

## Adsorption of Cadmium By Silica Chitosan

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### ABSTRACT

The adsorption behavior of silica-chitosan for cadmium ions has been investigated. The aim of this study to explore effects of initial concentrations of  $\text{Cd}^{2+}$ , and the ratio of silica to chitosan on the adsorption and recovery of  $\text{Cd}^{2+}$ . The present study deals with the competitive adsorption of  $\text{Cd}^{2+}$  ion onto silica graft with chitosan. Batch adsorption experiments were performed at five different initial  $\text{Cd}^{2+}$  concentrations (5, 10, 15, 20 and 25 ppm), on five different proportion from silica to chitosan (100%, 95%, 85%, 75% and 65%) as adsorbent at pH 5. The adsorption process depends on initial concentration of  $\text{Cd}^{2+}$  and ratio of chitosan in adsorbent. In the recovery process, the high recovery at 0.5 mg and observed the recovery decrease with increasing the initial concentration of  $\text{Cd}^{2+}$ , and the low recovery at 0.25 mg from  $\text{Cd}^{2+}$ . In this study, the adsorption capacity of  $\text{Cd}^{2+}$  in regard to the ratio of silica and chitosan hybrid adsorbents is examined in detail.

**Key word:** adsorption capacity, recovery, cadmium, silica, chitosan

### INTRODUCTION

Cadmium has been well recognized for its negative effects on the environment where it accumulates readily in living systems. Due to cadmium intake through food, water or smoke can cause chronic health problems, such as serious damage to human enzyme tissues specially kidneys and bones [1], lung edema, renal dysfunction, liver damage, anemia and hypertension [2]. The treatment of cadmium contaminated water is similar to that of many metal contaminated effluents. There are several methods to treat the metal contaminated effluent such as precipitation, ion-exchange, adsorption etc., but the selection of the treatment method is based on the concentration of waste and the cost of treatment [3].

Silica is an inorganic adsorbent, tend to polar, and less able to interact with Cadmium, because most of the active silanol groups less than the maximum adsorption process. Silanol (Si-OH) is a group that determines the surface properties including its adsorption effectiveness [4]. A large surface area of silica to determine its activity in adsorption of metal ions and ions exchange [5]. In general, the adsorption reaction has been presented as a reversible cation exchange between  $\text{Cd}^{2+}$  and silanol group (-SiOH) [6]. Chitosan is obtained by the deacetylation of chitin, Chitosan has been used for the adsorption ions such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  [7]. Silica has been proved to be a good material to modify chitosan and improve its adsorption ability for many heavy metals [8], [9]. The chitosan is reported to adsorb on silica particles via electrostatic attraction and hydrogen bonds. Bonding is between hydroxyl, amino, and carbonyl groups of chitosan and silanol groups of silica [10].

Adsorption is one of the effective ways to remove heavy metals from wastewater. The amount of  $\text{Cd}^{2+}$  adsorbed by Silica-chitosan is expected to increase with increasing the ratio of chitosan in adsorbent at pH 5, and the eluents used in this experiment were  $\text{HNO}_3$ .

The purpose of this research was to study sorbent behavior of silica chitosan when adsorb cadmium. During the experiment under this study, effects of different parameters such as initial concentration of cadmium and ratio of chitosan in adsorbent.

## EXPERIMENTAL

### Chemicals and reagents

All solutions were prepared using distilled water, cadmium stock solution was prepared from appropriate amount 0.150 g of the  $\text{CdCO}_3$  salt of this analyte, as 1000 ppm solution in 0.01M  $\text{HNO}_3$ . The concentration ranges of cadmium prepared from stock solution varied are 5, 10, 15, 20 and 25 ppm for both adsorbents. Before mixing the adsorbent, the pH of each solution was adjusted to the required value with diluted NaOH or  $\text{HNO}_3$ . All the chemicals used were an analytical reagent grade and were obtained from Merck.

### Apparatus

Metal determinants were made with spectra AAS, flame atomic absorption spectrometer (FAAS) SHIMADZU AA-6200, using air-acetylene flame. The pH values of the solutions were measured by a digital pH meter (Inolab). The amounts of chemicals and adsorbents were taken using analytical balance, and magnetic stirrer (IKAMAGRH).

