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Research Article

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Use of Chitosan Films for the Removal of Cd(II) from Aqueous Solutions by Adsorption and an Electrochemically-Assisted Method

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Abstract As Cd is considered as one of the toxic heavy metals affecting the human and the environment, this study was conducted to evaluate the potential of physically modified chitosan, chitosan film/membrane to remove Cd(II) from drinking water by adsorption and an electro-chemically assisted method. Chitosan films were prepared and surface morphology was analyzed by SEM. Batch adsorption studies were conducted to evaluate the effect of initial Cd(II) ion concentration, stirring time and adsorbent dosage on Cd(II) adsorption capacity of chitosan film at room temperature (29±1°C). Optimal Cd adsorption performance of the adsorbents was observed at 50.00 µg/L of initial Cd(II) concentration, at 0.025 g adsorbent dosage and at stirring time of 2 hours. Equilibrium data obtained for adsorption process of Cd(II) by chitosan films were tested with two common adsorption isotherm models, Freundlich and Langmuir isotherms and the results indicated that the experimental data at 29 ^{0}C were fitted well to both the tested isotherms. Langmuir monolayer maximum adsorption capacity (q^0) for the Cd(II) adsorption onto chitosan film was found to be 88.12 mg/g and which is significantly a higher value than the q_o values reported in the literature for adsorption of Cd(II) onto unmodified chitosan flakes and various other bio-adsorbents. Thus, it can be concluded that chitosan films could be considered as a low-cost and environmentally friendly material to remove Cd(II) from aqueous solutions by adsorption. Further, the results of the electro-chemically assisted method revealed that the chitosan membrane permeability for Cd(II) is significantly higher under an electric potential and further studies are required to develop it as a new method of water purification.

Keywords Adsorption capacity, Cadmium, Chitosan film, Electrochemically- assisted method

1. Introduction

Pollution of water sources specially drinking water sources is becoming a serious problem faced by the world today. Unlike organic pollutants, heavy metals are non-biodegradable and even trace amount of some of the heavy metals may cause deleterious health effects in humans [1-3]. As some of the common methods such as membrane filtration, precipitation, electrodialysis, photocatalysis, etc used to remove heavy metals in drinking water are associated with some drawbacks, intensive studies are conducted on the development of cost-effective, and efficient technologies. In recent years the search for efficient, low-cost and environmentally friendly natural material for the treatment of water by adsorption technology and electrochemical methods has intensified.

Among the many other low-cost adsorbents, chitosan is considered as one of the promising bio-adsorbent having a higher potential for heavy metal adsorption. As chitosan possesses hydroxyl and amine functional groups, the interactions of metals (metal cations) with chitosan are, possibly dominated by chemical adsorption by chelation in

near neutral aqueous solutions [4]. Chitosan is commercially produced by deacetylation of chitin. The main sources of chitin used for the production of chitosan includes exoskeleton of crustaceans such as crabs and shrimp. The chemical structures of chitin and chitosan are shown in figure 1.

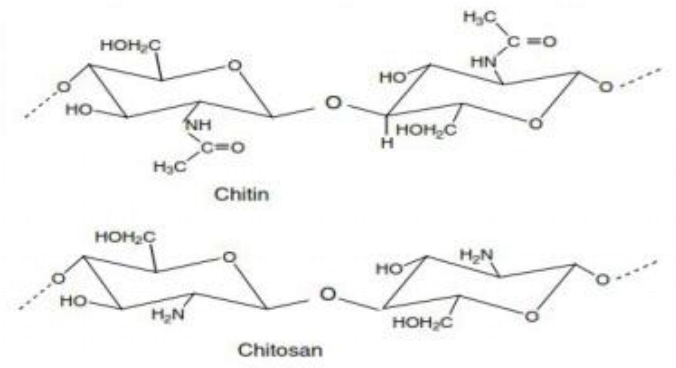


Figure 1: Chemical structures of chitin and chitosan [5].

Chitosan being a biopolymer is readily available, biodegradable [6], environmentally friendly, non-toxic and has no side effects if implanted in the body. Therefore, the current study focused on use of physically modified chitosan; chitosan film as a cost-effective heavy metal removal agent for drinking water purification by adsorption and an electrochemically-assisted method. Although chitosan has been used as a heavy metal removal agent for industrial wastewater, few attempts have been made to understand the ability of chitosan/physically or chemically modified chitosan to uptake heavy metals in the polluted drinking water, containing trace amounts (ppb levels) of metal pollutants.

