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EXPLORATORY STUDY TO ASSESS THE IMPACT OF CHITOSAN /BENTONITE RATIO ON THE METAL REMOVAL CAPACITY OF CHITOSAN MODIFIED BENTONITE CLAY

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ABSTRACT

Adsorption is one of the methods that can be used for metal removal. In this study five metals were used cadmium, chromium, lead, copper and nickel (Cd, Cr, Pb, Cu, and Ni) over a concentration range from 0.8 to about 7 mg l^{-1} for each metal. Adsorbents were prepared with increasing chitosan to bentonite ratio from 0 to 0.67 g chitosan/g bentonite. The study showed that adsorption of metals on plain bentonite and chitosan modified bentonite can fit well with Langmuir and Freundlich adsorption isotherms. Furthermore, the bentonite adsorption capacity will decrease with the increase of chitosan/bentonite ratio. This study concluded that bentonite is a good adsorbent. However, the applicability of bentonite as potential adsorbent may be limited by its physical properties such as slow settling rate and difficulty to use it as an adsorbent in adsorption columns. Despite the decrease of maximum theoretical adsorption capacity as a result of chitosan modification, the addition of small amount of chitosan can improve the physical characteristics of bentonite clay to be used as an adsorbent.

Keywords: Chitosan modified bentonite, Metal removal, Adsorption, water purification.

1. Introduction

The presence of heavy metal in water and wastewater are troublesome, and must be removed from effluent streams before disposal either to receiving water bodies or land. Over the past 20 years, the removal of heavy metals from water has been subjected to many developments and many experimental studies. Some of these studies are applicable and scalable to field applications; however, other applications are still in the experimental stages. There are severalmethods that can be used for removal of trace metals from water such as chemical precipitation, ion exchange, and membrane filtration, coagulation and adsorption. Chemical precipitation is a well-established technique characterized by simplicity, low cost (Ku and Jung, 2001), and ease of control of pH (Huisman *et al.,* 2006). The process involves precipitation of metals in the form of hydroxide or sulfide precipitates (Hosseini and Mirbagheri, 2003; Chen *et al.,* 2009).

Ion exchange process includes the use of either natural or synthetic metal exchangers. The process has high removal efficiency (Kang *et al.*, 2004) and short reaction time (Alyüz and Veli, 2009). Membrane filtration techniques are relatively new techniques which include ultrafiltration, reverse osmosis, electrodialysis, and nanofiltration. The membrane filtration techniques are promising techniques, but the process has some limitations such as high cost, complexity, the impact of influent suspended solids and the possibility of membrane fouling problems.(Barakat, 2011) Previous studies showed that membrane filtration techniques such as reverse osmosis can achieve almost complete metal removal (Kurniawan *et al.*, 2006).

Adsorption is one of the metal removal techniques that started to gain popularity over the last two decades. The main reasons for the popularity of the adsorption techniques are the possibility of preparing low cost bio-adsorbents from agricultural wastes (Sud *et al.*, 2008), availability of natural adsorbents such as clay (Jiang *et al.*, 2010), and the economic benefits of adsorbent regeneration (Barakat, 2011). Many studies have been done on the adsorption of metals on different types of clays such as bentonite (Barkat *et al.*, 2014), Illite (Echeverría *et al.*, 2002), kaolinite (Turan *et al.*, 2007). Despite the significant removal efficiency of bentonite clay, the process may be limited because of poor settling characteristics of adsorbent. This poor settling properties can be overcome by applying relatively long settling time, use of coagulants, or use of advanced filtration techniques such as ultrafiltration (Katsou *et al.*, 2011). The use of a suitable additional process to overcome poor settling characteristics of the clay can be considered as an added complexity to the operation. In other words, this can be considered as an additional cost to the overall process. In this study, chitosan was used to treat bentonite clay to modify its physical properties to be used as an adsorbent either in adsorption column or as added adsorbent followed by plain sedimentation. The impact of chitosan Bentonite ratio on metal adsorption capacity and effeciency using this modified adsorbent was tested in mixed metals solution.

