



CHARACTERIZATION OF SILICA-CHITOSAN AS ADSORBENT AND ADSORPTION EFFICIENCY TO REMOVAL CADMIUM

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Abstract: The removal of heavy metals from the environment is of special concern due to their persistence. In this study explain the ability of adsorbent to attracted Cd ⁺² and the adsorption capacity depends strongly on ratio of adsorbent and concentration of Cadmium ion in the solution. CEC of adsorbent was explain the greater value of Chitosan in adsorbent indicate to the largest of active group on adsorbent. It was also found that the Langmuir equation described very well the experimental adsorption data for metallic ion.

Keywords: Silica-Chitosan, Cadmium, Efficiency, Adsorption.

Introduction

Cadmium is a highly toxic compound and can cause various types of degenerative diseases. Yavuz et al reported that the acute toxicological effects of cadmium poisoning is the emergence of various diseases including hypertension, kidney damage, and damage to red blood cells[1]. Even, Bernard et al , had reported that cadmium is carcinogenic component that causes cancer in humans[2]. Cadmium levels in soils usually range from approximately 0.01 to 1.8 ppm, in natural freshwaters, cadmium sometimes occurs at concentrations of less than 0.1 µg/L. In salt waters with salinities from about 10 to 35 g/kg. The EPA has set a limit of 5 parts of cadmium per billion parts of drinking water (5 ppb or 0.005 mg/L). [3]

Silica is an inorganic adsorbent, tend to polar, and composed of SiO₄ tetrahedral units linked by siloxan (Si-O-Si). Silanol (Si-OH) is a group that determines the surface properties including its adsorption effectiveness. The surface of silica is characterized by reactive hydroxyl groups SiOH, called silanol groups, while its interior is connected by siloxane groups (Si-OSi) . these silanol groups determine the advantages of silica as sorbents.[4]

Chitosan is prepared from chitin by deacetylating its acetamido groups to a different degree. Chitosan can be easily crosslinked by reagents such as glutaraldehyde. As the polymer backbone of chitosan is highly polar, and capable of forming hydrogen bonds with adjacent chains, thus collapsing any low-density structure. To provide a stronger network support that would still allow a chitosan material with a high surface area to be prepared. Chitosan has both hydroxyl and amine groups that can be chemically modified, by reactions such as cross-linking [5]. Chemically modified chitosan has been proved to be highly efficient at removing heavy metal ions from dilute solutions. Because cross-linkers like glutaraldehyde [6], would weaken the adsorption efficiency of chitosan, the insertion of cross-linking agent with functional groups into chitosan is an effective way to get adsorbents with good adsorption capacity. Silica has been proved to be a good material to modify chitosan and improve its adsorption ability for many heavy metals [7][8]. Chitosan is a component polysaccharide family that is composed of several β -(1,4) bonds connected with N-acetyl -2-amino-2-deoxy-D-glucose residues.[9]

The use of adsorbents for adsorption metal ions from waste water takes in single or combined with different adsorbent. The used of polysaccharides-based adsorbent modified with other are more attractive, because it provides many advantages such as the formation of a combination of structure, strength, and chemical properties that enhance characteristics of the adsorbent surface and porosity. [10] Thus it can increase the effectiveness of metal ions extraction. Mortazavi et al published the high effectiveness various metal ions extraction using silica modified with 2-(3-silylpropylimino) methyl phenol [11]. Govindarajan et al, published the effectiveness of cadmium extraction using the mixture of chitosan and CMC (carboxymethyl cellulose) [12]. The effectiveness of solid phase extraction not only specified by adsorbent kinds, but also the initial concentration of metal ions.

EXPERIMENTAL METHODS

Chemicals and reagents

solutions were prepared using distilled water, The materials are CdCO_3 , Silica-Chitosan, Concentrated HNO_3 65%, HCl 37% (Merek), NaOH , Acetic acid 95% (Ajax), , NaCl 1 M. All of the reagents are of analytical-grade.

Apparatus

Metal determinants were made with spectra AAS, flame atomic absorption Spectrophotometer (FAAS) SHIMADZU AA-6200, using air-acetylene flame, digital pH meter (Inolab) , analytical balance, and magnetic stirrer (IKAMAGRH).

Preparation of Silica:

100 g dry rice husk was put in oven at 900° C (4-5 hours), the ash was transferred to beaker and treated by 100 ml HCl 6 M with heat (2 hours), until evaporated solution , neutralized the residual by distilled water until pH 7, heated again at 85° C 1 hour, balanced and kept in desiccator for using.

Preparation of silica-Chitosan

The amount of Chitosan to prepared 0.5, 1.5, 2.5, and 3.5 g, solve by stirring machine in 80 ml acetic acid 2% until change the solution to gel form, mix with silica 9.5, 8.5, 7.5 and 6.5 g, stirring the mixture 12 hours, neutralized the composition with 30 ml NaOH 1 M, decantation the residual and soak in 40 ml gluteraldehyde 0.5 % 24 hours, filter by filtration paper and dry at 105 C, keep adsorbent in desiccator.