Therefore, the main objective of this study was to prepare physically modified chitosan, chitosan film/membrane from commercially available chitosan and evaluate its Cd(II) removal ability from aqueous solutions by adsorption and electrochemically-assisted method.

2. Materials and Methods

2.1 Preparation of chitosan film/membrane

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). 1 % (w/w)) chitosan solution was prepared by dissolving chitosan powder in a 2 % (v/v) acetic acid solution. The mixture was stirred 48 hours at room temperature (29±01 ºC). Then the resulting solution was poured into a Petri dish and covered with polyethylene paper. It was dried at room temperature for couple of days and then washed with NaOH (0.10 M) solution followed by with distilled water. Finally, the films were air-dried.

2.2 Characterization of chitosan film/membrane

The surface morphology of prepared dried chitosan film/membrane and Cd(II) bound chitosan film was examined using scanning electron microscope (model of LEO-1420 VP using secondary electron microscopic method).

2.3 Study of the removal of Cd (II) from aqueous solutions using chitosan film by adsorption

Batch adsorption tests were carried out to examine the effect of initial Cd(II) ion concentration, adsorbent dosage, and stirring time on Cd adsorption onto chitosan films. All the experiments were conducted in triplicates.

2.3.1 Effect of initial Cd concentration on Cd adsorption capacity of chitosan film

A series of solutions containing different initial cadmium concentrations was prepared separately (30, 50, 70, 90, 110 µg/L) using Cd(II) standard (1000 µg/L). Then the prepared Cd solutions (50.00 mL) were added to polypropylene bottles. The prepared chitosan films were added (0.025 g) to each bottle. Then the pH was adjusted to 7.00 and capped tightly to prevent any leakages and stirred for 2 hours at room temperature (29±01 °C). The

samples were filtered and the remaining Cd concentrations in filtrates were determined by analyzing the filtrates using Graphite Furnace Atomic Absorption Spectrophotometer/GFAAS (GBC GF 3000). The cadmium adsorption capacities (q) were calculated using the equation 1 [7].

$$q\left(\frac{\mu g}{g}\right) = \frac{Iw(\mu g) - Fw(\mu g)}{Weight\ of\ chitosan\ used\ (g)} \quad (1)$$

Where, q = Cd adsorption capacity, Iw = Initial weight of Cd in the solution and Fw = weight of Cd in the solution after treatment with the adsorbent.

2.3.2 Effect of adsorbent dosage on Cd adsorption capacity of chitosan film

A solution with the initial concentration of Cd was prepared (50 µg/L) using Cd standard (1000 µg/L) in a volumetric flask. The Cd solution (50.00 mL) was added to three polypropylene bottles. The prepared chitosan film was added separately (0.025 g, 0.050 g, and 0.075 g) to each bottle. Then the pH was adjusted to 7.00 and they were allowed to stir for 2 hours at room temperature (29±1°C). The samples were filtered, and the filtrates were analyzed using GFAAS. Cd adsorption capacities were calculated using the equation 1.

2.3.3 Effect of stirring time on Cd adsorption capacity of chitosan film

Cd solution (50 µg/L, 50.00 mL) and chitosan film (0.025 g) were added separately to five polypropylene bottles. Then the pH was adjusted to 7.00 and stirred for 1, 2, 6, 12 and 24 hours separately at room temperature (29±1 °C). The samples were filtered, and the filtrates were analyzed using GFAAS for Cd.

2.4 Adsorption isotherm studies

Isotherm experiments were conducted by mixing chitosan films (0.025 g) with Cd solution (30, 50, 70, 90, 110 µg/L) separately in dry polypropylene bottles of similar size and shape. pH of the solutions was adjusted to 7 and bottles were capped tightly to prevent any leakages. The samples were allowed to stir at room temperature (30 ^{0}C) for 2 hours which was found to be the time required for the system to reach equilibrium. Then the samples were filtered and analyzed for Cd by GFAAS. The equilibrium adsorption data were analyzed using two most widely used isotherm models, Langmuir and Freundlich isotherm models.