2. Materials and methods

2.1. Preparation of Adsorbents

Adsorbents were prepared by adding different ratios of medium molecular weight chitosan (448877 ALDRICH) to Bentonite clay. The Bentonite used was highly expansive bentonite with a swell index of 20 ml g^{-1}. The Bentonite was obtained from a local supplier (Poudrszan Industrial and Mineral Group, Dubai, United Arab Emirates).

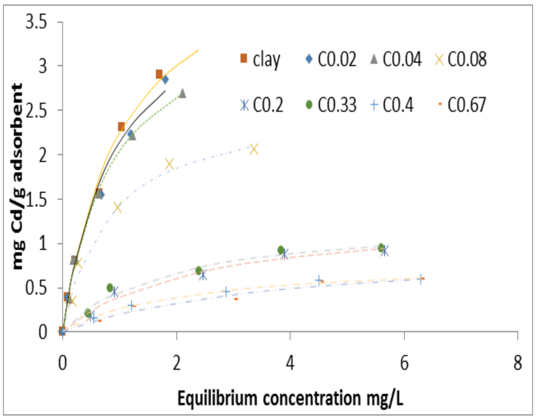
Adsorbents were prepared by dissolving 1 g of chitosan in 1% acetic acid. Hence, the dissolved chitosan was added to a specified weight of bentonite clay which was previously suspended in 0.5 liters of distilled water. The pH of the resulting chitosan clay mixture was adjusted to 7, and the mixture was agitated for 24 hours. After completion of agitation, the mixture was allowed to settle. Afterward, the supernatant was discarded. The resulting precipitate was washed with deionized water many times. After washing, the precipitate was filtered and dried at 60 °C for 24 hours. The resulting adsorbent was ground to a size range of 150 to 75 µm. The prepared adsorbents were stored in the desiccator for the batch adsorption experiment. In this study 8 adsorbents were used with chitosan/clay ratios of 0, 0.02, 0.04, 0.08, 0.2, 0.3, 0.4, and 0.67 g chitosan/g clay.

2.2. Batch adsorption experiment

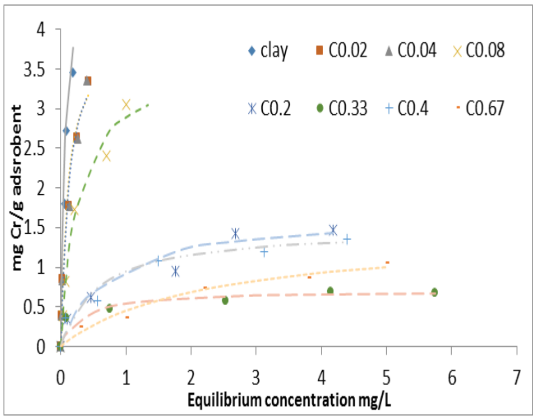
The experiment was conducted by agitating 50 ml of mixed metal solutions containing Cd, Cr, Pb, Cu, and Ni with different initial concentrations (0.8 to 8 mg l^{-1} of each metal) with chitosan clay adsorbents for 3 hours (Gupta and Bhattacharyya, 2006; Sen Gupta and Bhattacharyya, 2008). The pH of the different sollutions was controlled to be at 6 using either 0.1 M HCl or 0.1M NaCl. After 3 hours the flasks were allowed to settle for 30 minutes, and the supernatant was taken for the metal determination using inductivity coupled plasma optical emission spectrometry (Varian Vista MPX Simultaneous ICP-OES). Control samples that were treated with plain bentonite clay were centrifuged for 4 minutes at 300 rpm before measurements.

3. Results and discussions

The adsorption isotherms of the eight adsorbents for the five metals tested in this study cadmium, chromium, lead, copper, and nickel, are shown in Figures 1a, 1b, 1c, 1d, and 1e respectively.



