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

ELSERGANY M.[1], SHANABLEH A.[2] and AHSAN A.[3]

[1]School of Health and Environmental studies, Hamdan Bin Mohammed Smart University, Dubai, United Arab Emirates,[2] Department of Civil and Environmental Engineering, University of Sharjah, United Arab Emirate,[3]Dept. of Civil Engineering, and Institute of Advanced Technology, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
E-mail: Moetaz Elsergany: m.elsergany@hbmsu.ac.ae

ABSTRACT

Adsorption is one of the methods that can be used for metal removal. In this study 5 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 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 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

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 scalable to field applications however, other applications are still in the experimental stages. There are a large number of methods that can be used for removal of trace metals from waters such as chemical precipitation, ion exchange, and membrane filtration, coagulation and adsorption. Chemical precipitation is a well-established techniques characterized by simplicity, low cost (Ku & Jung, 2001), and ease of control of pH (Huisman, Schouten, & Schultz, 2006). The process involves precipitation of metals in the form of hydroxide or sulphide precipitaties(Hosseini & Mirbagheri, 2003) (Chen, Luo, Hills, Xue, & Tyrer, 2009).

Ion exchange process includes the use of either natural or synthetic metal exchangers. The process has high removal efficiency(Kang, Lee, Moon, & Kim, 2004) and short reaction time(Alyüz & Veli, 2009). Membrane filtration techniques are relatively new techniques which include ultrafiltration, reverse osmosis, electro dialysis and nanofiltration. The membrane filtration techniques are promising techniques but the process has limited to its high cost, complexity, impact of influent suspended solids and of membrane fouling problems.(Barakat, 2011) Previous studies showed that membrane filtration techniques such as reverse osmosis can achieve almost complete metal removal(Kurniawan, Chan, Lo, & Babel, 2006)

Adsorption is one of the metal removal techniques that started to gain popularity over the last two decades. The main reason for being popular technique for removal of metal from aqueous solutions are the possibility of preparing law cost bio-adsorbents from agricultural wastes (Sud, Mahajan, & Kaur, 2008), availability of natural adsorbents such as clay (Jiang, Jin, Lu, & Chen, 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, Churio, & Garrido, 2002), kaolinite (Turan, Doğan, & Alkan, 2007). Despite of good removal efficiency of bentonite clay, the process may be limited because of poor settling characteristics of bentonite clay. This can be overcome by applying relatively long settling time, addition of coagulates, or use of advanced filtration techniques such as ultrafiltration (Katsou, Malamis, & Haralambous, 2011). The use of additional process to overcome poor settling characteristics of clay can be considered as an added complexity or 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 new modified adsorbent was tested as an adsorbent for metals in mixed metals solution. Furthermore, the impact of chitosan/bentonite ratio on clay adsorption capacity was studied.

2. Material and methods

2.1. Preparation of adsorbent

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. It was obtained from a local supplier (Poudrszan Industrial and Mineral Group, Dubai, United Arab Emirates).

Adsorbents were prepared by dissolving 1 gm of chitosan in 1% acetic acid, hence the dissolved chitosan was added to a specified weigh of bentonite clay which was previously suspended in 0.5 liter 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 and supernatant were discarded. The resulting precipitate was washed with deionized water many times. The resulting precipitate was filtered and dried at 60 ^{O}C for 24 hours. The resulting adsorbent was ground to size of 150 to 75 µm and stored in 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 mls of mixed metal solutions containing Cd, Cr, Pb, Cu, and Ni with different initial concentrations (0.8 to 8 mg/l of each metal) with chitosan clay adsorbents for 3 hours (Gupta & Bhattacharyya, 2006; Sen Gupta & Bhattacharyya, 2008). After 3 hours the flasks were allowed to settle for 30 minutes and the supernatant were taken for metal determination using inductivity coupled plasma technique (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 8 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. The results showed that there is a decrease in adsorption capacity as the ratio of chitosan to clay increased. It was found that metals adsorption results were fitted using Langmuir and Freundlich isotherms (equations 1 and 2) respectively.

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

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

Where Qe = equilibrium adsorption capacity (mg adsorbate/g adsorbent); Qm = theoretical maximum adsorption capacity (mg/g); KL = Langmuir equation constant (l/mg);Ce = remaining concentration of adsorbate in solution at equilibrium (mg/L) , Kf is Freundlich constant related to adsorption capacity, and n is Freundlich constant related to adsorption intensity(Talaat *et al*., 2011).

