VNU Journal of Science, Earth Sciences 28 (2012) 37-43

Research on chromium removal in water by modified bentonite

Tran Van Son*, Tran Van Quy

Faculty of Environmental Sciences, VNU University of Science, 334 Nguyen Trai, Hanoi, Vietnam

Received 25 November 2011; received in revised form 26 December 2011

Abstract. This research was conducted to produce a new natural derivated material (bentonite), which can remove chromium from aquatic environment. Natural bentonite was activated by HCl acid, then by thermal factor at 110^0C. Results of SEM images show that spongy and surface area of modified bentonite larger than natural bentonite. Chromium adsorption ability on modified bentonite depends on pH of solution, and adsorption capacity is almost stable in the pH range from 3 to 6, then dramatically reduced from pH 6-11. Maximum chromium adsorption capacity of modified bentonite - B90at-2 (13,89 mgCr/g) was much more than natural bentonite - B90 (3,32 mgCr/g). The modified bentonite can be used for waste water treatment with high concentration of chromium (140 mg/L) meet the vietnamese standard (QCVN 24:2009/BTNMT, B column).

Keywords: Modified Bentonite, montmorillonit, chromium, acid, adsorption.

1. Introduction

Industries such as: electroplating, tanning, dyeing, ink… not only contribute much to the development of socio-economic, but also cause many risks on the environment. Waste water from these processes, including heavy metal irons (Cr, Ni, Zn, Cu...) in general and chromium in particular, has a lot of influence on the environment and negative effects on human health.

In each case, chromium treatment process from aquatic environment can apply some methods: oxidation – reduction, neutralization – precipitation, electrochemistry, biology, ion exchange, adsorption … Each method has its own advantages and disadvantages. However, the method using adsorbent material for chromium removal gives high efficiency and low cost. [1,2]

Bentonite is a type of clay minerals of smectit group, includes montmorillonit (MMT) with general formula $Al_2O_3.4SiO_2.nH_2O$ and some other clay minerals: saponit $Al_2O_3.[MgO].4SiO_2.nH_2O$; nontronit - $Al_2O_3.[Fe_2O_3]4SiO_2.nH_2O$, etc. This bentonite is a abundant and cheap source in Viet Nam. [3]

The research on manufacturing modified bentonite, having high ability on chromium treatment in aquatic environment, has theoretical and practical benefits in finding out new material for waste water treatment.

* Corresponding author. Tel: 84-987483211.
E-mail: transon_mt@hus.edu.vn

2. Materials and methods

2.1. Materials

- Bentonite (Ben) from Nha Me mine, Phong Phu commune, Tuy Phong district, Binh Thuan province has been refined to 90% MMT content (by weight); [4]

- Solutions $K_2Cr_2O_7$ containing different chromium concentrations;

- Sample of waste water containing chromium (140 mg/L) from plating sector of machine parts Joint stock Company No.1, Mo Che ward, Song Cong town, Thai Nguyen province.

2.2. Methods

In this research, using several methods such as: data collecting and processing method; material manufacturing method; analytical method by X-ray and scanning electron microscope (SEM) method to define properties of the material; chromium concentration analysis method by atomic adsorption spectrometer (AAS-6800 of SHIMADZU).

a) Manufacturing modified bentonite

Ben 90% MMT was modified by HCl (B90-ax), with acid concentrations (xM) were 0,5; 1; 2 and 5M, respectively. Then, it was burn at 110^0C as the protocol following figure 1.

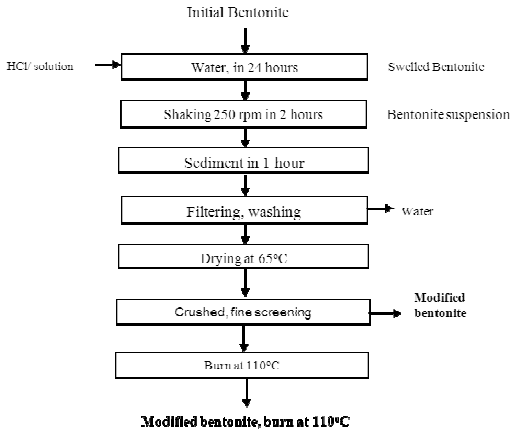

Figure 1. Steps of manufacturing modified bentonite.

b) Defining chromium adsorption ability of modified bentonite

+ Equilibrium time of adsorption

Experimental conditions: 10 mg/L chromium concentration, adsorber 0,1 g/100ml, stirring rate 250 rpm at 25^0C. Stirring time from 0 - 360 minutes.