2.5 Study of the removal of Cd(II) from aqueous solutions by an electrochemically-assisted method

2.5.1 Preparation of the initial setup of the cell for the metal removal studies

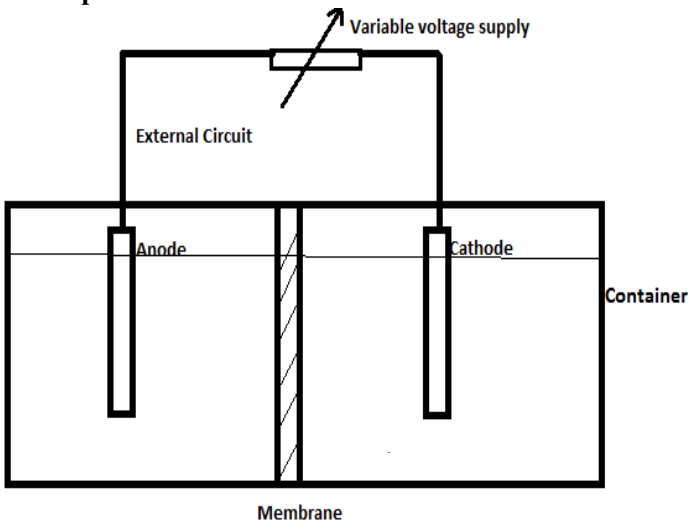


Figure 2: Schematic diagram of the setup prepared for Cd(II) removal studies

The schematic diagram of the cell constructed for the study is shown in figure 2. The chitosan membrane (5 cm x 3 cm) separates the container/cell in to two compartments. Water movement between two compartments occurred only through the membrane. Cu electrodes were used as a cathode and an anode of the electrochemical cell. Then two electrodes were connected to an external power supply (PS 500XTDC POWER SUPPLY Hoefer Scientific Instruments-San Francisco).

2.5.2 Cd removal studies using a Cd (II) solution with initial concentration of 40 µg/L

500 mL of Cd (40 µg/L) solution was placed in the electrochemical cell and then cell voltage (4 V) was supplied for one hour. After 1-hour period, samples of the solution were collected from both compartments at 10 minutes' intervals for 30 minutes after switching off the power supply and the Cd concentration of the samples were determined by GFAAS (GBC GF3000). The experiment was repeated without applying an electric current (control).

3. Results and Discussion

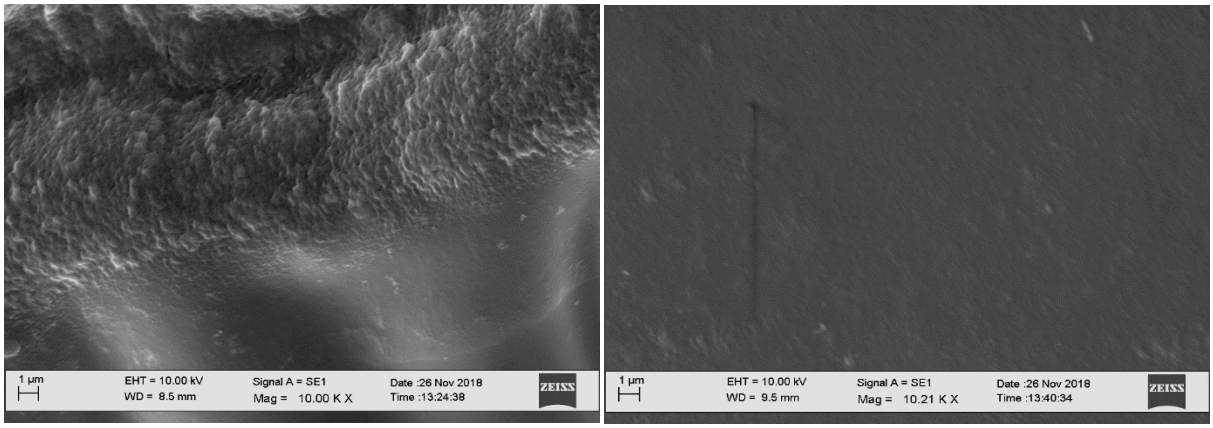
3.1 Preparation of chitosan film/membrane

Chitosan film was simply made by dissolving chitosan in acetic acid followed by pouring it to a petri dish. The prepared chitosan film is shown in figure 3.

Figure 3: Physically modified chitosan; chitosan film/membrane

3.2 Characterization of chitosan film/membrane

The SEM images of chitosan membrane/film before and after adsorption of Cd are shown in figure 4(a) and 4(b) respectively.