Determination of Cation exchange Capacity

Taken 0.100 g Silica chitosan as several ratio (Silica 100%, 95%, 85%, 75% and 65%) into conical flask, and added 10 ml NaCl 1 M, shake 2 hours at 100 rpm, filter and dry in oven 105° C until weight constant, transfer adsorbent to clean conical flask and added 10 ml HCl 0.01 M, shake again 2 hours, filtration and the filtrate titration with NaOH 0.01 M.

Adsorption process

Taken 0.100 g of adsorbent as several ratio (silica 65 % , 75 % ,85% , 95 % and silica 100 %) into conical flasks , and added 10 ml Cd²⁺ solutions of several concentration (5, 10, 15, 20 and 25 ppm)for each conical flask , shake 2 hours by shaker at 100 rpm ,filter the adsorbent by paper filter (Wattman 41), keep the filtrate in the plastic bottle, this procedure was repeated twice. Standard solution and filtrates of the samples measured by AAS at wavelength 228.8 nm.

RESULTS AND DISCUSSION

Characterization of adsorbent

Cation Exchange Capacity

Cation is an ion with a positive electrical charge. CEC is a measure of the Silica-Chitosan capacity to exchange ions. The Silica-Chitosan supplies negative

charges, opposites attract with any element have positive charge. Cations have the ability to be exchanged for another positively charged ion from the surfaces of adsorbent. Another term that is used in conjunction with CEC is base saturation which refers to elements that are basic or alkaline in their reaction. Hydrogen is an element with a positive charge and acts like a cation however Silica-Chitosan with significant saturation of hydrogen is acidic or has a lower pH. It is best to refer to cation exchange capacity rather than Base Exchange.

Results in Table (1) indicated that the reduction of Cd^{2+} adsorbed on silica-chitosan 75% composition was increased with the adsorption Cd^{2+} rate in the solid phase of silica-chitosan 85 % and 65 %. This increasing was based on CEC of solid phase, which showed that ions uptake on the solid phase were constant during the use of solid phase of silica-chitosan 85%-65%.

Table 1 Cation Exchange Capacity for adsorbent Silica:Chitosan

Adsorbent (Silica:Chitosan)	CEC (meq/g)
Silica 100%	0.035
Silica:Chitosan 95%	0.235
Silica:Chitosan 85%	0.550
Silica:Chitosan 75%	0.795
Silica:Chitosan 65%	0.895

Table (1) indicated that greater ratio of chitosan was added into silica-chitosan Therefore, CEC of solid phase increased. This increasing related with additional number of active groups in silica-Chitosan. Chitosan have active groups (-OH) that were functional in the adsorption process. The greater ratio of chitosan into solid phase it increased the number of active groups in the solid phase. The greater number of active groups would increase the mass of adsorbed ions same of exchange ions was increased. The results showed that silica-chitosan with biggest cation exchange capacity have lowest ratio of silica in solid phase. Silanol group at solid phase surface and OH^- group at chitosan were allowing Na^+ ion uptake on the solid phase due to electrostatic interaction with all active groups. Therefore all ions were easily interacted H^+ ion at OH^- group was easily due to its small diameter of Na^+ could replace H^+ in the electrostatic interaction mechanism [13]. This

interaction occurred because Na^+ ion electropositive and OH^- group electronegative.

Characterization by FTIR

Table (2) showed the IR characterization of several compositions from silica-chitosan, some other adsorptions with rather sharp intensity. The adsorption rate at wave number 1095.49 cm^{-1} indicated the presence of asymmetry extended vibration of Si-O function group which developed from siloxan (Si-O-Si).

Table (2). wave number of Function groups of Silica-Chitosan

Function group	Wave number Shown in (Silica-Chitosan) (cm^{-1})				
	100 %	95 %	85 %	75 %	65 %
OH (chitosan or Si-OH)	-	3431.13	3429.20	3413.77	3388.70
Si-O	1095.49	1093.56	1093.56	1093.56	1097.42
Si-O-Si	476.38	474.46	472.53	474.46	468.67
Si-O					
From Si-O-Si	792.69	792.69	790.76	792.69	794.62
C=N	-	1569.95	1573.81	1569.95	1568.02
CH_3	-	1406.01	1409.87	1411.80	1411.80

Si-O function group also absorbed asymmetry extended vibration at wave number 476.11 cm^{-1} . IR results indicated that the hydroxyl groups are responsible for Cadmium adsorbed. Results explaining IR Spectrum of silica-chitosan solid phase contained OH^- group with adsorption tape at the bands unfolded and the stretching of O-H is observed between 3200 and 3650 cm^{-1} . The adsorption of OH^- was uptake at 65 % silica-chitosan, explaining that the possibility of additional OH^- group existed was great because the ratio of chitosan in the solid phase was increased. OH^- group of all adsorbent its very significant group in the adsorption process. The strong sharp peak occurring around 1095.49 cm^{-1} can be ascribed to Si-O-Si functional group asymmetric stretching vibration. Slight shift to the right and an intensity increase of the 792 cm^{-1} peak denoted a conjugation between Si-OH group present on silica surface and Si-OH functional group [14]. Peak around 1411 cm^{-1} is indicative of $-\text{CH}_3$ group while those at 1411

cm⁻¹ are indicative of –CH groups. Peak around 1411 cm⁻¹ is indicative of –CH₃ group while those at 1411 cm⁻¹ are indicative of –CH groups.