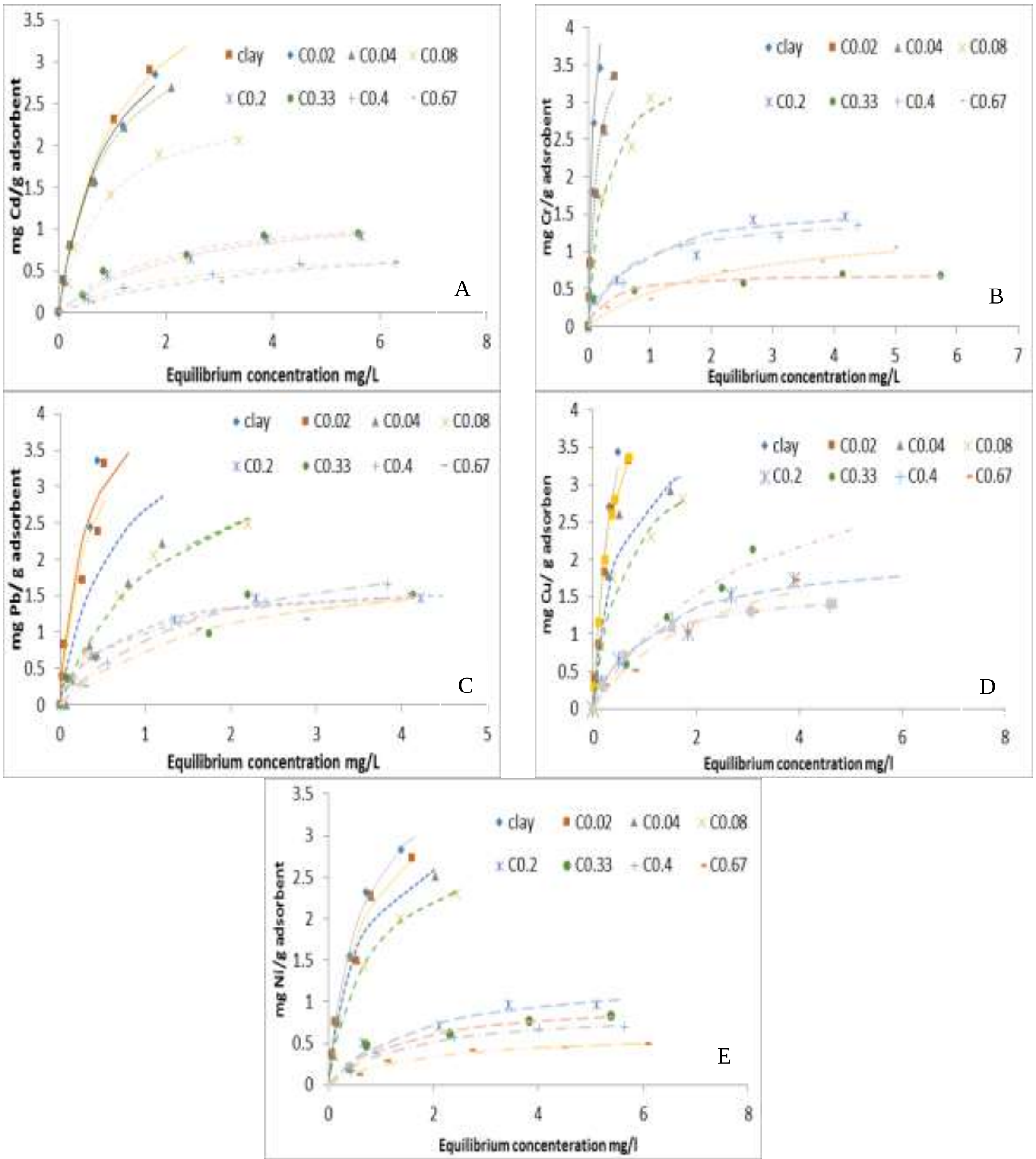

Figure 1: Adsorption isotherm of the prepared modified bentonite for different metals (a) cadmium, (b) Chromium,(c)Lead, (d)cupper and (e) Nickel.