(a) (b)

Figure 4: SEM images of chitosan film (a) before and (b) after Cd(II) adsorption

As depicted in figure 4(a) chitosan film has a curly or irregular and quite rough porous surface which provides a large surface area for metal ion adsorption. Upon binding with metal ions, the surface morphology of the chitosan film becomes smooth as shown in figure 4(b), indicating the interaction between Cd(II) and the chitosan film.

3.3 Study of Cd(II) removal by adsorption

3.3.1 Effect of initial Cd concentration on Cd adsorption

By changing the initial cadmium concentration, the Cd adsorption capacity of chitosan film was analyzed, and the results are presented in Figure 5.

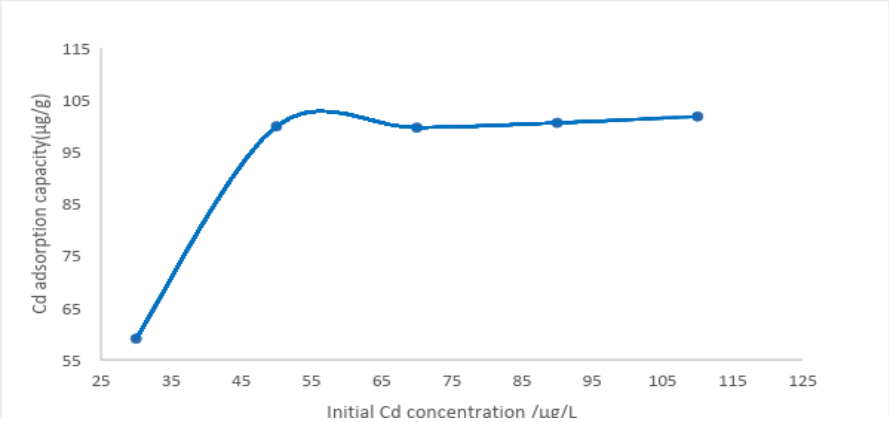


Figure 5: Effect of initial metal ion concentration on Cd adsorption capacity of chitosan film (Chitosan film dosage = 0.025 g, pH = 7, agitation period = 2 hours, ambient temperature)

By keeping the adsorbent dosage constant, the Cd adsorption capacity was measured by changing initial Cd concentration. According to the results, the maximum Cd adsorption capacity was observed when initial Cd concentration of the solution was 50 µg/L. When initial Cd concentration is increased from 50 µg/L, Cd adsorption capacity is not increased with the initial concentration. At low concentration, most Cd ions in the sample solution might contact the binding sites of the adsorbent and when the concentration is increased all the Cd ions may not be able to contact with the active surface due to the saturation of the binding sites.

3.3.2 Effect of initial chitosan film dosage on Cd adsorption

As tabulated in table 1, the maximum adsorption capacity of chitosan film for Cd was observed when chitosan film dosage was 0.025 g among the dosages selected at pH = 7 and initial Cd concentration of 50 µg/L.

Table 1: Adsorption capacity of chitosan film at different chitosan film dosages (initial cadmium concentration = 50 µg/L, pH= 7.0, agitation period = 2 hours, ambient temperature)

Chitosan dosage (g)	Cd adsorption capacity of chitosan film (µg/g)
0.025	99.94 (±0.28)
0.050	71.54 (±0.72)
0.075	55.80 (±0.15)

The Cd adsorption capacity of chitosan film was decreased from 99.94 to 55.80 µg/g with increasing adsorbent dosage from 0.025 g to 0.075 g due to the availability more unsaturated adsorption sites with increase in adsorbent dosage.

3.3.3 Effect of shaking time on Cd adsorption capacity

It was observed that the adsorption capacity of Cd ions increased with the increase in contact time up to some extent and later reached to a constant value when equilibrium is achieved due to the saturation of the adsorbent. The maximum adsorption capacity was observed at the shaking time of 2 hours.

The variation of the adsorption capacity of the prepared chitosan film with the shaking time is shown in the figure 6.

