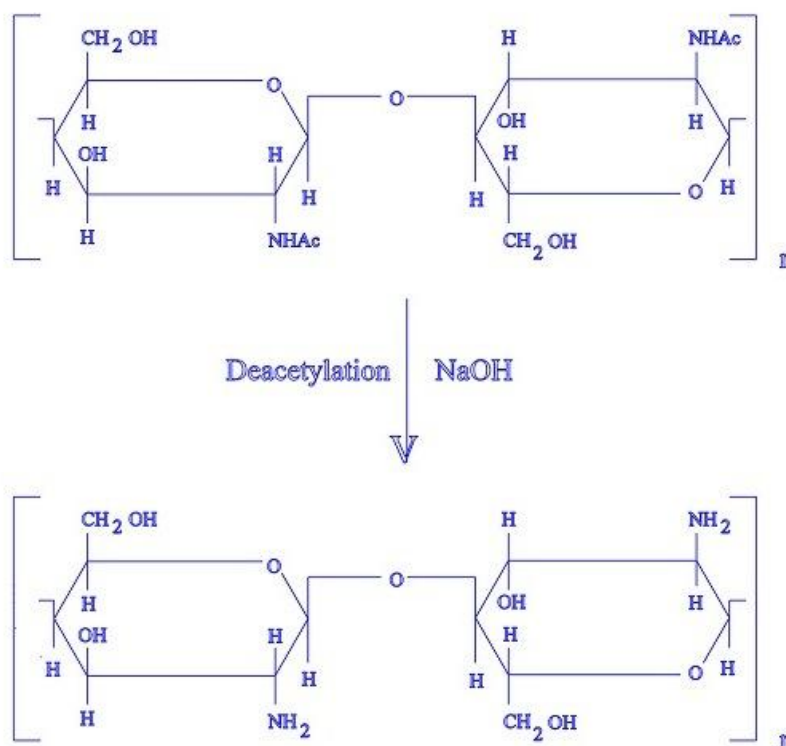
The social development of civilization, metropolitanization and industrialization has given rise to more and more discharge of polluted water. Numerous pollutants are immune to biochemical oxidation and reach obnoxious objectionable concentrations with multiple reuses of water. Toxicity and adverse effect of pollutants are well known and mostly unknown to general users. A huge quantity of colored waste effluent, contaminated with various dyes discharge from textile industries, which are sometimes mutagenic and carcinogenic to living beings (Crini, 2005). The existence of dyes are distinguished by their high oxygen demand, unstable pH with bulk loads of total dissolved solids, fastness to light, heat and reagents for oxidation and perseverance to biodegradability (Ozacar et al., 2005; Sivaraj et. al., 2001). The removal of such type of dye stuffs from effluent before flow into natural water bodies is essential requirements for an environmental aspect. The immediate visual effect of effluents is abnormal coloration to the running water which is able to block photosynthesis in bacteria and aquatic plants from sunlight. Recently, the decrement of dyes in an aqueous effluent has been investigated using adsorption as the most approved treatment process because of its simplicity, easy recovery, high efficiency and the reusability of the adsorbent (Garg et al., 2003). Activated carbon has been successfully accepted as an adsorbent for removing most of the dyes and most of the other pollutants from waste water, but it is an expensive adsorbent and suffers with difficulty in its regeneration. In order to come down the cost of treatment, numerous attempts have been made by technologists to find other alternatives having low cost, able to regenerate them, such as coir pith (Namasivayam and Kavitha, 2002), Clay minerals (Murray, 2007), rice husk (Han et al., 2008), leaf powder (Bhattacharrya and Sharma, 2004), fly ash (Acemioglu, 2004), bacterial biosorbents (Vijayaraghavan and Yun, 2008), and fungus (Fu and Viraraghavan, 2001) etc. for removing dyes from water. However, low adsorption capacities towards dyes for existing adsorbents make their limited applications in practical field.

A healthy environmental levels are chief requirement for today's society, hence it needs an enhancement in interest for the cleaning devices for general and industrial use from inexhaustible sources, keeping in view, more and more efforts are now being made in the area of research and development of usable derivatives as the materials for new applications, which would provide best results, undoubtedly chitosan is emerged as unique and attractive biosorbent used to treat wastewater. This is evident from enormous reports as appeared in the literature. Our literature survey produced an evidence that adsorbents generated from chitosan have outstanding adsorption efficiencies for metals and dyes.

## II. CHITOSAN

Biodegradable polymers which were derived from inexhaustible sources have nowadays generated much interest in controlling pollution by utilizing them as adsorbent. Chitosan is considered as a precious organic biocomponent polymer because of its nontoxicity, biodegradability (Gan et al., 2005; George and Abraham, 2006), easily bioabsorbability (Yalpani et al., 1992), mucoadhesivity (He et al., 1998; Schnurch et al., 1998) and also showing gel forming ability at acidic pH (Tseng et al., 1995). Due to all described interesting properties chitosan has been built as an ideal polymer for formulation of pollution controlling tools (Illum, 1998; Graham, 1990; Gupta and Ravi Kumar, 2000a; Mi et al., 2002).

Chitosan is prepared from N-deacetylation of chitin that forms a naturally occurring muco polysaccharide in abundance that forms the exoskeleton of aquatic animals, insects etc. It consists of 2-acetamido 2-deoxy- $\beta$ -D-glucose monomer units linked through a  $\beta$  (1 $\rightarrow$ 4) linkage (Ravi Kumar, 2000). Chitosan is prepared by alkaline hydrolysis of chitin with NaOH at 120°C for 1-3 hr as stated by chemical reaction in Scheme 1. The chemical reaction of chitin carried out as alkaline hydrolysis produces 40-80 % deacetylated chitosan. In fact, chitosan is a hetero polymer constituting (1 $\rightarrow$ 4) 2-amino 2-deoxy  $\beta$ -D-glucose unit with (1 $\rightarrow$ 4) 2-acetamido-2-deoxy- $\beta$ -D-glucose units of original chitin in polymeric chain.



Scheme 1 - Deacetylation of chitin into chitosan (Ac = COCH<sub>3</sub>)

The proportion of 2-amino-2-deoxy- $\beta$ -D-glucopyranose units to 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose, named as the degree of deacetylation is an important parameter, that determines the polymer's solution making properties. There are numerous methods for analyzing and estimating this parameter (Baxter et al., 1992; Domard, 1986; and 1987; Wei and Hudson, 1993; Maghami and Roberts, 1988; Sashiwa et al., 1991; Raymond et al., 1993; Niola et al., 1983; Sashiwa et al., 1993; Raathke and Hudson, 1993 and Pangburn et al., 1984) published in existing literature. Conversion of chitin into chitosan lowers the molecular weight due to deacetylation and the charge distribution in acidic solvent is originated due to amino group formation. Chitosan is an extensively alkaline polysaccharide, so it can be capable to obtain poly oxysalts, chelate with metal ions, and other molecular derivatives (Hench, 1998). It forms solution in weak acids like acetic acid, formic acid, etc. It has the characteristic of forming hydrogels that are highly swollen, hydrophilic polymer networks, competent to absorb water.

