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CHITOSAN BEADS AS A NATURAL ADSORBENT FOR THE REMOVAL OF Cd(II) FROM AQUEOUS SOLUTIONS

T.N. Batugedara[1] and C.S.K. Rajapakse[2]

[1]Department of Chemistry, University of Kelaniya, Kelaniya, Sri Lanka
[2]Department of Chemistry, University of Kelaniya, Kelaniya, Sri Lanka
E-mails: [1]batugedaratn@gmail.com, [2]shashikala@kln.ac.lk

Abstract: This project focuses on the synthesis of physically modified chitosan; chitosan beads and determination of the effect of contact time, beads dosage and bead size on Cd(II) adsorption capacity of chitosan beads from aqueous solutions at pH 7 and at temperature of 30±2˚ C. Further, the visual examinations of chitosan beads were conducted using SEM analysis. Isotherm experiments and kinetic studies were done to find out the maximum adsorption capacity and the order of the reaction respectively. According to the results obtained, the optimal performance of chitosan beads were achieved when initial Cd(II) ion concentration of the sample was 50 mg L^{-1} with chitosan bead diameter (1.11±0.02) mm, contact time of 150 minutes and chitosan bead dosage 0.40 mg. The isotherm experimental data at 30 ˚ C were satisfactorily fitted to Langmuir adsorption isotherm with R^2 value of 0.993. The maximum adsorption capacity value; Langmuir constant, q_o obtained for adsorption of Cd(II) onto chitosan beads was 62.5 mg g^{-1} which is considerably a higher value compared to q_o values for adsorption of Cd(II) onto various other biomass types reported in the literature. The kinetic data were fitted with the pseudo second order model with R^2 values of 0.992 and 0.988 for initial Cd(II) concentrations of 30 mg L^{-1} and 50 mg L^{-1} respectively. Therefore, the results revealed that the concentration of Cd(II) and amount of chitosan beads both may involve in the rate determining step and the adsorption process may be chemisorption.

Keywords: Cd(II), chitosan beads, adsorption, isotherms, kinetic.

Introduction

Environmental pollution has become a vital drawback with the increment of world population and also the giant development of industrial applications. Unlike organic pollutants, heavy metals are not biodegradable and cannot be metabolized or decomposed. They can simply enter the food chain via a number of pathways and then cause toxic effects with gradual accumulation in living organisms (i.e. Ismael, 2014). Water pollution by toxic heavy metals such as Cd(II), poses a threat to human health as it is a human carcinogen and causes dangerous impacts in lungs, kidneys, liver, and reproductive organs (i.e. Madala *et.al.,* 2013). Cd(II) is discharge into the environment from electro plating industries, batteries, phosphate fertilizers, mining, pigments, stabilizers, and alloys (i.e. Madala *et.al.,* 2013). Usually, in

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wastewater Cd(II) concentrations may vary from 2 mg L^{-1} to 80 mg L^{-1} (i.e. Ismael, 2014). According to the EPA guidelines, the maximum amount of Cd(II) that can be discharged to water surface along with water from industries is 0.01 mg L^{-1} and the maximum permissible level of Cd(II) in drinking water is 0.003 mg L^{-1} (i.e. Ismael, 2014). A lethal dose of Cd(II) is 2 mg per 1 kg of body weight (i.e. Ismael, 2014). It is much lower than that of other toxic metals (i.e. Ismael, 2014). Thus, remediation of Cd(II) contaminated wastewater is of high priority in order to safeguard the wellbeing of both the environment and human health.

Although a wide range of physical and chemical processes such as chemical precipitation, ion exchange, membrane filtration, solvent extraction etc. are available for the removal of heavy metals from water bodies; most of these methods are not practicable to developing country like Sri Lanka as some are extremely expensive while some methods produce toxic sludge. Therefore, development of low-cost methods to remove heavy metal ions in industrial effluent has received the attention of scientists worldwide and bio-sorption has been recognized as a cost-effective method of removal of heavy metal contaminants in water using low cost bio-adsorbents such as activated carbons, burned brick particles, clay, some aquatic weeds, agricultural and biological wastes, chitosan, and zeolites etc (i.e. Illeperuma, 2000).

Chitosan; de-acetylated product of chitin (Figure 1) is considered as one of the most valuable polymers for biomedical and pharmaceutical applications due to its biodegradability, biocompatibility, antimicrobial, non-toxicity, and anti-tumor properties (i.e. Younes, 2015). It is also used as a chelating agent due to its ability to bind with metal ions, cholesterol, fats and proteins (i.e. Younes, 2015). Nanoparticles, films, hydrogels, microspheres, and fibers are typical chitosan-based forms for several medical applications. Although chitosan has been used as a heavy metal removal agent for industrial wastewater, no previous attempts have been reported in Sri Lanka to understand the ability of physically modified chitosan to uptake heavy metals such as highly toxic Cd(II) in polluted water.