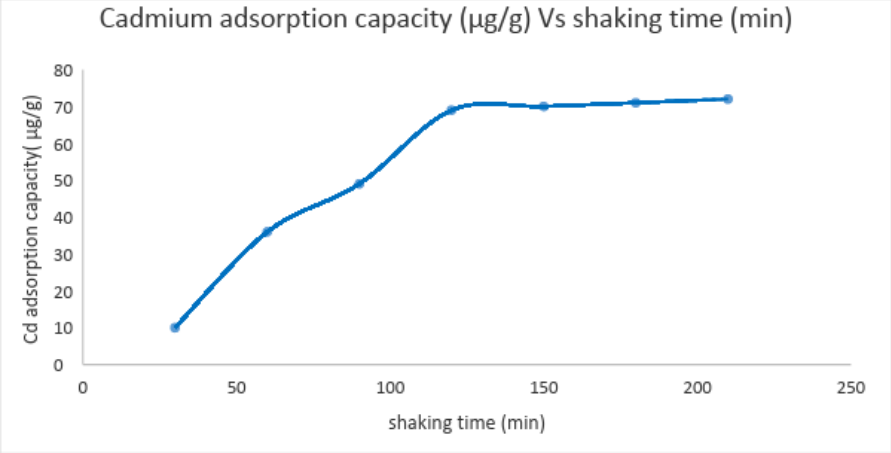


Figure: 6 Effect of stirring time on Cd adsorption capacity of chitosan film (Chitosan film dosage = 0.025 g, pH = 7, agitation period = 2 hours, ambient temperature)

3.4 Adsorption isotherm studies

Equilibrium data were mathematically modeled using two isotherm models, Langmuir and Freundlich, to describe the equilibrium isotherms at different Cd concentrations.

Langmuir model has been widely applied to describe experimental adsorption data based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with a constant energy and there is no transmigration of adsorbate in the plane of adsorbent surface [8]. The linear form of the Langmuir isotherm equation can be represented as equation 2;

$$\frac{1}{q_e} = \frac{1}{bq_oC} + \frac{1}{q_0}\frac{1}{q_e} = \frac{1}{bq_oC} + \frac{1}{q_0} \qquad (2)$$

Where, q_e is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium, C is the equilibrium concentration of adsorbate, b is adsorption coefficient and q_o is the amount of adsorbate adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites.

The q_e values at different initial Cd concentration were calculated and the constructed linear plot of the Langmuir isotherm is presented in Figure 7.

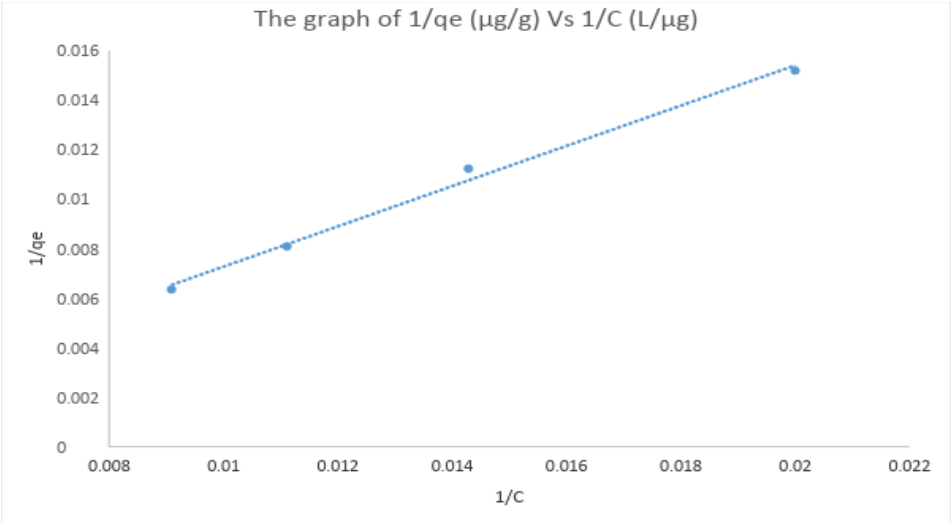


Figure 7: Linear plot of the Langmuir isotherm for Cd adsorption on to chitosan film (Chitosan film-0.025 g, Cd-50 µg/L, shaking time =2 hr, pH= 7, at 30±2 ^oC)

Freundlich's isotherm considers the adsorbent surface is energetically heterogeneous. Freundlich model is associated with physisorption and it is normally used with low concentrations of the adsorbate [9]. The linear form of the Freundlich isotherm is commonly given as equation 3;

$$logq_e = nlogC + logk \quad (3)$$

Where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium, C is the equilibrium concentration of adsorbate, and k is a constant related to adsorption capacity. Experientially obtained linear plot of the Freundlich isotherm is presented in Figure 8. Langmuir and Freundlich isotherm constants are presented in the table 2.