Sampling after 5, 10, 15, 30, 60, 120, 180, 240, 300, 360 minutes, then filtered through blue filter paper and analysed remain chromium concentration in samples.

+ Effects of pH to chromium adsorption process on modified bentonite

The experiment was conducted at pH from 3 to 11, chromium concentration 10 mg/L, adsorber 0,1 g/100 mL, stirring rate 250 rpm with suitable time was defined at the previous experiment, at 25^0C. Analysed remain chromium concentration in samples.

+ Adsorption capacity, Langmuir isotherm of chromium adsorption on modified bentonite

Pipetting 500ml $K_2Cr_2O_7$ solution with different choromium concentrations 1 - 100

mg/L, add 1 g modified Ben. Continuously shaking with 250 rpm rate in suitable period time and pH (defined at previous experiments), at 25^0C.

Samples were filtered through blue filter paper, then analysed chromium concentration.

+ Treating ability of modified Ben with actual waste water containing chromium

The experiment was conducted with follow conditions: chromium in waste water is 140mg/L, adsorber 8g/750ml, stirring rate 250 rpm at 25^0C. Stirring time varied from 0 to 360 minutes.

Sampling after: 5, 10, 15, 30, 60, 120, 180, 240, 300, 360 minutes, then samples were filtered through blue filter paper and analysed remain chromium concentration.

3. Results and discussion

3.1. Properties of the materials

a) SEM images of the materials

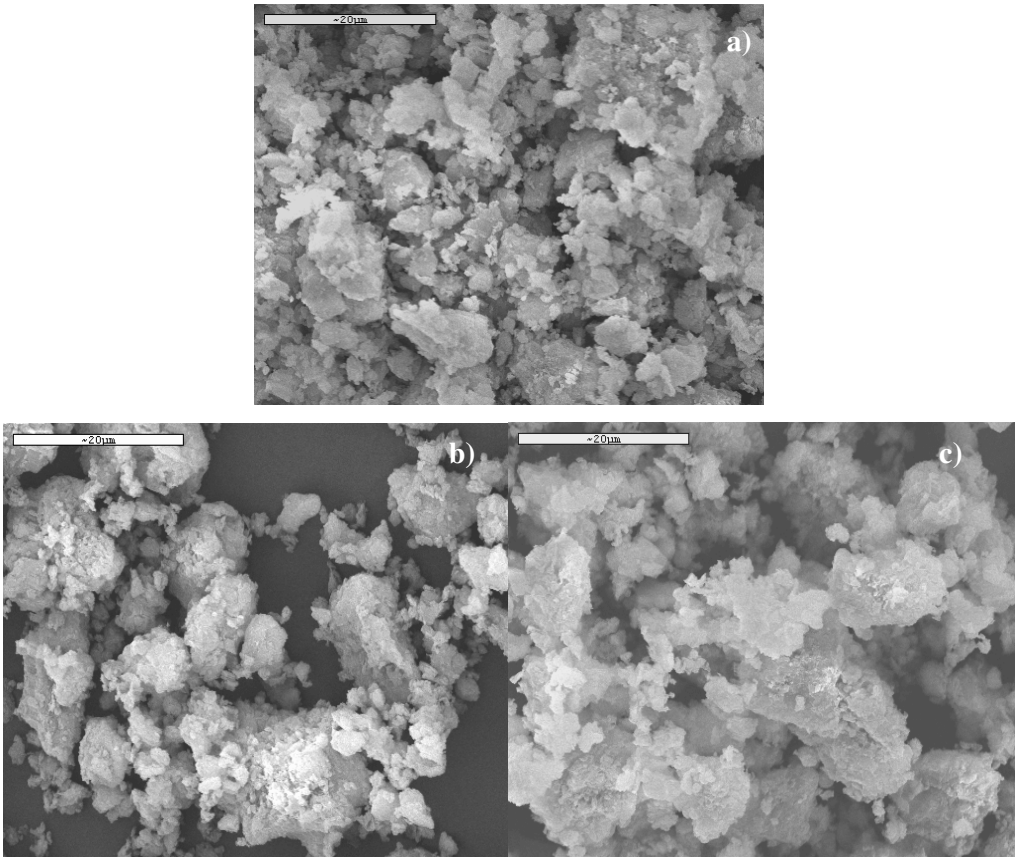

Figure 2. SEM images of the materials (x2500) magnification.