### Procedure determination of adsorption capacity

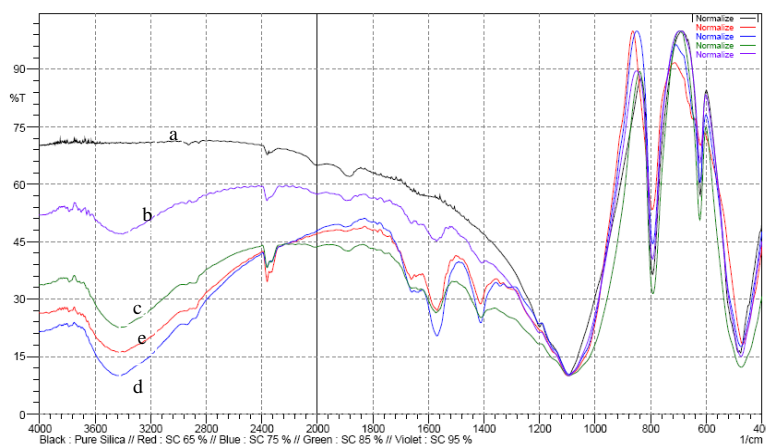
Taken 0.100 g of adsorbent as several ratio (silica 65 % , 75 % ,85% , 95 % and silica 100 %) transferred into conical flasks, and added 10 ml  $\text{Cd}^{2+}$  solutions several concentration (5, 10, 15, 20 and 25 ppm) for each conical flasks, shake 2 hours by shaker at 100 rpm. The solution was filtrated by filter paper (Wathman no. 41), the filtrate (filtrate 1) kept in the plastic bottle. This procedure was repeated twice, dried the absorbent in the oven at  $105^\circ\text{C}$  for 1 hour, and each absorbent transferred to the clean conical flasks and added 10 ml of  $\text{HNO}_3$  0.01 M for each conical flasks, the mixture filtered again and kept each filtrate (filtrate 2) in the plastic bottle, then all filtrates were measured by AAS at 228.8 nm.

## RESULTS AND DISCUSSION

### Characterization of adsorbent

#### IR Characterization of Silica-Chitosan

Figure 1 showed the IR characterization of several ratios from silica-chitosan, the appearance of a sharp peak of Si-O- functional group at wavelengths of around  $1095/\text{cm}$ . Si-O- functional group is a characteristic of the silica compound. Moreover, the groups of -OH are observed between  $3200$  and  $3650\text{ cm}^{-1}$ . The strong sharp peak occurring around  $1095\text{ cm}^{-1}$  can be ascribed to Si-O-Si functional group asymmetric stretching vibration. Peak around  $1411\text{ cm}^{-1}$  indicates of  $-\text{CH}_3$  group. The bond was shown of Si-O-Si at  $476\text{cm}^{-1}$ .



**Figure1.** IR Spectrum of Silica-Chitosan Adsorbent:  
(a) Silica100 %, b) 95 %, c) 85 %, d) 75 %, and e)65%

Two other vibrational modes with the medium intensity peaks occurring around  $792.69\text{ cm}^{-1}$  and  $476.38\text{ cm}^{-1}$  confirm Si–O–Si functional group presence on functionalized  $\text{SiO}_2$ . Slight shift to the right and an intensity increase to  $792\text{ cm}^{-1}$  peak denoted a conjugation between Si–OH group present on silica surface and Si–OH functional group [12].

### Effect of Silica-chitosan ratio

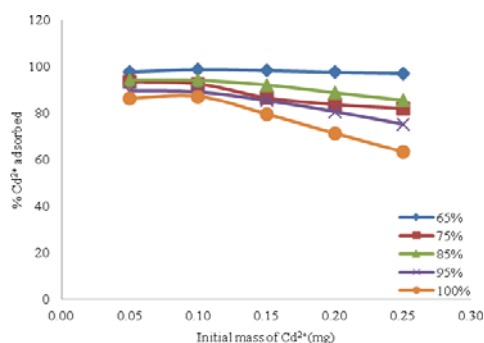
#### Adsorption capacity

The adsorption capacity is  $1.95\text{ mg/g}$  at silica100 % and it increases the adsorption capacity to  $2.46\text{ mg/g}$ ,  $3.14\text{ mg/g}$ , for silica-chitosan 95% and 85% respectively, at silica-chitosan 75% the adsorption capacity was decrease to  $2.81\text{ mg/g}$ , and at silica-chitosan 65% the adsorption capacity was increase to  $5.40\text{ mg/g}$ . According to results observed that the adsorption capacity of silica 65% is greatest, the increase of ratio of chitosan in adsorbent increasing ability to adsorbent to adsorb  $\text{Cd}^{2+}$ , these results indicated to the increase of active sites (–OH) on surface of increasing the adsorption capacity of adsorbent.

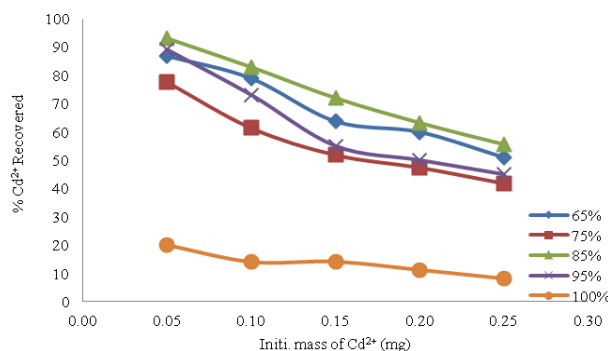
#### Adsorption and Recovery efficiency

According to Figure (2), show the amount of  $\text{Cd}^{2+}$  adsorbed per unit weight of silica-chitosan, at the end of the experiment, a net adsorption of  $\text{Cd}^{2+}$  was found to vary from Silica 100% to silica-chitosan 65% with an increasing initial mass of  $\text{Cd}^{2+}$  from  $0.05\text{ mg}$  to  $0.25\text{ mg}$ . This adsorption could be attributed to adsorption which depends in this case to chemical interaction instead of electrostatic attraction. The increase of  $\text{Cd}^{2+}$  solution concentration enhances the interaction between the  $\text{Cd}^{2+}$  ions and adsorbents. Figure (2) indicates the increase of initial mass of  $\text{Cd}^{2+}$  leading to an increase to the adsorption of  $\text{Cd}^{2+}$  on the adsorbents. The efficiency of  $\text{Cd}^{2+}$  adsorbed was affected with increase the initial mass of  $\text{Cd}^{2+}$  ions from  $0.5$  to  $0.25\text{ mg}$ , with decreasing adsorption percentages at constant pH at 5. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency [11].