Table 2: Langmuir and Freundlich isotherm constants for Cd adsorption onto prepared physically modified chitosan; chitosan films

Adsorbent	**Langmuir constants**		**Freundlich constants**	
	q_0	**b**	**k**	**n**
Chitosan film	88.12	0.021	1.056	0.765

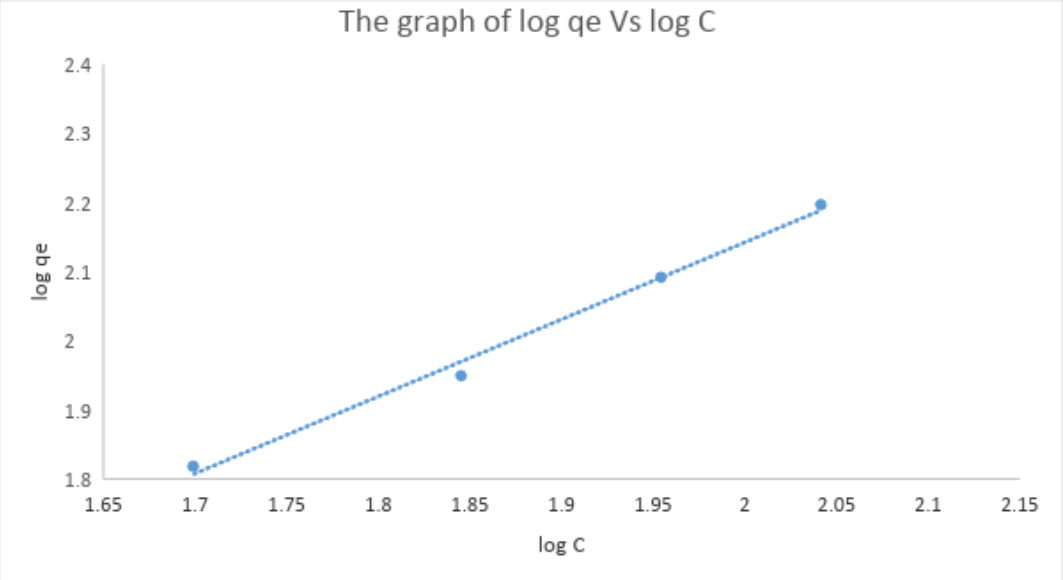


Figure 8: Linear plot of the Freundlich isotherm for Cd adsorption on to chitosan film (Chitosan film=0.025 g, initial Cd concentration = 50 µg/L, shaking time =2 hr, pH= 7 at30±2 ^oC)

Both Langmuir and Freundlich isotherms fit with the experimental data (correlation coefficient of Langmuir isotherm is R^2 = 0.9932 and that of Freundlich isotherms is 0.9925) but data fitted well to the Langmuir model confirming that homogeneous nature of the prepared chitosan film surface. Each Cd ion-chitosan film adsorption has equal activation energy and; the results demonstrates that the formation of monolayer coverage of Cd ions at the outer surface of the prepared chitosan film. Langmuir constant ($q_{0;}$ maximum adsorption capacity) for the physically modified chitosan, chitosan film was found to be 88. 12 mg/g and which was significantly higher than that of unmodified chitosan; chitosan flakes (q_0 = 40.1 mg/g) reported in the literature [10].

There are many experiments that have been carried out to remove Cd from waste water using low cost adsorbents and some q_0 values of low-cost adsorbents for the adsorption of Cd recorded in literature are shown in the table 3. Compared to those adsorbents chitosan film shows a better Cd adsorption capacity. However, it is also important to

note that these q_0 values depend on many parameters such as temperature, pH, particle size, other experimental conditions etc.

Table 3: Langmuir constants (q_o) for adsorption of Cd onto various types of adsorbents reported

Adsorbent	q_o (mg/g)	Reference
Natural clay	21.93	[12]
Montmorillonite	32.70	[11]
Fly ash	198.20	[13]
Peanut hull carbon	85.40	[13]
Red mud	66.80	[13]
Modified silica gel	33.72	[13]
Chitosan flakes	40.1	[10]
Chitosan beads	62.5	[14]
Chitosan film/membrane	88.12	This work

3.5 Study of Cd removal by an electrochemically- assisted method using a Cd(II) solution with initial concentration of 40 µg/L

Set up used to test the permeability of chitosan film for Cd(II) under an external power supply is shown in Figure 9.