### ADSORBING PROPERTIES OF CHITOSAN

Maursa, et al., 2012 investigated the removal of dyes like reactive red 3 (RR-3) and direct brown 95 (DB-95) from water streams by applying the batch method. They were accomplished their experiments by estimating as a function of the effect of contact time period, dye initial concentrations, temperature, solution pH and other

foreign ion concentration on adsorption capacity. The adsorption data were well suited for langmuir and Freundlich isotherms models. However, the thermodynamic and kinetic variables were used to validate the adsorption process. They concluded that the dye RR-3 was adsorbed preferably on chitosan adsorbing upto 151.52 mg/g at lower temperature (20<sup>0</sup>C) in comparison to dye DB-95 which was found to be retained upto 41.84 mg/g at high temperature of 50<sup>0</sup>C. Chitosan powder has been examined for its adsorbing properties for dye acid green 9 (AG9) from aqueous media by performing experiments applying batch method, at 20 ± 0.5 °C and the influence of different experimental parameters (pH, time period dye concentration initially, adsorbent dosage, temperature, ionic strength) on adsorption capacity were estimated (Asandei, et al., 2012).

Conclusions have been made by effectiveness that the dye is removed significantly and showed dependence on the ratio of initial dye concentration and chitosan dosage. At a given ratio of dye and chitosan, dye at optimum acid pH range of 4-6 was identified for acceptable percentage of dye removal. The increase in temperature and presence of Na<sub>2</sub>SO<sub>4</sub> in solution resulted in a decreased percentage of dye removal. The data obtained by experimentations were attempted to analyze for possible agreement with the langmuir, freundlich and temkin isotherm equations. The langmuir model was demonstrated to allow the best correlation with the experimental data.

Adsorption and thermodynamic investigations for congo red n°40 and food dye (FD) interaction on chitosan from water were performed by Piccin, et al., 2011. The determination of equilibrium time were carried out by using the batch method, at 298 to 338 K. Adsorption data were tried to satisfy to five isotherm models i.e. langmuir, freundlich, redlich-peterson, temkin and dubinin-radushkevich, with a view to determine which presented the best correlation to the observed data. Error analysis suggested that the isotherm model of langmuir was found fitted most appropriately for experimental data, having a monolayer for maximum adsorption of 3065.8 μMg<sup>-1</sup> at 308 K. Negative values of enthalpy, entropy and gibbs free energy for the system was calculated as -112.7 KJ, -0.338 KJ mol<sup>-1</sup> K<sup>-1</sup> and -15.6 to 1.0 KJ mol<sup>-1</sup> respectively, concluded the exothermic nature of the adsorption process also spontaneous, favorable, and randomness of the system decreases during the adsorption process.

## **MODIFIED CHITOSAN**

Preparation and characterisation report were published by Synowiecki and Al-Khateeb, 2003 and a survey by Ravi Kumar, 2000. Recently, complexation of metals by chitosan and its derivatives has been reported by Varma et al., 2004. The modified chitosan molecules also offer enormous opportunities. Through many kinds of chemical reactions, particularly crosslinking and grafting reactions, chitosan can produce interesting macro molecular super structures e.g. gels and hydrogel networks, polymeric resins, beads, membranes, fibers or composite materials. These materials can then be able to use as adsorbents which are neither soluble in neutral, acidic and alkaline mediums nor in organic solvents. Crosslinked chitosan gels are much stable hydrophilic polymeric materials. They become more prevented to shear, high temperature and low pH as compare to their parent materials. After crosslinking, they preserve their original properties, characteristics excluding the crystallinity and mechanical strength in solutions of different pH. These qualities are most important for an adsorbent so that it can be utilized in a different pH environment and the swelling nature of the beads prepared from chitosan in wastewater can be optimized. Crosslinking retards the extent of the crystalline with in the polymer and then can change the crystallinity of the polymeric raw material that notably impact the sorption activity of polymer because of controlling the accessibility to sorption sites. Crosslinked beads also have to show other benefits like faster kinetics, enhanced easiness of performance (Bailey et al., 1999) and existing diffusing characteristics. Due to the hydrophilic behavior of the crosslinking units of polymer, network hydrogels possess a remarkable increase in swelling capacity when keeping in water, as a result these networks are remarkably expanded and increased size of pores allow a fast diffusion process for the pollutants. Although crosslinked polymeric chain have better adsorbing characteristics, the adsorbing efficiencies can be more accelerated by the introduction of some functional groups onto the polymer network or the polymer backbone (Arrascue et al., 2003 and Jeon et al., 2003) which increases the density of sorption sites. The production of novel reactive functional groups on the exterior of the beads results in an increase of surface polarity and hydrophilicity and this will again increases the sorbing efficiency of charged adsorbates and promotes the selective sorption for the targeting pollutant at the sorption site. Structural chemical changes may also be created by varying the pH range of adsorbate solutions so that the optimum sorbing efficiency can be regulated by controlling diffusion properties and decreasing the sensitivity of sorption with environmental conditions (Guibal et al., 2000 and Arrascue et al., 2003).

After adsorption, the crosslinked polymeric chains may also be easily regenerated by using desorbing solvents or by solvent extraction. Despite these predefined properties and characteristics, crosslinked networks have not been used at the industrial scale. There are several drawbacks in transferring the procedure to industrial applications because of the variability of the bead characteristics affected by the choice of the crosslinking agent

which produced signified influence on the adsorbing capacity because the chemical behaviour of the synthesized beads influences the porosity and the degree of crosslinking (Chiou and Li, 2003; Wan Ngah et al., 2002 and Yoshizuka et al., 2000). Seidel et al., 2001 explained that the crosslinking chemical has a remarkable influence on the textural strength of the material. Crosslinking alters both the physical properties and also the thermal transition characteristics of the polymer (Chung et al., 2004).

The circumstances in which the crosslinking reaction takes place, is another important factor to control adsorption process, as the conditions govern the determination of the variation in crosslinking density which again decides the adsorption efficiency of the adsorbing mass and further direct the success for selectivity of the adsorption site, determining the diffusion rate of pollutants enter the polymeric gel network. It is well known fact that the diffusion rate of pollutant becomes slower with increase of the crosslinking density which decreases the adsorption efficiency. Furthermore, highest crosslinked beads have lower swelling capacities.

The excessive three dimensional polymeric networking may produce result with low accessibility due to increase in the hydrophobic character (Shiftan et al., 2000). This phenomenon can have an explanation that the decreased hydrophilicity grows by the destruction of the crystalline structure. The stability, mobility and accessibility of the polymer further decided the adsorption rates. Although crosslinking add increments of the resistance in polymeric structures against acid, alkali and chemicals, these occurs more or less loss in the chain flexibility (Shiftan et al., 2000), reducing the diffusion rate of chelating groups and their accessibility, and produces a significant decrease in pollutant uptake efficiency and finally, we can say that there would be lesser values of the maximum adsorption capacities of the adsorbent. However, the lowering of adsorption capacity is equally required to produce the most stable adsorbing material (Bailey et al., 1999). This restricting factor can be lowered by using a polymer like chitosan, because its structure is able to modify physically that allows expansion of the polymer networking which increases the diffusion rates of bulk molecules and decreased the crystalline nature of the polymer (Dzul et al., 2001). The variations in the sorption characteristics are noticed because of crosslinking of polymeric beads. It has been proved that the sorption ability of crosslinked chitosan beads was found to be lower than the pure chitosan beads, Despite it, they showed their usefulness even in acidic solution of low pH level.