a) Ben90 - initial bentonite; b) B90a-2 - bentonite was modified by HCl 2M; c) B90at-2 - bentonite was modified by HCl 2M, then burn at 110^0C

Figure 2 shows that, modified Ben is finer and better dispersion than initial Ben (Ben90). So, by the acid modified process, H^+ ions could have been added into structure of Ben and replaced ions Na^+, K^+, Ca^{2+}…, as well as dissolved binders and separated particles, increasing the fineness of modified Ben. When Ben was modified by acid then burn at 110^0C, it has more porous, finer than when modified by acid only.

b) X-ray results of the material

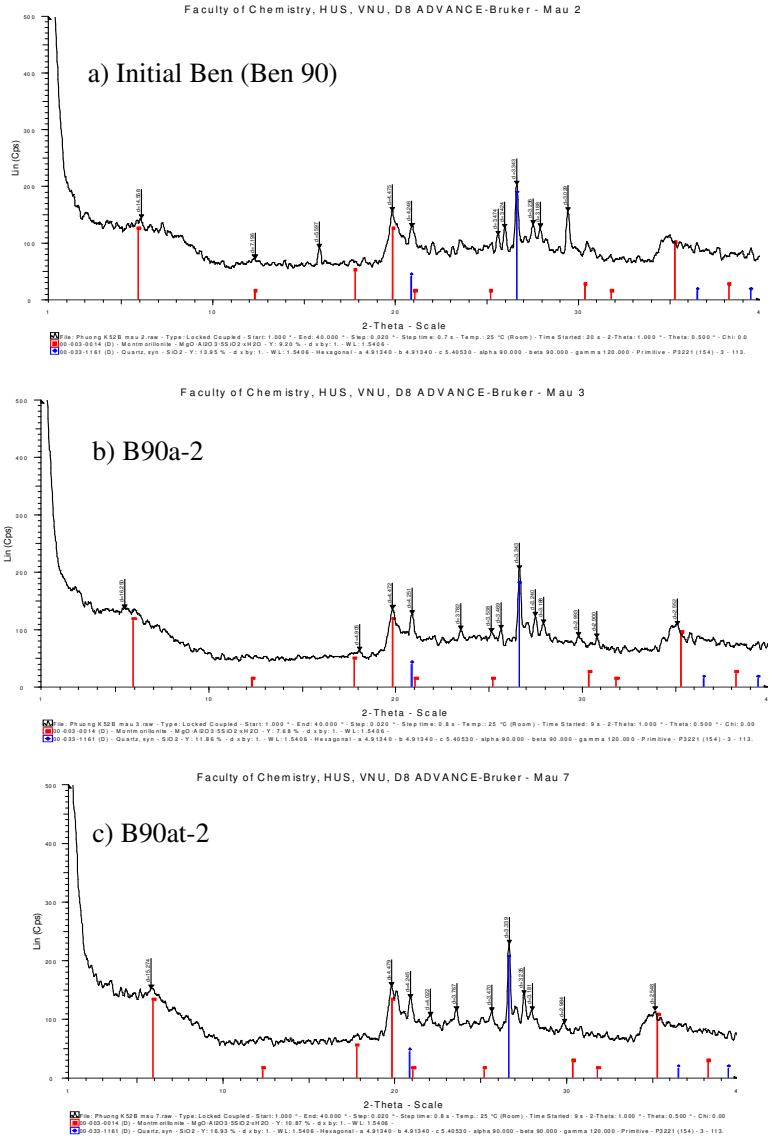

Figure 3. X-ray results of B90, B90a-2, B90at-2.

a) Ben90 - initial bentonite; b) B90a-2 - bentonite was modified by HCl 2M;
c) B90at-2 - bentonite was modified by HCl 2M, then burn at 110^0C

X-ray results show that there was a few change of distance between layers (d001 from 14,558 to 16,25 Å) after bentonite was modified.