Figure 9: Set up used to test the permeability of chitosan film for Cd(II) under an external power supply

The samples were collected from both the cathodic and anodic compartments separately after supplying current for an hour (4 V). Then samples were taken every 10 minutes for 30 minutes from both compartments. The change in Cd concentration in both compartments with time after the removal of power supply is shown in Figure 10 (a) and change in Cd concentration in both compartments with time without applying an electric current is depicted in figure 10(b)

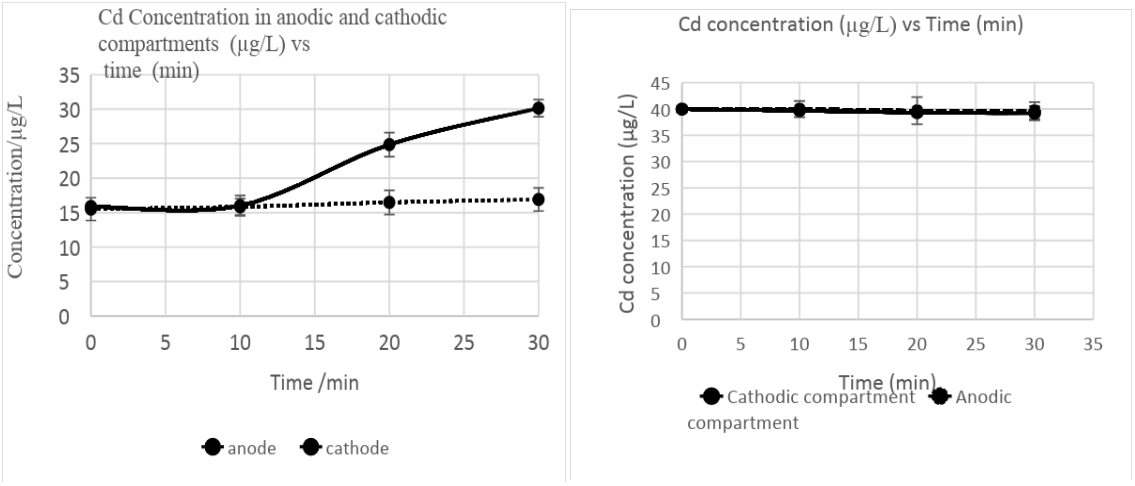


Figure 10: Graph of Cd Concentration vs. sampling time interval (a) after turning off the power supply(4 V) and (b) graph of Cd Concentration vs. sampling time interval (after one hour) without the power supply (0 V). (Total volume 500 mL, pH = 7, ambient temperature, initial concentration of Cd(II) = 40 µg/L)

The preliminary results revealed that the initial Cd (II) concentration has reduced (15 µg/L) in both chambers when current was passed through the cell for 1 hour. This indicates that Cd (II) was allowed to move through the chitosan film towards the cathode when an electric current was applied to the system [15]. However, the collected Cd(II) at the cathodic compartment did not significantly migrate back to the anodic compartment through the chitosan membrane when the current was switched off indicating that the chitosan membrane permeability for Cd(II) is significantly higher under an electric potential. Hence the Cd content in the anodic compartment is less than that in the cathodic compartment after the process.

4. Conclusion

The results of the batch adsorption studies revealed that the Cd adsorption capacity of physically modified chitosan; chitosan film depends on initial adsorbate (Cd) concentration, adsorbent dosage (chitosan film) and stirring time/contact time. It was found that maximum adsorption of Cd(II) by chitosan film was occurred at initial Cd(II) concentration of 50 µg/g, adsorbent dosage of 0.0025 g and at stirring time of 2 hours. The equilibrium adsorption data were fitted to both the Langmuir isotherm model and the Freundlich isotherm model. Langmuir constant, q_o value obtained for Cd(II) adsorption onto chitosan film was found to be 88.12 mg/g and which is significantly higher than that of the unmodified chitosan flakes (40.1 mg/g), indicating that physical modification of chitosan flakes to obtain chitosan films has enhanced the adsorption potential of the adsorbent. As the results of the study on Cd removal by electro-chemically assisted method revealed that the chitosan membrane permeability for Cd(II) is significantly higher under an electric potential, the electrochemically-assisted method could be further studied to develop it as a new method to purify water contaminated with heavy metals.

Acknowledgement

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