Chitin is extracted mainly from shrimp and crab shells which is, at present, merely a waste material of the sea food industry of Sri Lanka. Development of a water purification method using chitosan as a bioadsorbent will also give a value addition to the waste material, which is dumped into the environment polluting the surrounding. Further, treatment of water with chitosan would be a cost effective and safer method over the traditional methods of removal of toxic metal species using chemicals. Therefore, the current study focuses on potential of using physically modified chitosan; chitosan beads as low cost, environmentally friendly bio-sorbent for the removal of Cd(II) from wastewater.

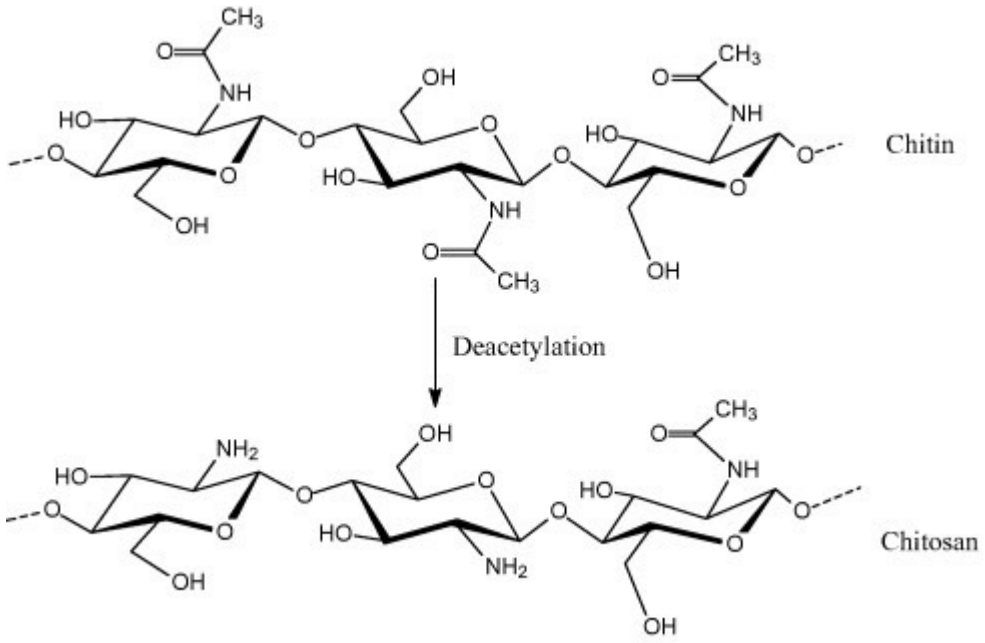


Figure 1- Structures of chitin & chitosan

Materials and methods

Preparation of the adsorbent

Medical grade chitosan was purchased from PT. Biotech Surindo, Cireban, West Java, Indonesia. (Average molecular weight = 191000 g/mol, deacetylation percentage = 80-85%, purity = 95%, solubility = over 99% in 1% acetic acid). Chitosan (3 wt %) solution prepared in acetic acid (1% v/v) was added as drops using a syringe (10.0 mL) into a NaOH (0.50 M) bath. The formed chitosan gel beads were kept in NaOH solution for 24 hours and then the wet chitosan beads were rinsed with distilled water to adjust the pH to 7 and the beads were air dried until they gain a constant weight.

Characterization of Adsorbent

The surface morphology of chitosan beads was analyzed using scanning electron micrographs.

Preparation of adsorbate solution

Synthetic wastewater solutions were prepared by using 1000 mg L^{-1} Cd(II) solution. The prepared Cd(II) solution was diluted using deionized water to the required concentration for experiments. The pH of the solution was adjusted to pH 7 using NaOH (0.01M).

Batch adsorption tests

Batch adsorption tests were carried out to examine the adsorption behavior of chitosan beads on Cd(II) removal under different conditions. For this purpose, the effect of adsorbent dose

(0.05 g - 0.95 g), contact time (0 min - 210 min) and bead size (1.11 mm – 1.96 mm) on the Cd(II) adsorption on chitosan beads were determined. In each experiment, a known amount of chitosan beads was contacted with 50 mL of desired synthetic wastewater solution agitated in a mechanical shaker at a speed of 60 rounds per min. All the experiments were carried out at room temperature 30±2˚C and at pH 7±0.5 as the previous studies showed that chitosan is very efficient in removing Cd(II) at pH 7 (i.e. De Silva *et.al.*, 2014). The solutions were filtered by using Whatman 01 filter papers and filtrates were analyzed by Flame Atomic Absorption Spectrophotometer (Thermo Scientific iCE 3300, / GBC 93.2 plus) to determine the amount of Cd(II) remaining in the solutions after treatment with chitosan beads. The Cd(II) adsorption capacity of chitosan beads under selected conditions was calculated using the following relationship;

$$q\ (mg/g) = \frac{adsorbed\ weight\ of\ cadmium\ onto\ chitosan\ beads\ (mg)}{weight\ of\ chitosan\ beads\ used\ (g)}$$

Where, q is the adsorption capacity of chitosan beads.