(a)



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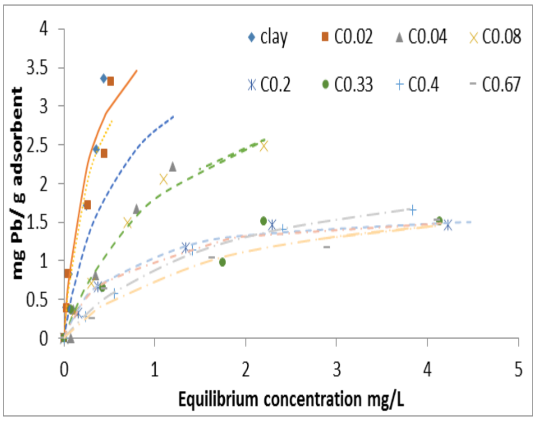

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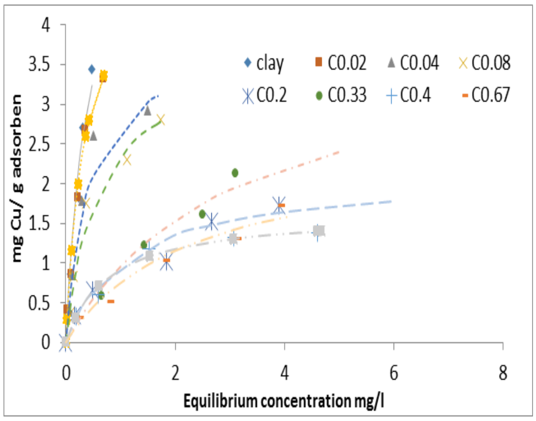

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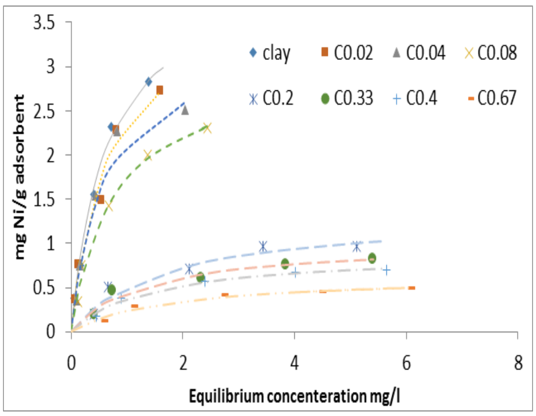

(e)

Figure 1. Adsorption isotherm of the prepared modified bentonite for different metals (a) cadmium, (b) Chromium, (c) Lead, (d) copper and (e) Nickel.

The results revealed that there is a decrease in adsorption capacity as the ratio of chitosan to clay is increased. It was found that metals adsorption results were fitted using Langmuir and Freundlich isotherms (equations 1 and 2) respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (1)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Where Qe = equilibrium adsorption capacity (mg adsorbate/g adsorbent); Qm = theoretical maximum adsorption capacity (mg g^{-1}); KL = Langmuir equation constant (l mg^{-1}); Ce = remaining concentration of adsorbate in solution at equilibrium (mg l^{-1}), K_f is Freundlich constant related to adsorption capacity, and n is Freundlich constant related to adsorption intensity (Freundlich, 1906; Langmuir, 1918; Weber Jr; 1985).

Parameters of both Langmuir and Freundlich models are presented in Table 1 and 2 respectively. R^2 values for both models showed that adsorption of metals on bentonite and chitosan modified bentonite can fit well with both models where the R^2 value was above 0.9 in most experimental runs. Previous studies on bentonite adsorption found that adsorption can fit well with either Langmuir adsorption isotherm (Talaat *et al.,* 2011) or with both models (Jiang *et al.,* 2010; Zhang *et al.,* 2011; Barkat *et al.,* 2014).

Table 1. Impact of chitosan bentonite ratio in the range of 0 to 0.67 g chitosan to g clay on the parameters of the Langmuir adsorption isotherms

Ct/B	Cd			Cr			Pb			Cu			Ni		
ratio	Q_m	K_i	R^2	Q_m	K_i	R^2	Q_m	K_i	R^2	Q_m	K_i	R^2	Q_m	K_i	R^2
0.00	4.60	0.96	0.97	5.22	10.52	0.95	4.70	3.49	0.77	5.43	3.32	0.94	4.11	1.60	0.96
0.02	4.11	1.09	0.98	3.98	9.45	0.97	4.44	3.30	0.81	4.94	2.94	0.89	3.80	1.57	0.96
0.04	3.79	1.16	0.98	4.09	8.15	0.95	4.32	1.63	0.91	3.91	2.28	0.94	3.33	1.71	0.96
0.08	2.63	1.19	0.99	3.62	3.94	0.98	4.00	0.70	1.00	3.73	1.67	0.95	3.04	1.33	0.97
0.20	1.34	0.42	0.95	1.67	1.41	0.94	1.70	1.77	0.99	2.12	0.85	0.92	1.33	0.59	0.94
0.33	1.28	0.54	0.97	0.71	3.36	0.99	1.70	1.64	0.94	3.84	0.33	0.98	1.02	0.74	0.98
0.40	0.82	0.46	0.99	1.48	1.76	0.98	2.43	0.58	1.00	1.63	1.29	0.99	0.90	0.68	0.99
0.67	0.97	0.26	0.90	1.44	0.45	0.90	2.05	0.59	1.00	2.48	0.44	1.00	0.65	0.56	0.98