#### **MECHANISM OF ADSORPTION ON CHITOSAN**

The direct example of the chitosan interaction with metal species or dyes is a chemical or physical interaction, so the adsorption, is strongly pH dependent (Varma et al., 2004 and Ruiz et al., 2000). Metal with chitosan give rise to complex formation involves two different mechanisms which are chelation versus ion exchange reactions. These are depending on the pH since this parameter is responsible to affect the hydrogen ion concentration through protonation of the macromolecule (Varma et al., 2004). Chitosan is identified by estimating higher nitrogen percentage and it runs as amine groups which provide a site for metal ion boundation or adsorption through chelation mechanisms. Amine groups are the main adsorption site for metal ions via hydroxyl groups

(-OH), particularly in the carbon at third position, may also donate to adsorption (Ravi Kumar, 2000 and Varma et al., 2004). However, chitosan is also a cationic polymer and its pKa value ranges from 6.2 to 7 according to the degree of deacetylation and the ionization extent within the polymer (Arrascue et al., 2003). In this way at lower pH < 7 it is protonated (-NH<sub>3</sub><sup>+</sup>) and exhibits electrostatic properties and thus, also able to interact metal ions due to anion exchange mechanisms (Ruiz et al., 2000). Although numerous contradictory mechanisms have been suggested, metal adsorption on chitosan and chitin based materials is now supposed to take place through single or several mixed interactions which are as follows-

- (i) Chelation or coordination at amino groups in a pendant fashion or by participation of vicinal hydroxyl groups
- (ii) Complex formation or electrostatic attraction in acidic media
- (iii) Ion exchange with protonated amino groups (-NH<sub>3</sub><sup>+</sup>) through either proton (H<sup>+</sup>) or anion (X<sup>-</sup>) exchange, the counter ion being exchanged with the metal anion (Ravi Kumar, 2000 and Ruiz et al., 2000).

Physical adsorption does not play much role in attracting pollutants towards crosslinked chitosan for ion exchange mechanism as beads have comparatively smaller surface area. The pH may also influences the speciation of metal ions, hence the speciation differences of the metal may result in turn the changing of chelation mechanism into the electrostatic attraction mechanism. Another factor that, can govern a valuable part for deciding the mechanism are the occurrence of ligands grafted on the chitosan chains. For crosslinked polymeric substances, physical adsorption occurs in the polymer structure and chemisorption of the pollutant via acid base interactions, hydrogen bonding, complexation and/or ion exchange or both involved process of sorption (Delval et al., 2002 and 2003). In most cases, although an incorporation of these interactions was supposed to explain adsorption mechanisms, the efficiency and the selectivity of the adsorbents are principally allocated to their chemical network.

The extensive survey of literature concluded that chitosan and its various modified molecular derivatives in form of beads has been utilized as an adsorbent as follows-

## **CHITOSAN BEADS**

Azlan Kamari et al., 2009 prepared two kinds of beads— Pure chitosan beads and crosslinked chitosan ethylene glycol diglycidyl ether beads and compared their removal efficiencies for the acid red 37 (AR-37) and acid blue 25 (AB-25) from aqueous solution. Ethylene glycol diglycidyl ether is a crosslinker for chitosan which increase its chemical resistance and mechanical strength. Experimentation has been carried out dyes in influencing adsorbed amount of dyes on adsorbents to decide factors like pH, agitation time and quantity of AR-37 and AB-25 in solution. It was deduced by scientists that the adsorption capacities of uncrosslinked chitosan for both the studied dyes were significantly high than that of crosslinked chitosan with ethylene glycol diglycidyl ether. The reason of it is that cross-linking reduces the major adsorption sites  $-NH_3^+$  on chitosan. Adsorption process followed langmuir model of isotherm and pseudo second order kinetics. The used adsorbent is undergone for recycling studies and desorption is attempted by NaOH and HCl. Experimental results regained almost total of the adsorbed dye so it proved that the adsorption of both studied dyes onto chitosan based adsorbents was a physical adsorption. It also concluded that beads obtained from pure chitosan and crosslinked chitosan beads with ethylene glycol diglycidyl ether were proved to be good adsorbers and could be employed as low cost alternatives for the removing both the dyes to purify wastewater. Chitosan hydrogel beads are easily formed by dispersion of droplets of chitosan solutions in to alkaline media, and the beads prepared after taking place chemical crosslinking reactions were found to show a great interaction for heavy metal ions. In adsorption experimentation, however the beads at equilibrium were clogged with metal ions at the outer sphere of beads surfaces and could not completely show their capabilities in a region of low initial concentration for metal ions (Juang and Shao, 2002).

The beads performed excellently and proved to be much more selective and efficient. The conclusion made by Coughlin et al., 1990 according to their studies performed that sorption of pollutants on chitosan is competitive against precipitation techniques. Wan Ngah et al., 1998 told that sorption capacities were remarkably higher for chitosan in order to recover copper than for commercial synthetic resin. The studies for removing reactive textile dyes by using beads obtained either from chitosan or crosslinked chitosan to absorb pollutants were accomplished by Deepika et al., 2003. The beads were obtained by dissolving chitosan in acetic acid (0.3 N) and then cross linking was achieved with 40% glyoxal and 0.05M glutaraldehyde. The extent of adsorption was estimated by removing acid orange-10 and direct black-22 from the textile dyeing waste water. The influence of the factor affecting adsorption like initial dye concentration, adsorbent concentration, temperature, equilibrium time and pH were evaluated. The obtained results were compared for the adsorption equilibrium for beads of chitosan and crosslinked chitosan. They also investigated that the observed data was found to correlate significantly with the well known langmuir isotherm model. The chitosan beads are noted worthy less cytotoxic than those crosslinked by glutaraldehyde, hence, they may also be tried for bio medical applications. Cao et al., 2001 suggested the preparation of crosslinked chitosan resins by microwave irradiation. The experimental results as obtained by Chiou et al., 2004 made some suggestions on the basis of observations of his experimentations that the adsorption capacities of crosslinked chitosan beads for anionic dyes were much greater (3–15 times) than commercial activated carbons at the same pH.