The silanol groups are in the form of silicon dioxide structure (–Si–O–Si–OH). This structure is similar to the silanol groups of silicic acid. The peak at 1095 cm⁻¹ is due to Si–O–Si and –C–O–H stretching and –OH deformation. The presence of polar groups on the surface is likely to give considerable cation exchange capacity to the adsorbents. [13]

Adsorption capacity

The capacity of the sorbent is an important factor that determine how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively, for investigation of adsorption isotherm of Cd²⁺ ion, the same volumes of Cd²⁺ ion solution with different concentrations of Cd²⁺ ion were contacted with 0.100 g of sorbent (Silica-Chitosan) in the batch mode. Then the concentration of the remaining Cd²⁺ in the solution was determined by AAS, the adsorption isotherm that is the number of milligram of ion adsorbed per gram of adsorbent.

Table (3) Adsorption capacity of Silica-Chitosan

Adsorbent (Silica: Chitosan)	Adsorption Capacity (mg/g)
100:0	1.95
95:5	2.46
85:15	3.14
75:25	2.81
65:35	9.70

Adsorption efficiency

Figure (1) show the amount of Cd²⁺ adsorbed per unit weight of Silica-Chitosan as a function of Silica-Chitosan dosage and adsorption time. At the end of the experiment, a net adsorption of Cd²⁺ was found to vary from Silica 100% to Silica-Chitosan 65% with an increasing initial mass of Cd²⁺ from 0.5 g to 0.25 g. This adsorption could be attributed to adsorption which depends in this case to chemical interaction instead of electrostatic attraction. The increase of Cd²⁺ solution concentration enhances the interaction between the Cd²⁺ ions in the aqueous phase and the adsorbents. The results indicates the increase of initial mass of Cd²⁺ leading to

an increase to the adsorption of Cd^{2+} on the adsorbents. The increase of initial concentration of Cd^{2+} ions at range 5 to 25 ppm allows a lot of Cd^{2+} ions to contact with silica-chitosan. Adsorption behavior of Cd^{2+} depend on the proportion of chitosan. However, shows that the actual amount of Cd^{2+} adsorbed increases with the increase of initial mass of Cd^{2+} . Higher initial mass of Cd^{2+} resulted in a higher gradient which accelerated the diffusion of the adsorbate from solution into the adsorbent.

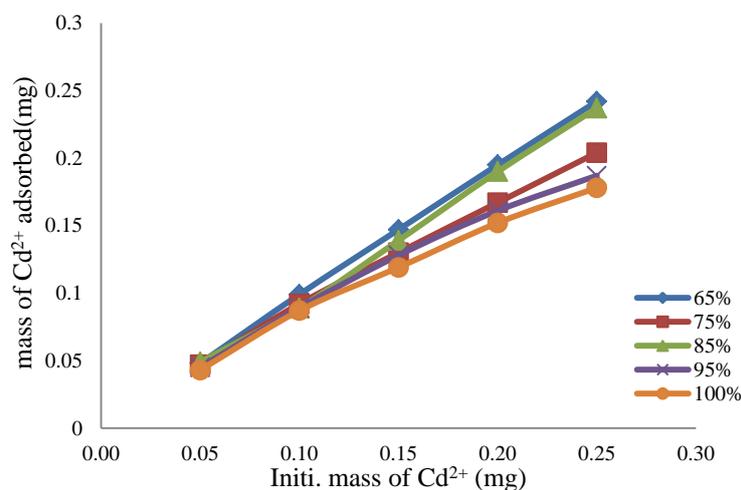


Figure (1) mass of Cd^{2+} adsorbed

In acid solutions $\text{pH} = 5$, amino group on chitosan react with H^+ to producing NH_3^+ group which cannot bonding with Cd^{2+} ions because similar charge (positive charge) on Cadmium and NH_3^+ , (NH_3^+ nonactive in this case). The increase of amount of cadmium ions adsorb with increasing ratio of chitosan in adsorbent, due to the availability of a larger bonding of adsorbent as (-OH) group on surface of dsorbent.

Conclusion

Conditions of adsorption were determined and the most efficient condition for cadmium adsorption was examined at $\text{pH}=5.0$. The adsorption behavior followed the Langmuir adsorption isotherm with adsorption capacity of silica 100% is 1.93 mg/g and a adsorption capacity of silica 65 % is 9.83 mg/g. From the results we observed increase the adsorption capacity with decrease the ratio of chitosan in adsorbent. From the experimental results the adsorption of Cd^{2+} increase with the ratio of chitosan increasing in adsorbent, also the best recovery accrued at 5 ppm of Cd^{2+} concentration , and decrease the recovery with increasing concentration of cadmium solution.

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