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 on the parameters of the Langmuir adsorption isotherms.

Ct / B ratio	Cd			Cr			Pb			Cu			Ni		
	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 3: Impact of chitosan bentonite ratio on the parameters of the Langmuir adsorption isotherms.

Ct / B ratio	Cd			Cr			Pb			Cu			Ni		
	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 reduced the maximum adsorption capacity (Qm) from 4.6 to 0.97 mg /g for cadmium, 5.22 to 1.44 mg/g for chromium, 4.7 to 2.05 mg/g for lead, 5.4 to 2.48 gm/g for copper, and 4.11 to 0.65 mg/g for nickel. These findings imply that bentonite alone is a good adsorbent at the bench scale, however its applicability on a large scale may be limited because of settling properties and its particle size. The findings of this study suggest 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 particle size of the bentonite clay. The modified chitosan can be either used by direct addition to metal containing wastes, or in continuous flow adsorption column. 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 small ratio of chitosan to bentonite clay (0.02 gm chitosan/gm bentonite) is to improve solid liquid separation characteristics of bentonite. This benefit can outweigh the insignificant decline in the metal removal efficiency inherited with chitosan addition. Previous studies showed that bentonite is a good adsorbent, either modified or in its natural state, which 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). This necessitate the use of artificial modification of this bentonite clays to be suitable for use either in column adsorption, or even by direct addition followed by plain sedimentation or filtration.

4. Conclusions

It can be concluded that 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.

REFERENCES

1. Alyüz, B., & Veli, S. (2009), Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. Journal of hazardous materials, 167(1), 482-488.
2. Barakat, M. A. (2011), New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry, 4(4), 361-377.
3. Barkat, M., Chegrouche, S., Mellah, A., Bensmain, B., Nibou, D., & Boufatit, M. (2014), Application of Algerian Bentonite in the Removal of Cadmium (II) and Chromium (VI) from Aqueous Solutions. Journal of Surface Engineered Materials and Advanced Technology, 2014.
4. Chen, Q., Luo, Z., Hills, C., Xue, G., & Tyrer, M. (2009), Precipitation of heavy metals from wastewater using simulated flue gas: Sequent additions of fly ash, lime and carbon dioxide. Water Research, 43(10), 2605-2614.
5. Echeverría, J. C., Churio, E., & Garrido, J. J. (2002), Retention mechanisms of Cd on illite. Clays and Clay Minerals, 50(5), 614-623.
6. Gupta, S. S., & Bhattacharyya, K. G. (2006), Adsorption of Ni(II) on clays. Journal of colloid and interface science, 295(1), 21-32.
7. Hosseini, S., & Mirbagheri, S. (2003), Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. Int. J. Environ. A, 28, 369-374.
8. Huisman, J. L., Schouten, G., & Schultz, C. (2006), Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy, 83(1), 106-113.
9. Jiang, M.-q., Jin, X.-y., Lu, X.-Q., & Chen, Z.-l. (2010), Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. Desalination, 252(1), 33-39.
10. Kang, S.-Y., Lee, J.-U., Moon, S.-H., & Kim, K.-W. (2004), Competitive adsorption characteristics of Co2+, Ni2+, and Cr3+ by IRN-77 cation exchange resin in synthesized wastewater. Chemosphere, 56(2), 141-147.
11. Katsou, E., Malamis, S., & Haralambous, K. J. (2011), Industrial wastewater pre-treatment for heavy metal reduction by employing a sorbent-assisted ultrafiltration system. Chemosphere, 82(4), 557-564.
12. Ku, Y., & Jung, I.-L. (2001), Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Research, 35(1), 135-142.
13. Kurniawan, T. A., Chan, G. Y. S., Lo, W.-h., & Babel, S. (2006), Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Science of The Total Environment, 366(2–3), 409-426.
14. Sen Gupta, S., & Bhattacharyya, K. G. (2008), Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. Journal of Environmental Management, 87(1), 46-58.
15. Sud, D., Mahajan, G., & Kaur, M. P. (2008), Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. Bioresource Technology, 99(14), 6017-6027.
16. Turan, P., Doğan, M., & Alkan, M. (2007), Uptake of trivalent chromium ions from aqueous solutions using kaolinite. Journal of hazardous materials, 148(1-2), 56-63.