The adsorbed quantity of dye onto crosslinked chitosan beads has been studied by Chiou and Li, 2003 and 2002. Chitosan based materials were prepared as beads and crosslinked with glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether using as crosslinking agent. The beads have a capability for adsorption of 1642 g/kg adsorbent for reactive dye 189. The quantity of dye adsorbed increased as the particle size of beads decreased due to the effective surface area becomes higher for the same mass of smaller particles. The extent of adsorption is again influenced by the temperature and the weight ratio of epichlorohydrin with chitosan. It was proposed that the chitosan epichlorohydrin beads have shown a remarkable adsorption capacity than glutaraldehyde and ethylene glycol diglycidyl ether resins. Although the beads preserved a high adsorption capacity, yet they were soft with poor mechanical properties. There was a need to improve their mechanical strongness for practical applicability. Recently, Chiou et al., 2005 obtained another kind of calculated beads which were crosslinked using tripolyphosphate for producing more rigidity. They had very large values of 1911–2498 g of adsorbed dye per kg of bead. Wan Ngah et al., 2002 also used the same adsorbents to remove  $Cu_2C$  from aqueous solutions. The uptakes were 59.6, 62.4 and 45.9 mg  $Cu_2C/g$  beads on chitosan glutaraldehyde, chitosan epichlorohydrin and chitosan ethylene glycol diglycidyl ether beads respectively. The adsorbed metal amount was highly pH dependent. The beads can be efficiently regenerated. Ruiz et al., 2000 investigated the utilization of crosslinked glutaraldehyde chitosan beads as effective chelating resins for adsorbing palladium from solutions of low concentrations. Sorption kinetics was regulated by bead size, degree of crosslinking and metal concentration. Crosslinked chitosan beads exhibited good uptake of heavy metals as proposed by Juang and Hao, 2002 who pointed out that the nature of crosslinking agent chiefly determines the extent of adsorption. The increasing pH of the solution tends to increase the extent of adsorption due to competition between proton and metal ions during adsorption process.

## **CHITOSAN DERIVATIVES BEADS**

Arrascue et al., 2003; Guibal et al., 1998; 2000 and 2002 and Dambies et al., 2002 were performed an important work on chitosan derivatives. They reported that crosslinked chitosan derivative have shown their utility as beads for removing and the recovering toxic or valuable, precious metals for example arsenic (Dambies et al., 2002), vanadium (Guibal et al., 1998), molybdenum (Guibal et al., 1999a and 1998), platinum (Guibal et al., 2000 and Guibal et al., 1999b), osmium (Ruiz et al., 2003), palladium (Guibal et al., 2002), iridium (Ruiz et al., 2003) and gold (Arrascue et al., 2003). Sulphur group containing chitosan beads are very efficient for gold removal from their low concentrated acidic solutions and maximum uptake of metal was estimated 600 mg of Au per gm of beads (Arrascue et al., 2003).

### **Grafted chitosan beads-**

Among the various process of modification, graft copolymerization is a promising technique for modifying the chemical and physical features of chitosan (Crini, 2005). In grafting process a functional derivative is found between chitosan and another molecule through a covalent bond called the graft lying on the chitosan backbone. The two kinds of functional groups, one is free amino group (-NH<sub>2</sub>) and another is hydroxyl group (-OH) which are able to grafted (Alves and Mano 2008). Crini et al., 2002 and Janus et al., 2003 investigated the synthesis of new monomers by grafting vinyl groups on chitosan. Newly synthesized derivatives showed benefits of being a monomer ready to polymerize to form reticular structure, which permits the involvement of a polysaccharide into a material like chitosan without the usual chemical crosslinking of the polymer.

In fact the crosslinked chitosan beads have proved as an excellent adsorbent still not replaced reliably used activated carbons or ion exchange resins, further studies must be necessary to demonstrate the possible technology on an industrial scale. Mousa Sadeghi et al., 2013 has been prepared a biopolymeric adsorbent of chitosan ethylacrylate (Ch-g-Ea) and utilized inable of removing the effluent dyes basic red 18 (BR-18) and basic blue 41 (BB-41) from textile effluent. The adsorbent has been analyzed and characterized using techniques like fourier transform infra-red, <sup>1</sup>H nuclear magnetic resonance and <sup>13</sup>C nuclear magnetic resonance. The technologists confirmed an acceptable relation for the chemical structure of Ch-g-Ea (Chitosan-g-Ethylacrylate) characterising from spectral data. Batch experimental studies for evaluation of parameters like adsorbent dosage, pH, time of contact and temperature effects was successfully employed for investigating and optimizing the process of dyes removal. It was noticed that the structural modification in chitosan as Ch-g-Ea significantly increased removal efficiency of dyes. This increasment is due to the introduction of a large number of carboxyl groups through grafting to the chitosan backbone. The kinetic experimental data exhibited fitness very well to pseudo second order kinetic model ( $R^2 > 0.99$ ) whereas adsorption data to langmuir model ( $R^2 > 0.98$ ). The investigated results proved that Ch-g-Ea can be applicable as an efficient biopolymer adsorbent that remove dyes from textile effluents.

In 2013, Perolatto and Ferrero worked on cotton fabric which was ecofriendly functionalized by chitosan, UV grafting and used as dyes adsorbent. The parameters controlling adsorption efficiency for the treated fabric were optimized in terms of extent of chitosan add-on, time of impregnation, temperature, pH, radiation time and curing intensity. The cotton grafted by chitosan was differentiated by scanning electron microscopy (SEM), fourier transform infrared analysis, attenuated total reflection (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS). The substance was then examined towards different dye classes: acid, reactive and direct dyes. Batch, kinetic and also continuous flow assessments were performed, to calculate the dye removal efficiency by measuring spectrophotometrically. They observed that it exhibited high rates for adsorption for all classes of dye studied. Besides, when the experimentation for adsorbing capacity were set up by using chitosan functionalized cotton as a filter, it gives better adsorption even at lower temperature of 25 °C and significantly increasing adsorption capacity was noted in acid conditions. Finally, regeneration of adsorbent was performed in NaOH solution with good recovery by good release of the desorbing dye. Studies revealed that results show good perspectives for use of chitosan treated cotton in wastewater filtration.

N- Maleilated chitosan was synthesized by treatment of chitosan and maleic anhydride in N, N-dimethyl formamide. The copolymer, named as N-Maleilated chitosan-g-methyl methacrylate was polymerises through free radical mechanism for which ceric ammonium nitrate (CAN) was functioned as the initiator. The effective variables that control the polymerization include the concentrations of ceric ammonium nitrate (initiator) and monomer, the temperature were studied to produce grafted product and conclusion made that increase in variable for polymerization were also increased grafting and then grafted product during a phase and afterward decreased. The maximum extent of grafting was produced at 1.6g of initiator (CAN), 2g of the monomer (Methyl methacrylate) at 70°C. The copolymer synthesised was characterised by Fourier transform infrared analysis, X-ray differaction, Thermal gravimetric analysis and differential scanning calorimetry. This graft co polymer was attempted as an adsorbent in the treatment of textile effluent. It was proved more potent as compare to pure chitosan. Equilibrium sorption attempts were produced positive results and the observed data was precisely fitted to the langmuir adsorption isotherm.