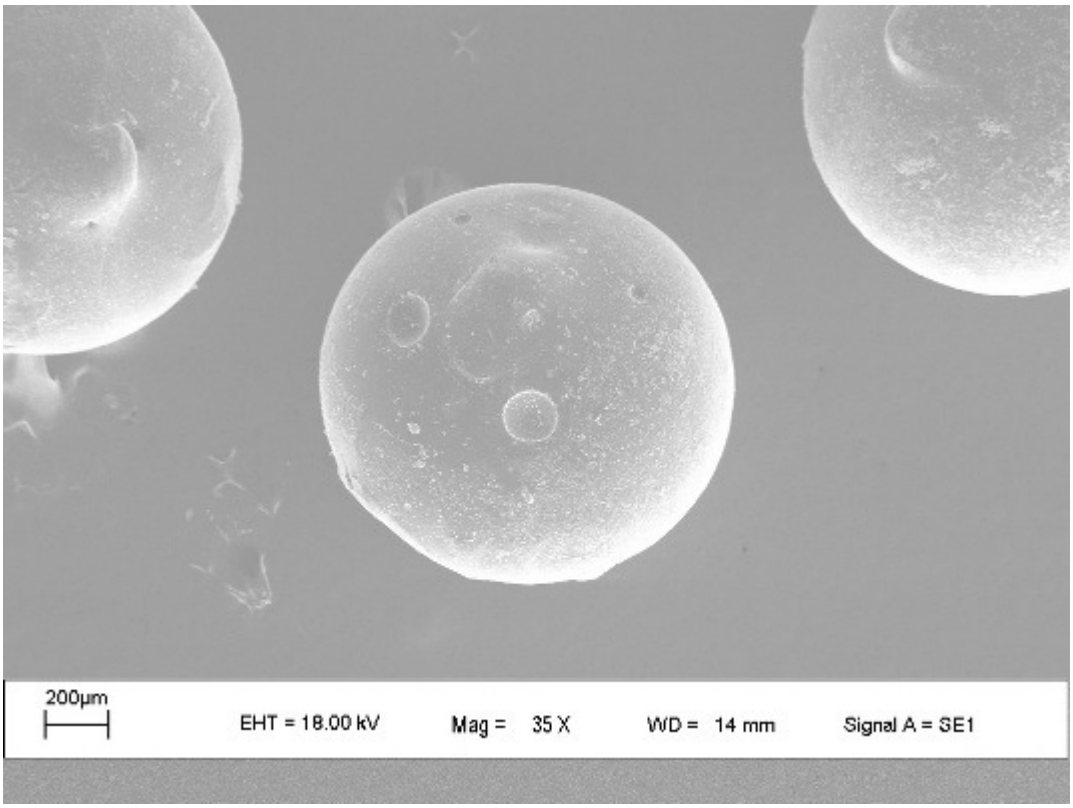
Isotherm experiments

Equilibrium isotherm experiments were conducted by mixing 0.1500 g of chitosan beads with 20.00 mL of Cd(II) solution for a range of initial metal ion concentration from 20 to 100 mg L^{-1}. The mixtures were shaken at 30˚C for 2.5 h, which was found to be the equilibrium time for adsorption. Then the solution was filtered and the filtrates were analyzed for Cd(II) using FAAS (Flame Atomic Absorption Spectrophotometer) and Langmuir and Freundlich isotherm models were applied to relate the distribution of Cd(II) ions between the liquid phase and the solid phase.