3.2. Effects of time to chromium adsorption ability of the material

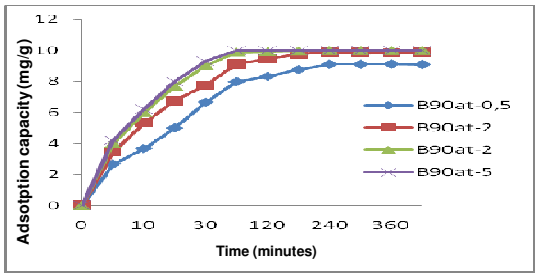

Figure 4. Effects of time to chromium adsorption ability of modified bentonite.

Figure 4 illustrates that, similarity to modified Ben samples at room temperature, modified Ben samples at 110^0C adsorbed chromium fastest in the first 60 minutes and then gradually decreased and reached equilibrium adsorption after 240 minutes.

3.3. Effects of pH to chromium adsorption ability of modified bentonite

Adsorption capacity is almost stable in the pH range from 3 to 6 (adsorption capacity of B90at-2 and B90a-2 at pH 3 were 5.51 and 4.33 mg/g, respectively), then dramatically reduced when pH at 6. When the pH from 7 to 11, adsorption ability slightly decreased (adsorption capacity of B90at-2 and B90a-2 at pH 11 were 3.49 and 2.78 mg/g, respectively). The effects of pH can be explained as follows: at high pH, surface of adsorption materials are negatively charged and thus promote more interaction between the negatively charged ions in the solution. On the other hand, the high pH, OH^- ion concentration is relatively high, lead to competitive adsorption between OH^- ion and the anion of chromium in the solution. [5,6]

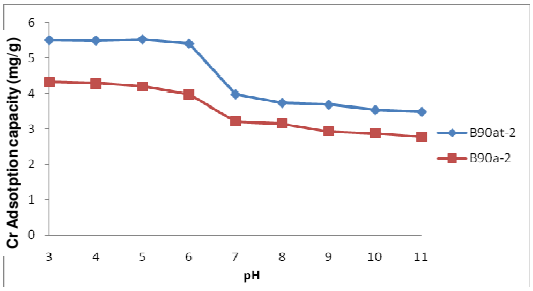

Figure 5. Effects of pH to chromium adsorption capacity on modified Ben.

3.4. Langmuir isotherm of chromium adsorption on modified bentonite

Langmuir isotherm equation was applied for chromium adsorption process on initial and modified Ben:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L . Q_{max}} \quad *$$

Where: Q_e - equilibrium adsorption capacity (mg/g); C_e - chromium concentration at equilibrium (mgCr/L); Q_{max} - maxium adsorption capacity (mg/g); K_L - Langmuir constant.

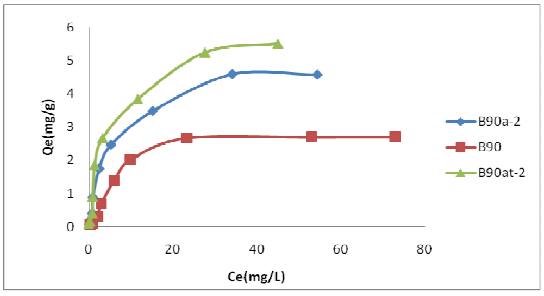

Figure 6. Langmuir isotherm chromium adsorption on initial and modified Ben

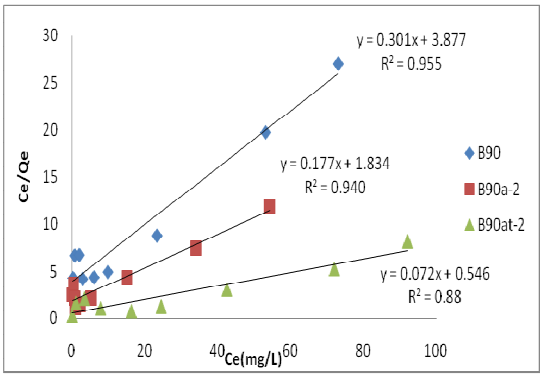

Figure 7. Linear form of Langmuir isotherm of chromium adsorption on initial and modified Ben.