### **Chemically modified chitosan beads-**

Polymeric chitosan based substances can also be attempted to acquire success for the decontamination of effluents and to recover valuable metals. Dambies et al., 2002 introduced a new procedure for the production of molybdate impregnated chitosan sorbent. Direct coagulation was caused to impregnate the beads in a molybdate bath. These modified beads were attempted for adsorbing As (III) and As (V) from solutions with success. Recently other modified beads of chitosan were also proposed. (Nehal et al., 2015) formulated poly oxy propylene diamine modified chitosan (D2000-Cs) in which chitosan was crosslinked with epichlorohydrin (ECH) and finally chemically modified by utilizing polyoxypropylene diamine. D2000 Cs was distinguished by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA). The study to test stability of D2000-Cs in acidic solution was carried out. They investigated positive adsorption of an acidic dye, acid green 25 (AG-25) onto D2000-Cs from low pH aqueous media. Different variables like pH, initial concentration of dye and temperature were evaluated to control adsorption by performing a number of set up of experimentations. The adsorption process obeyed pseudo-second order kinetic model well fitted in langmuir model.

Zhang et al., 2011 prepared the chitosan modified diatomite to explore the removal efficiency of acidic dyes reactive red M-8B (RR) and direct green B (DG). The experimental set up characterise adsorbent, evaluating adsorption isotherms and the factor affecting it like adsorption time, temperature and pH. They explained after getting positive results that the adsorption capability of modified diatomite was much better than natural diatomite. The maximum values for adsorption capacities on chitosan modified diatomite for RR and DG were 94.46 and 137.0 mg/g respectively. A positive impact on the dye adsorption was noted with increasing equilibration time and temperature. Within the experimental limits and results, electrostatic attraction is reflected as the main reason of the chemisorption mechanism.

A new magnetic nano adsorbent from chitosan transformed by N,N- bis carboxy methyl glutamic acid (G-MCTS) was synthesized by Xiaohong Zhu et al., 2016 using covalently bounded tetra sodium N,N- bis (carboxy methyl) glutamic acid onto the exterior of Fe<sub>3</sub>O<sub>4</sub> coated chitosan nano particles. The adsorbent was distinguished by scanning electron microscope (SEM), infrared spectrum vibrational sample magnetometer and X-ray powder diffractometer. It was concluded that chitosan nanoparticles were round shaped whose size ranges from 100-150 nm with a value of saturation magnetization of 21 emu/g. Meanwhile, G-MCTS was tested for their adsorption performance by adsorbing methylene blue. Correspondingly, adsorption kinetics, isotherms and adsorption thermodynamics were investigated by evaluating the adsorption variables like Initial dye concentration, pH, contact time and temperature. It was noticed that the adsorption equilibrium time was calculated as 30 min, besides the adsorption kinetics has possess to obey pseudo second order kinetic model, and the adsorption data fitted nicely with freundlich model and also langumir model. More importantly, the maximum adsorption efficiency was estimated as 3.3 g/g by langmuir model and above 90% desorption of the dye took place. Hence, it concluded that G-MCTS can employ as a competent adsorbent for removing Methylene Blue efficiently.

### **Chitosan composition beads-**

In recent period, many valuable new hybrid substances (Jessis and Peng, 2003; Aoki et al., 2003; Jime'nez et al., 2003; Chen and Wang, 2001; Martel et al., 2001; Tojima et al., 1999; Sakairi et al., 1999; Tanida et al., 1998; Furusaki et al., 1996; Yi et al., 2003; Yang et al., 1999; Tan et al., 1999 and Peng et al., 1998) to eliminate various hazardous wastes from water have been produced and reported, using other mineral give rise to glass beads (Liu et al., 2003 and 2002), silica gel (Crini and Morcellet, 2002; Mocanu et al., 2001; Janus et al., 2003; Fan et al., 2003; Phan et al., 2002 and 2000), polyamine beads (Crini and Morcellet, 2002; Nayak et al., 2001; Crini et al., 1999 and wan et al., 2004), alginate beads (Gotoh et al., 2004), polyethyleneterephthalate (Zhang and Bai, 2003), polyurethane (Jessie et al., 2003), polyvinylalcohol (Hamai and Kikuchi, 2003), polysiloxane (Kalfat et al., 2000), alumina (Steenkamp et al., 2002), polyacrylic acid (Kusumocahyo et al., 2004), polypropylene (Le et al., 2000 and Martel et al., 2002), polyester (Martel et al., 2002a and 2002b) etc.

#### *Chitosan- inorganic materials compositions*

Composition beads of chitosan with zinc oxide

With the view of Norzita et al., 2014 ethyl orange is a typical azo dye, soluble in water and utilized in industries of textile, printing, paper manufacturing, pharmaceutical and food. Now a days azo dyes have a wide range of production and excessive application so cause a huge amount of polluted wastewater and can attack health seriously. Chitosan considered as a low cost adsorbent and has been extensively used to make water azo dye free. Technologists carried out researches to mix the less expensive adsorbent chitosan and semiconductor zinc oxide to obtain a new hybrid material efficiently remove azo dyes than that of pure chitosan. The experiments were carried out to set pH variation from 5-9, adsorption variables such as change in temperature from 25 to 60 °C and the range of initial dye concentration in between 0.10 to 1.00 mg/l. The results concluded that the studied

dye ethyl orange had been removed successfully with mixture of chitosan and zinc oxide as a new adsorbent. The maximum removal efficiency for ethyl orange (85%) was achieved using conditions such that temperature of 60°C, with adsorbent having mixture of .08 g chitosan and .02 g zinc oxide, used to study aqueous solution of dye concentration (1.0 mg/l), at pH 7 and equilibrating for two hours. In this research, results were obtained for the adsorption equilibria and data was observed to fit with more accuracy to the freundlich isotherm than that of the langmuir isotherm.

Composition chitosan with kaolin

Kaolinite is a 1:1 aluminosilicate, consists of  $\text{Al}_2\text{O}_3$  (15.61 mol%),  $\text{SiO}_2$  (42.14 mol%), and  $\text{H}_2\text{O}$  (42.25 mol%) (Nandi et al., 2009). The novel chitosan beads were formulated by Zhu et al., 2010 which was blended with maghemite ( $\text{Fe}_2\text{O}_3$ ) and kaolin using the SEM and tunneling electron microscope (TEM) images studies, it was noticed that there were many pores and folds at the exterior of the particles obtained which provided active sites able to entrap the dye molecule. Excellent ability of adsorption was exhibited by these usual CS composites as it could be able to adsorb upto 70% methyl orange from slightly acidic (pH 6.0) solution. The effect of competitive sorption of foreign negative ions on the adsorption efficiency of dye was studied, which involved  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ . The decolorization of dye was observed in the order:  $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{PO}_4^{3-}$ . It means, the contamination of anions had decreased the adsorption of methyl orange. This could be explained by the preferential adsorption of  $\text{PO}_4^{3-}$  in comparison to bearing methyl orange due to higher negative charge on phosphate anion.

Composition beads of chitosan and montmorillonite

Results were presented by Wang and Wang, 2007 for utilizing a natural phyllosilicate of montmorillonite in preparation of chitosan composites for removing well known dye of congo red. The detailed structure of these composites was discussed by them. Researchers studied the effect of various molar ratios of chitosan and montmorillonite (Wang et al., 2004). They observed the adsorption properties were affected by the molar ration that was responsible for the changes of chemical behaviour of these composition beads. The increases in the adsorption capacity of dye studied was noted on increment in the molar ratio of chitosan to montmorillonite upto exceeding 1:1 beyond the adsorption remains almost constant. Scientists give two possible explanations for this scenario. Firstly it is because of stabilizing negative charge on montmorillonite initially by chitosan which would enhance the dye removal capacity for congo red. On the other hand, it may be created by the montmorillonite being saturated by the quantity of intercalated chitosan.