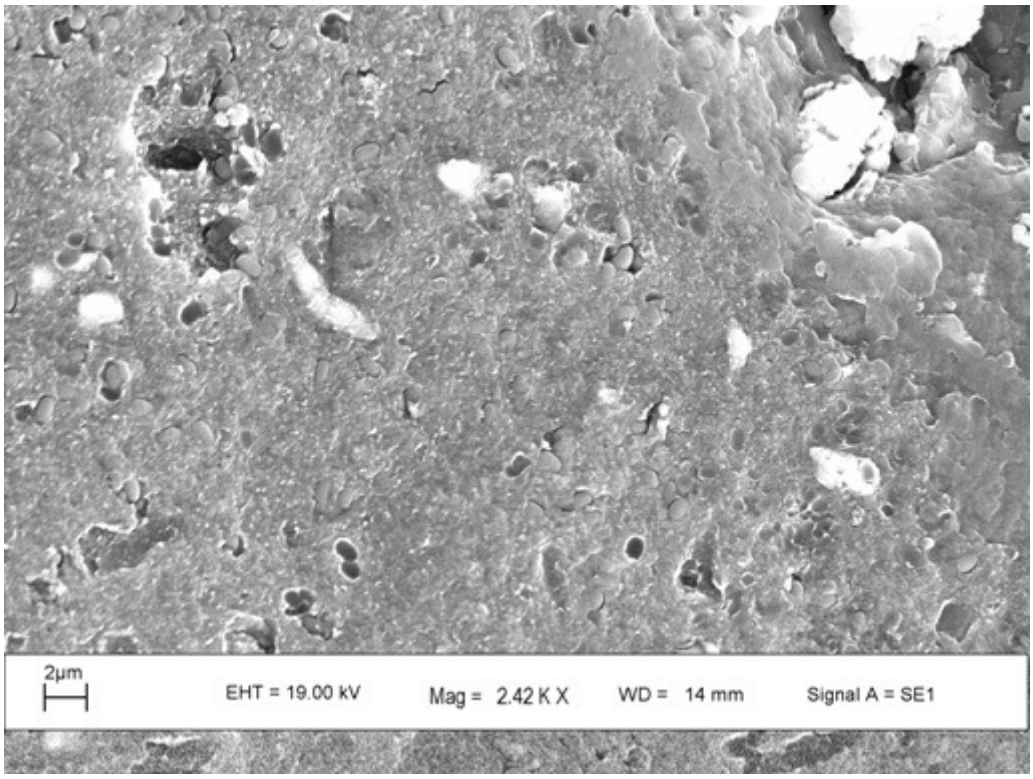
Results and discussion

Characterization of chitosan beads

Scanning Electron Microscope (SEM) was used to observe the surface morphology of the chitosan beads and SEM images of chitosan beads produced from commercially available chitosan flakes are shown in Figure 2. Micro-pores present on spherical shaped chitosan beads can act as active sites for metal adsorption and increase the surface to volume ratio of the adsorbent.



(a)



(b)

Figure 2 (a) - SEM micrographs of chitosan beads, **(b)** - surface of a chitosan bead

Batch adsorption tests

Effect of contact time on Cd(II) adsorption

Cd(II) adsorption capacity of chitosan beads as a function of contact time was investigated in order to establish the equilibration time for the maximum uptake and to determine the kinetics of the adsorption process. Figure 3 shows the relationship between the contact time and the Cd(II) adsorption capacity. In the initial stages, the removal of metal ions increased with increasing contact time and according to the results, the system approached equilibrium within 150 minutes. Results revealed that further increase in contact time did not show significant change in Cd(II) adsorption capacity of chitosan beads as the adsorbent get saturated.

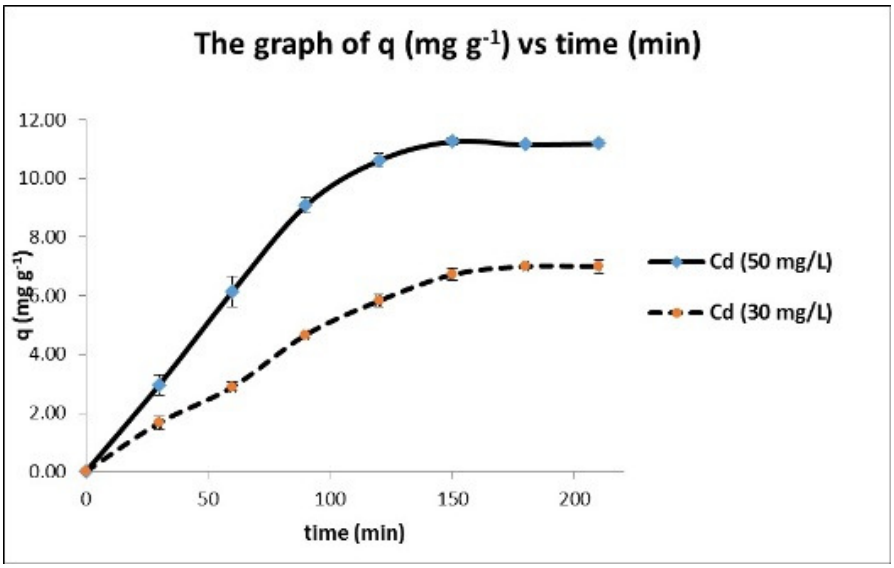


Figure 3- Effect of contact time on adsorption capacity of Cd(II) (30 mg L^{-1} and 50 mg L^{-1}) onto chitosan beads (adsorbent dose 0.1500 g, temperature: 30±2˚C, pH: 7)

Effect of bead dose on Cd(II) adsorption

Figure 4 shows the effect of adsorbent dose on percentage adsorption of Cd(II) onto chitosan beads. The results revealed that percentage adsorption of Cd(II) increases with increase in chitosan bead dose up to 0.40 g. Further increase in adsorbate dose yields a negligible change in percent adsorption. As the available sites for metal binding increase with the increase in adsorbent dose, percentage Cd(II) adsorption increases up to 98 % and it becomes almost a constant when bead dosage is greater than 0.40 g.