Table 1. Parameters of chromium adsorption process on initial and modified Ben

Sample	Qmax (mg/g)	Constant K_L	R^2
B90	3.32	0.78	0.96
B90a-2	5.65	0.10	0.94
B90at-2	13.89	0.13	0.88

Maxium adsorption capacity of B90at-2 (13.89 mg/g) was the highest, B90 (3.32 mg/g) was the lowest. These results proved that chromium adsorption ability was much higher when Ben was modified. On the other hand, it could be seen that Ben was modified by acid then burn at 110^0C has higher adsorption ability than was only modified by acid (Q_{max} of B90a-2 and B90at-2 were 5.65 and 13.89 mg/g, respectively.

3.5. Results of treating on actual waste water

Figure 8 demonstates that, in the first 60 minutes period, chromium adsorption rate from waste water of plated process of B90at-2 was the highest, then gradually decreased and reached adsorption equilibrium at 240 minutes. After 240 minutes, chromium concentration from 140 mg/L (initial) decreased to 0.09 mg/L.

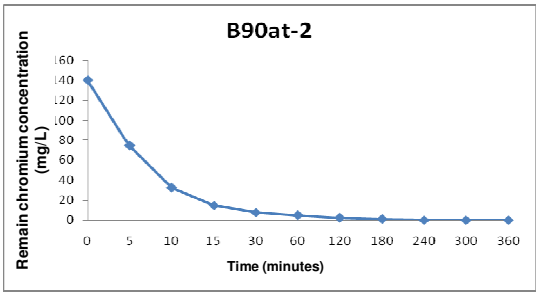

Figure 8. Remain chromium concentration after treated by Ben90at-2 through time.

Compare with QCVN 24:2009/BTNMT, B90at-2 can treat waste water containing chromium meet standard, B column.

4. Conclusion

Has created modified Ben by HCl which has good ability of chromium removal in aquatic environment. Results of SEM images show that, modified Ben is finer and better dispersion than initial Ben; particles size of modified bentonite also smaller than initial Ben. When bentonite was modified by acid then burn at 110^0C, it has more porous, finer than when only modified by acid.

The ability of chromium adsorption on modified Ben depends on the pH of solution, at pH 3 - 6 it was stable. But from 6 - 11, it dramatically reduced.

Chromium adsorption capacity is much higher after Ben was modified, especially Ben was modified by HCl and burn at 110^0C. Maximum chromium adsorption capacity (Q_{max}) of B90at-2 (13,89 mgCr/g) was much higher than initial Ben (3,32 mgCr/g).

The sample of modified Ben by HCl 2M and burn at 110^0C (B90at-2) has chromium treatment ability in plated waste water, with

high concentration of chromium (140 mg/L), waste water after treatment process meet standard QCVN24:2009/BTNMT, column B for industrial waste water containing chromium.

Acknowledgements

This paper was finished with helping of Laboratoty for Environmental Analysis, Faculty of Environmental Sciences, Ha Noi University of Science, VNU.

References

[1] Deng.B, *Chromium(VI) reduction by naturally occurring organic compounds-kinetics of direct and surface catalyzed reactions,* Ph.D. Theis. Thejohns Hopkins University (1995).

[2] Sonya Abbasi; Hind Wahba; Mohammad Saaed Al-Masri. Abbasi- Wahba-AL-Masri. Removal of Chromium from Waste Water of Tanning Industry Using Bentonite. *Damascus University Journal* Vol. (25) - No. (2) 2009.

[3] Truong Minh Luong, Research on preparing and modifying of Thuan Hai bentonite to produce catalyst for ankylization reaction of aromatic hydrocacbon. *Doctoral thesis* (2001) (in Vietnamese).

[4] Than Van Lien et al, *Report of National level sciencetific research,* code KC.02.06/06-10 "Research on manufacturing technology of Montmorillonite (MMT) from natural mineral to supply as material for nanoclay", Ha Noi - 2009.

[5] S. Arfaouia*, N. Frini-Srasraa,b, E. Srasraa aUnité Matériaux Technopole, Borj Cédria, B.P. 95-2050, Hammam-Lif, Tunisie bDepartement de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 2092 El Manar 2, Tunisie. *Modelling of the adsorption of the chromium ion by modified clays.*

[6] Abbasi- Wahba-AL-Masri. Activation of Bentonite to Remove the Chromium from Waste Water Produced by Panning Industry. And Studying the Chromium Recovery Efficiency. *Damascus University Journal* Vol. (26) - No. (1) 2010.