Chitosan (CTS) was modified by montmorillonite (MMT) to obtain a nanocomposite i.e. chitosan coated montmorillonite and utilized for adsorption of azo dyes for example methyl orange (MO) and reactive black (RB5) from waste water by the batch adsorption process (Sakew, and Umpuch, 2013). The MMT and CTS/MMT specimen were differentiated by CHNS-analyzer and X-ray diffraction (XRD). Adsorption studies were acquired using batch method into 3 steps. Firstly, removal efficiency for dye was performed and should realised that CTS/MMT showed higher percentage of removal efficiency for both of the dyes as compare to montmorillonite. In second step, the experiments were set up to investigate the dye equilibrium adsorption and data was correlated with freundlich and langmuir equations. It was concluded by results obtained from experiments that the data was best fitted to langmuir isotherm. Finally, the kinetic experiments for adsorption were made to know the contact time effect and then correlating it to different kinetic models. They observed that initially the rate of adsorption is fast and reaches equilibrium in 60 min and follows pseudo second order kinetic model with the best correlation.

Umpuch and Sakaew, 2013 published their research work for adsorbing a dye methyl orange (MO) by forming an adsorbent from a montmorillonite modified with chitosan. The montmorillonite and chitosan infused as to a nano composite CTS/MMT which were examined by means of SEM and BET-analysis. The observations of adsorption experiments reported that MO was adsorbed rapidly in initial phase and finally the equilibrium was reached in 1 hr. Adsorption kinetics were best explained by the pseudo second order model. An aqueous solution of pH 2.0 was favorable for the adsorption. The equilibration data were correlated better by langmuir isotherm compared to the freundlich isotherm. The extent of MO dye adsorption was found to be increased with the increase of operating temperatures. This indicated an endothermic nature of adsorption process. Desorption studies reflected that the reutilization of the chitosan montmorillonite composite was possible. These results clearly suggested that the CTS/MMT has been proved an efficient adsorbent for removing methyl orange (MO) from textile effluent.

Composition beads of chitosan and ceramic alumina

The usability of composite beads obtained from mixing chitosan and ceramic alumina have been worked out as an adsorbent to purify waste waters by removing heavy metals like As(III), As(V) (Veera et al., 2008a), Cr(VI) (Veera et al., 2003), Cu(II) and Ni(II) (Veera et al., 2008b). Instead of the acetic acid, Oxalic acid was used for preparing the composites as it is a dicarboxylate and behaves as a bridge between alumina and chitosan. One of the carboxylic group form ionic bonds with amine group of chitosan while another one forms a strong chelate at



surface via ester linkage with the alumina (Dobson and McQuillan, 1999). The oxalic acid is also able to form hydrogen bonds with  $-OH$ ,  $-CH_2OH$ , or  $-NH_2$  group in the biopolymer (Veera et al., 2003). For example uptake of heavy metal ions was caused by various phenomena like adsorption, ion exchange and chelation (Veera et al., 2008). Chelation occurred when the chitosan binds to the metal ions via amino group. It involves two or more complexing groups. According to Veera et al., 2008, in the chelation, two separate amino groups are involved from different glucosamine residues of the polymeric chain. The amino group is an active centre for residing the pollutant ions during adsorption process due to having an oxo anion or chloro complex anions of metals adsorb on chitosan composite from the sample solutions through ion exchange mechanism.

#### Composition beads of chitosan with perlite

Chitosan perlite composition beads have been attempted to adsorb heavy metals like chromium (Shameem et al., 2003), cadmium (Shameem et al., 2006), nickel (Kalyani et al., 2009) and copper (Kalyani et al., 2009; Shameem et al., 2008). They adopted a little difference between the process described found in literatures (Shameem et al., 2003; 2006 and 2008; Veera et al., 2009). Any dissolved contaminant in the oxalic acid was removed by shaking the perlite powder and it also inserts carboxylic groups onto perlite surface which may strengthen the attachment of chitosan to perlite (Shameem et al., 2008). Washing and defloculating of perlite powder was helpful to maintain an appropriate ratio of acid to chitosan in the mixture during beads preparation (Shameem et al., 2008).

#### Composition beads of chitosan with bentonite

Wan Ngah et al., 2010 formulated chitosan bentonite composition beads crosslinked with epichlorohydrin being to adsorb tartrazine, an azo dye harmful to living beings. The crosslinked chitosan composites were able to bring increment in the performance of chitosan as an adsorbent (Crini and Badot, 2008). The choice of a suitable crosslinking reagent can make chitosan stable in acid solutions so that chitosan becomes insoluble. According to Wan Ngah et al., 2010, the adsorbate solution pH value plays a crucial part in the adsorption phenomenon. The surface of the adsorbent would carry positive charge at pH lower than  $pH_{ZPC}$  and tartrazine molecules would be attracted on adsorbent by increasing pH because the exterior of the adsorbent getting more negatively charged.

#### Composition beads of chitosan with bamboo charcoal

Chitosan and bamboo charcoal composition beads were formed by intermixing chitosan with bamboo charcoal. The composites were examined for adsorbing reactive dye. The equilibration time for maximum dye removal was estimated to 8 hours, when the weight ratio 1:1 composite adsorbent had the highest adsorption efficiency. The maximum dye removal occurs at the initial pH value of 4.0. The optimal dose of adsorbent for removing dye was 6.0 g. Under all these conditions the maximum dye removal was 98.4%. The adsorption isotherm for chitosan and chitosan based bamboo charcoal composition beads were compared and observed to be agreed best with the langmuir model. The maximum adsorption capacity was 4.32 mg/g for chitosan bamboo charcoal composite beads and 3.47 mg/g for chitosan beads. SEM micrographs after adsorption proved the appearance of packed pores on the exterior of beads with reactive red 152.

#### Composition beads of chitosan with oil palm ash

The crosslinked chitosan oil palm composite beads have been prepared by Hameed et al., 2008 to take up reactive blue 19. The researchers concluded that pH had a significant influence on the amount of dye adsorbed onto the chitosan composition beads. More protons were present at lower pH and protonated the free amino groups to  $NH_3^+$  in chitosan, thus attracting more strongly the negatively charged dye ions towards the positively charged active sites thus grow the high value of adsorption quantity of dyes. When pH becomes greater than 10.0, the adsorption capacity diminished tremendously because of lesser number and lower size of the pores in crosslinked chitosan beads. This has created difficulty in particle diffusion of dye due to crosslinking with in the beads. Hameed et al., 2008 studied four types of isotherms these are langmuir, freundlich, temkin and redlich peterson and noted the data obtained was fitted better to the last one than the other isotherms.