Table 2. Impact of chitosan bentonite ratio in the range of 0 to 0.67 g chitosan to g clay on the parameters of the Freundlich adsorption isotherms

Ct/B	Cd			Cr			Pb			Cu			Ni		
ratio	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2
0.00	2.14	0.68	0.98	12.55	0.69	0.98	4.94	0.65	0.98	5.78	0.6723	0.99	2.55	0.64	0.98
0.02	2.00	0.64	0.97	5.52	0.54	0.97	4.41	0.64	0.95	4.44	0.62	0.98	2.29	0.63	0.96
0.04	1.90	0.63	0.96	5.57	0.56	0.99	2.81	0.66	0.93	3.07	0.66	0.88	2.10	0.63	0.90
0.08	1.25	0.56	0.92	3.24	0.56	0.96	1.99	0.83	0.98	2.29	0.61	0.89	1.58	0.59	0.92
0.20	0.37	0.61	0.91	0.85	0.39	0.88	0.91	0.46	0.93	1.15	0.50	0.98	2.22	0.56	0.86
0.33	2.41	0.55	0.90	0.51	0.16	0.98	0.92	0.38	0.96	0.90	0.70	0.97	2.51	0.48	0.88
0.40	0.24	0.54	0.97	0.82	0.34	0.96	0.79	0.64	0.98	1.28	0.46	0.95	2.44	0.72	0.92
0.67	5.15	0.65	0.93	0.43	0.53	0.96	0.70	0.58	0.98	0.71	0.59	0.98	2.44	0.72	0.90

The adsorption of metals on clay was in the order Cu>Cr>Pb>Cd>Ni according to Langmuir adsorption model, and Cr> Cu> Pb> Cd ≈ Ni according to Freundlich adsorption model. The maximum theoretical adsorption capacity (Qm) values for each metal showed a significant declining trend with the increase of chitosan to bentonite ratio. Similarly, Kf showed the same trend of decline with the increase of chitosan to bentonite ratio. Qm and Kf values are used to reflect the adsorption capacity in Langmuir and Freundlich isotherm respectively. It was found that increasing the chitosan to bentonite ratio from 0 to 0.67 g chitosan / g bentonite resulted in the reduction of the maximum adsorption capacity (Qm) from