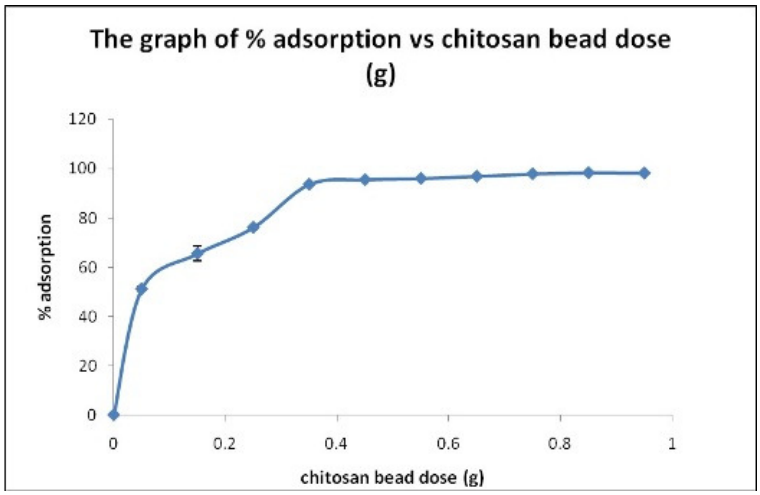


Figure 4- Effect of adsorbent dose on percent adsorption of Cd(II) (50 mg L^{-1},) onto chitosan beads, (contact time: 2.5 h, temperature: 30±2˚C, pH: 7)

Effect of bead size on Cd(II) adsorption

Effect of bead size on adsorption of Cd(II) onto chitosan beads is shown in figure 5. For a better adsorption, adsorption sites should expose to the metal ion solution to occur solid to metal ion interactions efficiently. If the surface area of an adsorbent is high, the exposure of surface sites facilitates more solid to metal ion interactions; hence, the efficiency of adsorption increases. When the bead size gets smaller the surface area gets enhances; therefore, the percentage of adsorption as well as q value increases. According to the results the highest adsorption capacity was observed when the smallest sized chitosan beads were used as the adsorbent.

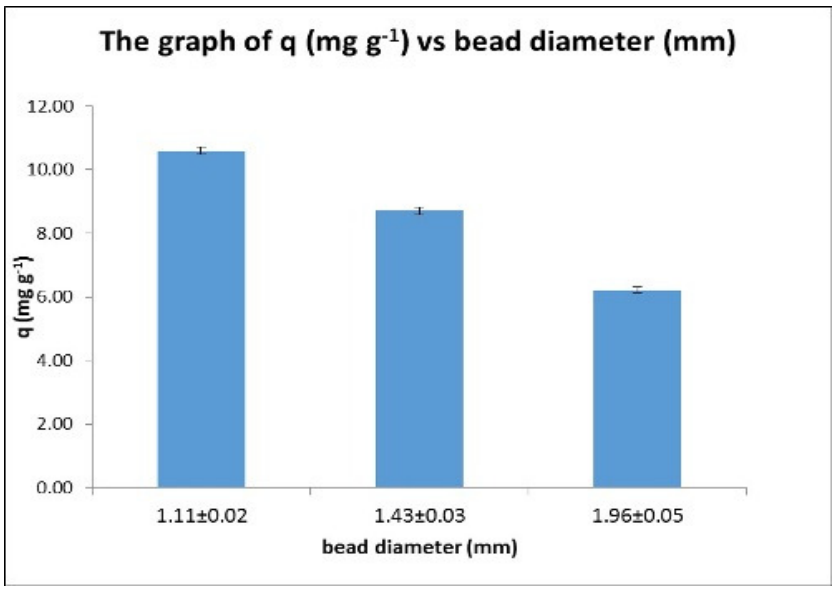


Figure 5 -Effect of bead size on adsorption of Cd(II) (50 mg L^{-1}) onto chitosan beads (bead dosage = 0.1500 g, shaking time: 2.5 h, temperature: 30±2˚C, pH: 7)