#### Composition beads of chitosan with sand

Adsorption capability have shown to be better by chitosan sand composition beads than any of its component used alone as adsorbent. The reason behind it is the three dimensional structure of the adsorbent used. In chitosan amine groups provide reactive sites for forming the complexes with metallic ions, which are stabilized by coordination. The highest value for adsorbed amount of heavy metals decreases as the number of acetyl groups with in the bead structure increases (Wan et al., 2007). Isotherm data was fitted best to the Langmuir isotherm with maximum capacity of adsorption i.e. 10.87 mg/g.

#### Composition beads of chitosan with activated clay

Modification of clay was attempted for removing dyes (Mouzdahir et al., 2010) and heavy metals (Mabrouk and Mourad, 2010). Chang and Juang, 2004 carried out studies by synthesizing the composition beads of the chitosan activated clay. The authors estimated the specific gravity of the resulting beads containing different weight percentage of clay. They explained that specific gravity of beads was 1.0197 while the beads of chitosan containing 50% clay by weight showed the value of 1.0055 so that they described that the adsorption phenomenon of chitosan activated clay and their maximum adsorption capacity are linked with their specific gravity values and made a conclusion that the capability of chitosan to agglomerate has been increased and improved the strongness of the beads based on the stokes laws for formation of beads. It is valuable because it facilitates the solution containing adsorbent within the solution without swelling. The adsorption studies were performed for methylene blue and reactive dye (RR22) and found that the chitosan composition beads had a comparable adsorption than the chitosan beads.

#### *Chitosan - Organic material compositions*

##### Composition beads of chitosan with Polyurethane

The method adopted for preparing the composition beads of chitosan contained polyurethane is quite different, as chitosan does not dissolve when using acetic acid. According to Lyoo et al., 2009 at 0.25 wt% of glutaraldehyde concentration, chitosan was proved to be the most applicable in immobilizing into the foam matrix of polyurethane. The micrographs obtained from scanning electron microscopy (SEM) revealed that researchers as described the beads to have open porous structures which had also been suggested by other existing literature (Jang et al., 2008 and Moises et al., 2006). The open structure of the composition beads increases the penetrability and approachability of acid dyes towards active sites into the chitosan matrix to make them inactive and immobilized in the beads with foams (Lyoo et al., 2009). A study was performed to make comparison to adsorb acid dyes between the adsorbents of neat polyurethane foams and chitosan polyurethane composition beads. The results obtained that the adsorption capacity of chitin polyurethane composite was comparably higher than the neat polyurethane. It is further proved that the amino groups inside the neat polyurethane specifically could not react as an active site to reside dye molecule.

##### Composition beads of chitosan with cellulose

Some literatures have reports on the advantage of cellulose immobilization on chitosan forming chitosan cellulose composition beads. Li and Bai, 2005 and Sun et al., 2009 prepared chitosan cellulose composition beads by adopting similar method. Sun et al., 2009 used 1-butyl-3-methyl imidazolium as the solvent instead of acetic acid to dissolve chitosan. Recently, ionic solvents have received great recognition as green solvents and proved promising substitutes for the traditional volatile organic solvents due to easier usability and their unique characteristics like non volatility, thermal stability, nonflammability, and recyclability (Ueki and Watanabe, 2008; Hameed and Guo, 2009 and Zhang et al., 2006). Sun et al., 2009 made conclusion based on adsorption experiments that the adsorption capacity of freeze dried chitosan composition beads was nearly three times lower than that of naturally dried chitosan biosorbent which clearly indicated the better stability of freeze dried chitosan cellulose composition beads. Li and Bai, 2005 noticed that the acid resistance of the composition beads was improved by crosslinking reaction and presented the evidence that the crosslinking reactions were consumed numerous amino groups with in chitosan or shielded as supposed by zeta potential studies. A novel beads as magnetic cellulose chitosan composition was formed by combining two methods of preparations which were the emulsification and regeneration of cellulose chitosan from ionic solvent without modifying process surface. The composition microbeads have porous structure, large surface area, and greater affinity for metals, upto the efficient capacity of  $\text{Cu}^{+2}$  ions (Peng et al., 2014).

##### Composition beads of chitosan with alginic acid

Gotoh et al., 2003 mixed alginic acid and chitosan simultaneously as both of them, were recognized as most powerful adsorbents to eliminate lower concentrations of heavy metallic ions from industrial waste waters. They formed a stiff reticular mass of beads as a result of electrostatic attractive forces existing between amine groups of chitosan and carboxylic groups of alginic acid, and named them as alginate chitosan hybrid gel beads. It could be possible by utilizing water solubilized chitosan in first attempt and chitosan having 36-39% degree of deacetylation was prepared from chitin. The water soluble chitosan formed in stabilized form also remained as solution by adding of sodium alginate to form in and this homogeneous mixture of chitosan and alginate was dispersed cupric chloride aqueous solution to give gel bead particles. The obtained beads were then undergone to crosslinking reaction by using glutaraldehyde. The crosslinking reaction made durable beads in acidic situation. The rates of adsorption of  $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$ , and  $\text{Cd}^{+2}$  on beads was so fast that the equilibrium attained within 10 min only at 25 °C. Adsorption isotherms of the metal ions on the beads exhibited freundlich and langmuir behavior.

#### Composition beads of chitosan with polyvinyl alcohol

Polyvinyl alcohol has been used to immobilize chitosan to produce chitosan polyvinyl alcohol composition beads (Wan Ngah et al., 2004 and Kumar et al., 2009) which showed appreciable removal of  $\text{Cd}^{+2}$  (Kumar et al., 2009) and  $\text{Cu}^{+2}$  (Wan Ngah et al., 2004) from wastewater. A slightly different method is applied to prepare of the composition beads by scientists. Kumar et al., 2009 raised the system temperature upto  $90\text{ }^{\circ}\text{C}$  to distill out little water as an azeotropic mixture. A surfactant tween 80 was added for preparing the beads which acts as an emulsifier during the formulation of droplets from suspension (Malgorzata et al., 2007 and Avranas et al., 1998).

#### Composition beads of chitosan with alginate

The sodium alginate and chitosan were attempted by Quin, et al., 2006 for treatment of waste water polluted due to containing heavy metals. The proportion of chitosan and sodium alginate used for preparing beads affected the cupric ions removal efficiency from water was tested on different treatment temperatures and time of contact with adsorbing ions and proved to be far better if using in combined form than alone to remove  $\text{Cu}^{+2}$  from aqueous solutions. The treatment was too applicable to other ions of heavy metals like cadmium, lead and silver ions and the removal efficiency was compared. It was noted that when CS and sodium alginate adsorbent were taken in combinations the separation of pollutants by polymeric adsorbents from waste water is better than chitosan or sodium alginate are used alone.

#### Composition beads of Chitosan with cotton fiber

Composition beads had been obtained from chitosan and cotton fiber to remove Au (III) (Qu et al., 2009a), Hg(II) (Qu et al., 2009b) and Ni(II), Cd(II), Pb(II), Cu(II) (Zhang et al., 2008). For synthesising the composition beads, cotton fibers were reacted with sodium periodate and then added into the solution of chitosan. Oxidation of periodate ion oxidized the glycon cleavage in carbohydrates. It was a well known classical method used for deciding the structure of complex carbohydrates.