4.6 to 0.97 mg g^{-1} for cadmium, 5.22 to 1.44 mg g^{-1} for chromium, 4.7 to 2.05 mg g^{-1} for lead, 5.4 to 2.48 mg g^{-1} for copper, and 4.11 to 0.65 mg g^{-1} for nickel. These findings imply that bentonite alone is a good adsorbent at the bench scale level. However, its applicability on a large scale may be limited because of settling properties and its particle size. The findings of this study suggest the addition of small concentration of chitosan in a ratio of 0.02 g chitosan /g of clay to improve the settling characteristics as well as the particle size of the bentonite clay. The modified chitosan/bentonite clay can be either used by direct addition to water and wastewater containing metals, or in continuous flow adsorption column.In case of direct additon of the adsorbent there should be a setling tank to separate the settled adsorbent after the compeletion of metal remoal process.These suggestions should be studied more deeply in terms of optimum operating contitions. Use of chitosan modified clay at the smallest chitosan ratio (0.02) will not significantly impact the predicted Q_m i.e. the overall metal removal efficiency. The predicted decline in the value of maximum adsorption concentration as a result of adding 0.02 gm chitosan/gm of bentonite will be 11, 24, 5.5, 15 and 7 % for Cd, Cr, Pb, Cu, and Ni respectively. The main purpose of adding this small ratio of chitosan to bentonite clay (0.02 gm chitosan/gm bentonite) is to improve the solid-liquid separation characteristics of bentonite. This benefit can outweigh the insignificant decline in the metal removal efficiency associated with chitosan addition. Previous studies showed that bentonite is a good adsorbent, either modified or in its natural form. This implies that bentonite would be preferred as the future adsorbent because of its abundance, low cost and its adsorption capabilities which can pave the way for bentonite clays as an alternative to activated carbon. On the other hand, the physical properties of bentonite such as swelling characteristics and its permeability can limit its applicability as an adsorbent in its natural form (Zwain *et al.*, 2014). the finding of this study can serve as a base for preparing a low cost adsorbent with relatively similar advantages of the plain bentonite in addition to an improved physical properties that can expand the bentonite applicability for metals removal . The results obtained in this study is in agreement with the findings of many studies that have reported the ability of bentonite to remove heavy metals (Alvarez-Ayuso and Garćia-Śanchez, 2003; Bereket *et al.,* 1997; Fu & Wang, 2011; Lin and Juang, 2002). Talaat *et al.,* (2011), evaluated the use of different type of Egyptian clay in the form of kaolin, calcium bentonite and sodium bentonite for the removal of 5 metals as Ni, Cd, Cu, Zn, and Pb. The study showed that the three types of clays have the ability to remove heavy metals. Calcium bentonite showed the highest adsorption capacity for the tested metals. The study showed that the metals adsorbed were in the order of Pb>Cr>Cd>Cu>Zn>Ni (Talaat *et al.,* 2011) however the current study showed a difference in metal adsorption order as follow Cr> Cu> Pb> Cd ≈ Ni. There are many factors that can impact the adsorption order. One of these factors might be the working pH of the batch adsorption experiment. In addition to that, the initial metal concentration applied in the experiment may impact the metal adsorption order. Additional study will be conducted to assess the impact of operating conditions such as initial metal concentration on the metal adsorption order.

It is well known that chitosan is soluble at low pH values of less than 6 (Qin *et al.*, 2006), accordingly low pH values may be detrimental to the modified chitosan bentonite adsorbent. Therefore, it is important to use the modified chitosan bentonite absorbents under relatively elevated pH equal or more than 6. Fortunately, previous studies suggest that the adsorption of heavy metals is pH dependent where the efficiency of removal increases with the pH increase. In a study conducted on the adsorption of Cr and Cd onto natural bentonite, it was found that the adsorption of Cr enhanced from 2.3 mg g^{-1} at pH 0.5 to 5.1 mg g^{-1} at pH 6. Similarly, the Adsorption of Cd onto bentonite increased from 6.34 at pH of 0.5 to 14.97 mg g^{-1} at pH of 6 (Barkat *et al.*, 2014).This explains why the current study was conducted at pH 6 as this enables to get the advantage of increased efficiency at relatively elevated pH (pH= 6) while maintaining the consistency of chitosan bentonite adsorbent.

Other studies showed that chitosan alone has the ability to remove heavy metals from water and wastewater(Gerente *et al.*, 2007). Accordingly, the main hypothesis of this study was to investigate the efficiency of chitosan and bentonite clay together. The authors expected to have a higher removal efficiency when chitosan is used for modifications of the bentonite clay. The obtained results of this study indicated that mixing chitosan with bentonite clay at high chitosan/bentonite ratio may be detrimental to the overall removal efficiency of heavy metals. On the other hand, keeping bentonite clay as an adsorbent is limited because of the poor settling characteristics. Accordingly, the main advantage of chitosan addition to bentonite clay is to modify the physical properties of the bentonite clay which in turn will enhance the separation of the adsorbent from the treated effluent. Based on this study, the addition of chitosan should be in small ratios of about 0.02 g chitosan to 1 g of bentonite clay.

4. Conclusions

It can be concluded as the chitosan bentonite ratio increases the metal removal capacity of the modified chitosan bentonite clay will decrease. Accordingly, the use of small amount of chitosan as a modifier to bentonite clay can improve its solid separation characteristics and can help producing good adsorbent that can be used in field applications. The advantage of using small amounts of chitosan to the bentonite for the purpose of modifying its physical characteristics can outweigh the decreased efficiency compared to the unmodified bentonite clay.

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