Adsorption isotherm

Valuable information such as theoretical capacity of the sorbent exhaustion and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms (i.e. Ansari, 2001). For this purpose, two commonly used isotherms namely Langmuir isotherm and the Freundlich isotherm were used. The linear form of the Langmuir equation is given as;

$$\frac{1}{q_e} = \frac{1}{bq_oC} + \frac{1}{q_o} \quad (1)$$

Where, q_e is the amount of grams of adsorbate per gram of adsorbent, C is the equilibrium concentration of Cd(II) metal ion solution. b is the adsorption coefficient and q_o is the amount of adsorbate adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites. The linear form of Freundlich isotherm is given as:

$$logq_e = nlogC + logk \quad (2)$$

Where q_e is the grams of adsorbate per grams of adsorbent, C is the equilibrium concentration of Cd(II) metal ion solution and n is a system specific constant. The Langmuir isotherm best describes chemisorption processes and it fits mainly with gaseous phase adsorptions as well as aqueous phase monolayer adsorption while the Freundlich model widely fits with aqueous systems with multilayer adsorptions. In figures 6 and 7 the Langmuir isotherm and Freundlich isotherm curves for adsorption of Cd(II) onto chitosan beads are shown respectively. Langmuir and Freundlich isotherm constants for Cd(II) onto chitosan beads at 30˚C are given in table 1.

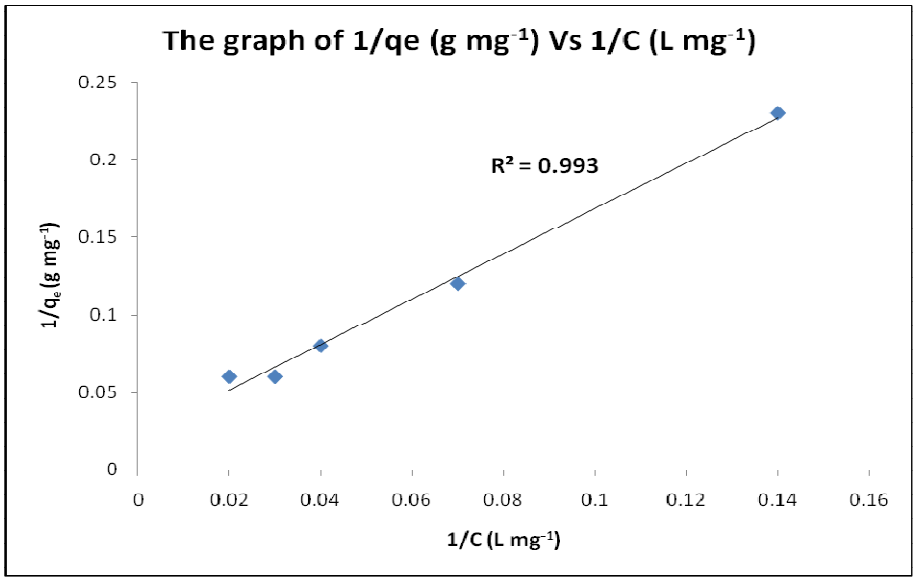


Figure 6- Langmuir isotherm for adsorption of Cd(II) onto chitosan beads at 30˚C. (Eq. 1)

Langmuir constant b is the equilibrium constant of adsorption. It is a constant at higher concentrations of the adsorbate molecules if the enthalpy of adsorption is independent of coverage; Θ (Θ = q_e/q_o) (i.e. Ansari, 2001) Since the experimental data fits with the Langmuir model with R^2 value of 0.993 it can be concluded that under these experimental conditions and concentrations of adsorbate used, b act as a constant independent of Θ.

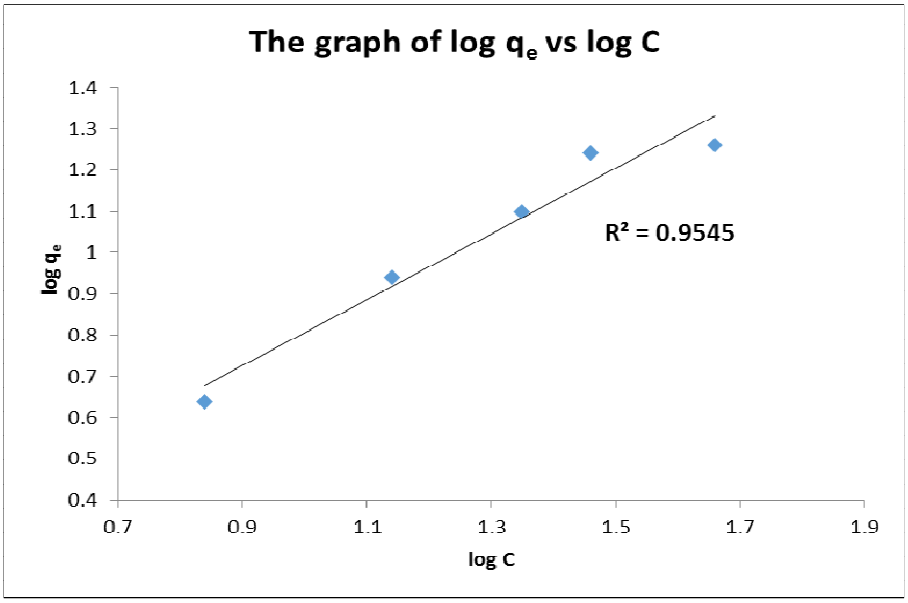


Figure 7- Freundlich isotherm for adsorption of Cd(II) onto chitosan beads at 30˚C. (Eq. 2)