#### *Chitosan derivative-other material compositions*

Aoki et al., 2003 described that the derivatives of chitosan containing cyclodextrine are good adsorbing material for the selective resolution of p-nonylphenol and bisphenol. Martel et al., 2001 invented the addition of a monochlorotriazinyl derivative of cyclodextrine with chitosan to get a novel suspended composition material which was useful in decontamination of polluted water with textile dyes. The result reflects that the new derivatives could work as an excellent adsorbent for dyes. Cyclodextrin was to immobilised chitosan beads covalently via a reductive amination method (Tojima et al., 1999). The immobilised chitosan sorbents were able to prepare inclusion complexes with p-nitrophenol. The utilization of chitosan derivatives constituting crown ether has been proposed by Yi et al., 2003; Yang et al., 1999; Tan et al., 1999 and Peng et al., 1998. They had shown large extent of adsorption for  $\text{Pb}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$  and also shown better selectivity properties than crosslinked chitosan which not constituted crown ether. Studies proved that the material could be regenerated. This is very interesting as it is already known that crown ethers are not easily recycled after using once and hence their applications are limited.

Batch methods of adsorption to carry out experiments were attempted by (Lin et al., 2004) for adsorbing methylene blue dye from waste waters utilizing composites of chitosan-g-poly (acrylic acid) and attapulgit as adsorbent. The effects of attapulgit percentage as constituent, dye initial concentration, solution pH value and temperature on adsorption were studied and the outcomes showed that attapulgit content of chitosan-p-poly (acryl acid) composites had influenced the adsorption capacities. They explained that involvement of a small amount of attapulgit had improved adsorption capacity of chitosan-g-poly (acrylic acid) attapulgit composites to a certain extent. Kinetic experimental results revealed that the rate of adsorption for MB on chitosan-p-poly (acrylic acid) and chitosan-poly (acrylic acid)-attapulgit composite with 30% of attapulgit was so fast, that more than 90% of dyes were adsorbed within the initial 15 min. The kinetic procedure was shown to follow pseudo second order equation and the maximum adsorption capacities as obtained from langmuir equation, reached 1873 and 1848 mg/g for Chitosan-p-poly (acrylic acid) and Chitosan-p-poly (acrylic acid)-attapulgit composite respectively. The desorption studies were also carried out using distilled water of pH 2.0, The studies revealed that Chitosan-p-poly (acrylic acid) and Chitosan-p-poly (acrylic acid)-attapulgit composite can be used as promising adsorbents for removing of methylene blue dye from wastewater.

The composition of chitosan and poly ( N-2 aminoethyl acryl amide) or PAEA were made by Perju and Dragan, 2010 and then crosslinked with glutaraldehyde (GA) to test their adsorption capacity for congo red and direct blue-1 (azo dyes). The composite hydrogels constituting different molar ration have been prepared for crosslinking and the primary amino groups ( $\text{GA}/\text{NH}_2 = 5.3$  and  $12.5$ ) with similar total concentration of polycations (CPC =2 wt%) and two molar ratios for polycations (PAEA:CS =0.25 and 1.2) were obtained. Pseudo first order model, pseudo second order model and the intraparticle diffusion model were tried to analyze the experimental data for establishing the mechanism of adsorption. The pseudo second order model has

described the kinetics of adsorption process. The temperature effect on the adsorbing capacity of both of the dyes has also been investigated.

Feng et al., 2012 has been prepared an adsorbent from chitosan and modified flax shive (CFS) which has been investigated for adsorbing reactive red dye from textile effluent. A by product from flax fiber separation, was characterized by the Brunauer Emmett Teller (BET) method, Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). Adsorption studies were conducted by batch method under various conditions of contact time, initial concentration, solution pH and adsorbent dosage. Conclusion has been made on the basis of experimental results that the BET and Langmuir surface area of CFS were  $1.722 \text{ m}^2 \text{ g}^{-1}$  and  $3.057 \text{ m}^2 \text{ g}^{-1}$  respectively. Results proposed that CFS has the similar pores as FS and the proper adsorption site on CFS is  $-\text{NH}_2$  group. Maximum adsorption capacity found to be reached within 8 h and uptake of RR 228 at pH 2.0 was satisfactory. The total amount of dye gets adsorbed when initial concentration of dye was 10 mg/l to 20 mg/l at solution pH 2.0 while the percent dye removal were estimated 90% and 85% in same conditions for dye concentrations respectively. Observed data proved accuracy for correlating with pseudo second order model and Langmuir isothermal equation. It is proposed that CFS be used as a low cost adsorbent in dyes removal from wastewater.

### III. CONCLUSION

The chitosan biopolymer sorbents are capable in using to remove contaminants from effluents for separation or recovery process and also for analytical or solid phase extraction purposes. Hence, our present discussion introduced various chitosan based adsorbents that originating auspicious substitute for conventional adsorbents for the removing pollutants. Although, in acidic medium, chitosan itself is soluble, yet crosslinking, derivative promotion or modification in its molecular structure, improved the dissolution character of chitosan, allowing it to function well in acidic solutions. The adsorption capabilities of chitosan is because of its electropositive nature as it has amino group that can undergo protonation ( $-\text{NH}_3^+$ ) and able to provide site for adsorbing metal ions or dye molecule through a variety of interaction mechanisms like electrostatic interactions and chelation. Literature review indicated that a wide range of chitosan based adsorbents have been prepared which are raw or flakes chitosan, chitosan derivatives, chemically and physically modified chitosan and composites etc. which one type of adsorbent is better, it is still a subject of research. There is no accurate answer to this argument as each and every adsorbent has its own advantage to use because parameters and the adsorbates are different in different studies. In this way, this field has a wider spectrum for improvement actually either chitosan based materials would be applied commercially instead of only at laboratory scale. We worked to throw light or uncover some facts that might help in future research.

Considering the cost factor, low production cost with greater adsorption efficiencies are well preferred. It is the main principal to decide either the adsorbent is appropriate for implementation in large scale. Economically chitosan based materials are found feasible as they can easily be prepared with simple process using inexpensive reagents. Regeneration studies are required to perform as it will much decrease the product cost. The regeneration study provides idea about reusability of adsorbent which increased the potency of adsorption phenomenon. Many literatures did not discuss about regeneration and the mechanism involved in this process. Literature explained that regeneration can be achieved and sorbent extraction can be obtained by using some common solvents like hydrochloric acid, nitric acid, sodium chloride, sodium hydroxide etc. Based on the adsorption equilibria and kinetic studies, assumptions have been made. Hence exact mechanism involved during the process is not well defined in existing studies. However, some recent molecular technology like scanning electron microscopy, X-ray powder diffraction, electron spin resonance and differential scanning calorimetry provide valuable information for characterizing the adsorbents.

Therefore, more efforts will be required to acquire a better picture in explaining the adsorption mechanism for a process in which removal of different pollutants would be attempted. Actually research should not be limited up to laboratory scale batch methods. It is needed an investigation for the simultaneous removal of numerous coexisting pollutants so that a multipurpose adsorbent can develop a more realistic approach.

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