According to the results, the efficiency of  $\text{Cd}^{2+}$  adsorb was effected by the initial mass of ions, with decreasing adsorption percentages as mass increase from  $0.05$  to  $0.25\text{ mg}$ , because all the active groups on adsorbent interacted with  $\text{Cd}^{2+}$  ions.



**Figure 2.** Adsorption efficiency of silica-chitosan adsorbed  $\text{Cd}^{2+}$



**Figure 3.** Recovery efficiency of silica-chitosan adsorbed  $\text{Cd}^{2+}$

Elution of  $\text{Cd}^{2+}$  from silica-chitosan was investigated by using concentration of nitric acid 0.01 M, after recovery process it was seen that not all  $\text{Cd}^{2+}$  ions adsorbed on silica-chitosan could be liberated using nitric acid. Review on the difference between  $\text{Cd}^{2+}$  mass and the desorbed  $\text{Cd}^{2+}$  mass. Decreased of recovery efficiency with increased the mass of cadmium ions return to increase of bonding of metal ions with adsorbent, and Lack of ions that are linked with silica-chitosan. The decrease of recovery in silica 100 % (20.05-8.27) % indicates that adsorption is not favorable and that desorption can take place easily since the  $\text{Cd}^{2+}$  is not strongly bonded with silica, while, increase of recovery at other ratio indicated to the uptake the heavy metal ion on adsorbent with two function groups (-OH) on chitosan and (Si-OH) silanol group on silica.

However, after desorption it was seen that not all  $\text{Cd}^{2+}$  adsorbed on silica-chitosan adsorbent could be liberated using  $\text{HNO}_3$  0.01M. The desorption of  $\text{Cd}^{2+}$  from adsorbent silica-chitosan with diluted  $\text{HNO}_3$  to evaluate the feasibility and regeneration of adsorbent,  $\text{H}^+$  ion were needed to displace the  $\text{Cd}^{2+}$  ions adsorbed on silica-chitosan, the metal ion adsorbed by adsorbent could be described by an ion exchange mechanism where two ion of hydrogen was released from silica-chitosan surface per one ion of  $\text{Cd}^{2+}$ .

## CONCLUSION

This study was under taken to investigate the capability of silica-chitosan to adsorption of cadmium. Batch adsorption experiments were performed at five different initial  $\text{Cd}^{2+}$  concentrations (5, 10, 15, 20 and 25 ppm), on five different ratio of silica to chitosan (100%, 95%, 85%, 75% and 65%) as adsorbent, the adsorption except cadmium at pH 5. the results reported that the best ratio of adsorbent in adsorption process was silica 65 %, and the best ratio of adsorbent in recovery process was silica 85 %. The adsorption process depends on initial mass of  $\text{Cd}^{2+}$  and ratio of chitosan in adsorbent. The adsorption capacity of adsorbent was increase with increasing of ratio of chitosan.

## REFERENCES

- [1] Hasan, S., S. Krishnaiah, T.K. Ghosh, D.S. Viswanath and V. M. Boddu., *Ind. Eng.Chem. Res.* **2006**, 45, 5066-5077.
- [2] Waalkes, M.P., *J. Inorg. Biochem.*, **2000**, 79, 241-244.
- [3] P. S. Kumar, *Brazilian J. Chem. Eng.*, **2010**, 27, 2, 347-355.
- [4] Filho, N. L. D., Carmo, D. R, *Marcel Dekker, Inc.*, New York, **2004**.

- [5] Jal, P.K., Patel, S., Mishra, B.K., *Talanta*, **2004**, 62(5):1005-28.
- [6] A. A. Chuiko, *Izvestiya Academy*, **1990**, 10, 2339-2406.
- [7] Jianlong Wang, *Biotechnology Advances*, **2009**, 27, 195–226.
- [8] Coelho, T.C.; Laus, R.; Mangrich, A.S., *React. Funct. Polym.* **2007**, 67, 468–475.
- [9] Birinci, E.; Gulfen, M.; Aydin, A. O., *Hydrometallurgy*, **2009**, 95, 15–21.
- [10] S. T. Koev, *Lab Chip*, **2010**, 10, 3026-3042.
- [11] A. B. Dekhil, *J. Env. Sci. Tech.*, **2011**, 4 (5), 520-533..
- [12] Mirela Diaconu, *U.P.B. Sci. Bull., Series B*, **2010**, 72, 3.