Freundlich model is associated with physisorption and it is normally used with low concentrations of adsorbate. Experimental data fits with Freundlich isotherm with R^2 value of 0.954 which is lower than Langmuir model R^2 value. Thus, it is concluded that the Langmuir model is an appropriate model to represent the adsorption equilibrium data.

Table 1- Langmuir and Freundlich isotherm constants for adsorption of Cd(II) onto chitosan beads at 30˚C

Freundlich constants		Langmuir constants	
K	n	q_o	b
1.0715	0.777	62.5	0.0112

There are many experiments that have been carried out to remove Cd(II) from wastewater using low cost adsorbents and some q_o values of low cost adsorbents recorded in literature are tabulated in the table 2. According to the results, the q_o obtained for adsorption of Cd(II) onto chitosan beads was 62.5 mg g^{-1} which is considerably a higher value compared to q_0 values

for adsorption of Cd(II) onto various other biomass types reported in the literature. Interestingly, the Cd(II) adsorption capacity of physically modified chitosan; chitosan beads is significantly higher than the unmodified chitosan; chitosan flakes indicating that physical modification has enhanced the surface area and the porosity of the chitosan beads. The highest q_o value was reported for fly ash. However, these values depend on many parameters such as temperature, pH, particle size, other chemical treatments etc.

Table 2- Langmuir constants (q_o) for adsorption of Cd(II) onto various types of adsorbents reported in literature

Adsorbent	q_o (mg g^{-1})	Reference
Activated Carbon from Coconut Coir Pith	93.4	(i.e. Kadirvelu, 2003)
Natural clay	21.93	(i.e. Mariadas *et.al.,* 2012)
Montmorillonite	32.7	(i.e. Khalfa, 2011)
Fly ash	198.2	(i.e. Kadirvelu, 2003)
Peanut hull carbon	89.4	(i.e. Kadirvelu, 2003)
Red mud	66.8	(i.e. Kadirvelu, 2003)
Modified silica gel	33.72	(i.e. Kadirvelu, 2003)
Waste cork	2.4	(i.e. Grudić, 2015)
Red alga	53.1	(i.e. Grudić, 2015)
Untreated coffee grout	15.65	(i.e. Grudić, 2015)
Chitosan flakes	40.1	(i.e. Mendez, 2008)
Rice husk	8.58	(i.e. Grudić, 2015)
Saffron leaves charcoal	68.75	(i.e. Dowlatshahi *et.al.,* 2014)
Chitosan beads	62.5	This work

Adsorption kinetics

Adsorption kinetics is used to explain the adsorption mechanisms and characteristics. Pseudo-first order and pseudo-second order kinetic models which are considered as the widely used models to study the kinetics of adsorption, were applied to experimental data in order to investigate the kinetics of sorption of Cd(II) onto chitosan beads. Lagergren's pseudo first

order model can be expressed by Eq. (3) and (4) (i.e. Amarasinghe, 2007). The pseudo second order model is given by Eq. (5) and (6) (i.e. Amarasinghe, 2007).

$$\frac{dq}{dt} = k_1(q_e - q) \quad (3)$$

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (5)$$

$$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2 t} \quad (6)$$

Where q and q_e are the amount of metal ions adsorbed per unit weight of adsorbent (mg g^{-1}) at time t and at equilibrium respectively. k_1 and k_2 are the adsorption rate constants for first order and second order respectively.

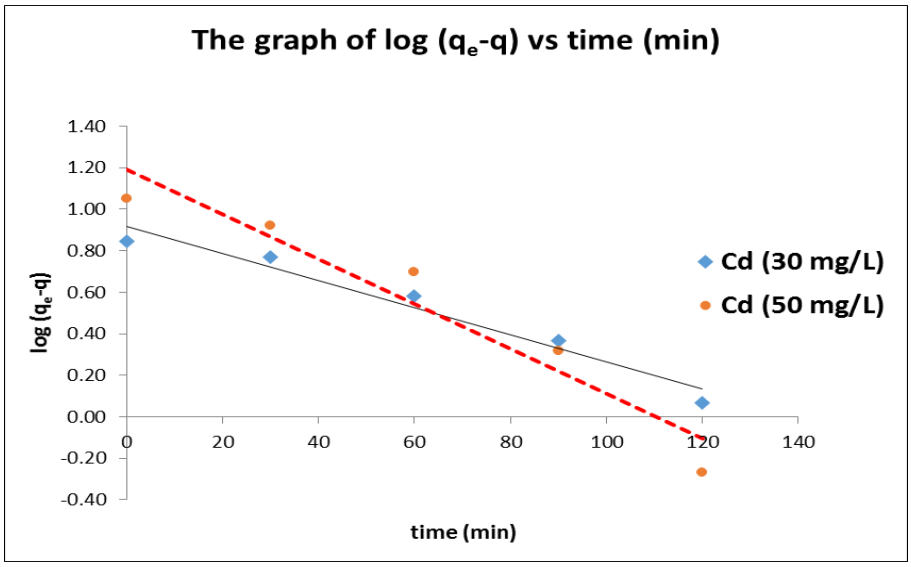


Figure 8 - Pseudo first order kinetics of adsorption of Cd(II) (50 mg L^{-1} and 30 mg L^{-1}) onto chitosan beads (dosage =0.1500 g, temperature =30˚C).

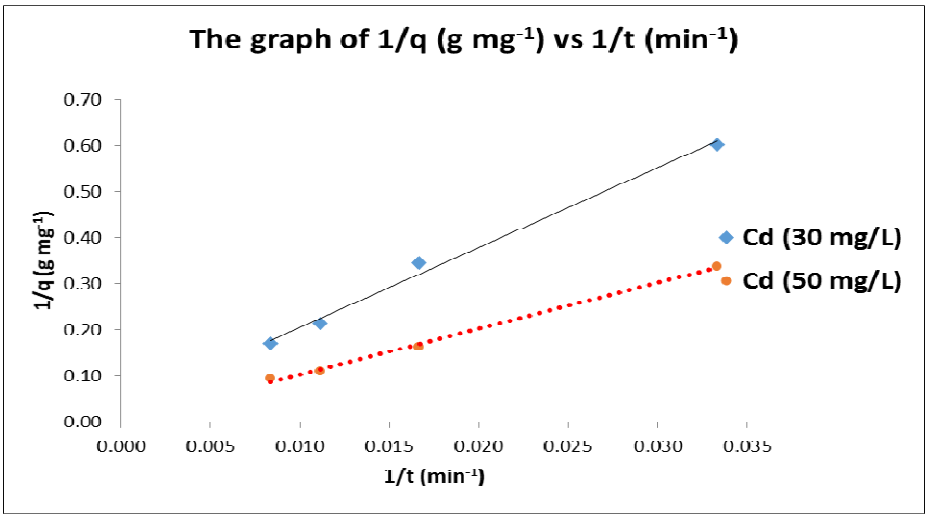


Figure 9- Pseudo second order kinetics of adsorption of Cd(II) (50 mg L^{-1} and 30 mg L^{-1}, 50.00 mL) onto chitosan beads (dose = 0.1500 g, temperature = 30˚C).

According to the results, the pseudo-second-order model (figure 9) fits to the experimental data better than the pseudo first order model (figure 8) for the Cd(II) adsorption as the pseudo-second order model fits to the experimental data with higher R^2 values (0.992 and 0.988 for 30 mg L^{-1} Cd(II) solution and 50 mg L^{-1} Cd(II) solution respectively) than the pseudo-first order R^2 value (0.959 and 0.935 for Cd(II) solutions 30 mg L^{-1} and 50 mg L^{-1} respectively). The higher R^2 values confirm that the pseudo second-order model well represents the adsorption data. These results reveals that the concentration of Cd(II) and the amount of chitosan beads used, both involve in the rate determining step of the adsorption process. Therefore, the adsorption process may be chemisorption.

Conclusions

Optimal performance of physically modified chitosan; chitosan beads was observed with chitosan bead diameter 1.11±0.02 mm, contact time of 150 minutes and chitosan bead dosage of 0.40 g for 50 mg L^{-1} of initial Cd(II) ion concentration.

Isotherm data at 30˚C were satisfied Langmuir model with R^2 value of 0.993. The kinetic data fits with the pseudo second order model with R^2 values of 0.992 and 0.988 for Cd(II) concentrations 30 mg L^{-1} and 50 mg L^{-1} respectively. Results obtained by the experiments revealed that chitosan beads are more efficient compared to number of alternative low cost natural adsorbents reported in literature, in purifying water samples contaminated with Cd(II) as the Langmuir constant q_o value obtained for adsorption of Cd(II) onto chitosan beads is 62.5 mg g^{-1}. Further, it can be concluded that physically modified chitosan; chitosan bead

made using commercially available chitosan flake is a better adsorbent for removal of Cd(II) from wastewater.

Acknowledgments

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