



## NOTE

### Effectiveness of Biopolymer-Bentonite Clay Composites in Wastewater Treatment

N.M. MUPASI<sup>1</sup>, D. DUBE<sup>1</sup>, H. CHIRIRIWA<sup>2,\*</sup> and E.B. NAIDOO<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry, National University of Science & Technology, P.O Box AC939 Ascot Bulawayo, Zimbabwe

<sup>2</sup>Biosorption and Water Research Laboratory Department of Chemistry, Vaal University of Technology, Private Bag X021, Vanderbijlpark, 1911 andries Potgieter Blvd, South Africa

\*Corresponding author: E-mail: [harrychiririwa@yahoo.com](mailto:harrychiririwa@yahoo.com)

Received: 26 June 2017;

Accepted: 17 October 2017;

Published online: 31 December 2017;

AJC-18724

The feasibility of employing wood-bentonite clay composite material as a low-cost and effective adsorbent for removal of cations from wastewater has been investigated. The wood-bentonite clay composites were prepared by a solution intercalation method. Results showed that the percentage adsorption of  $Pb^{2+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$  from the effluent water was 88.46, 81.12 and 95.76 % respectively, using 10 g/L of the adsorbent. The desorbed wood-bentonite clay composites could be reused for adsorption of the cations.

**Keywords:** Adsorption, Wood-bentonite clay composite, Kinetics.

The presence of heavy metals in wastewater, even at low concentrations, is highly undesirable and can pose serious threats to human health. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries manufacturing [1]. Heavy metals can successfully be recovered from solution by precipitation as hydroxides or carbonate, by membrane filtration and by capture on synthetic ion exchangers [2,3]. These methods are much less efficient for concentrations lower than 100 mg/L for which they can be prohibitively expensive and can even fail to achieve legal limits. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost [4]. However, conventional adsorbents such as granular or powdered activated carbon have disadvantages as they are not economically viable and sometimes are technically inefficient [5].

Many studies have been done for removing  $Pb^{2+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$  ions from aqueous solutions using adsorption [6]. It has been reported that algae, wheat shell, seafood processing waste sludge and sawdust have been studied to define the adsorption capacity of these ions [7-9]. Adsorption is proposed as an economical and effective method for the retention of lead ions from aqueous industrial wastes [10]. However, adsorption on to the surface of activated carbon is the most widely used method despite its disadvantages [11]. Therefore there is need for continuous search for low cost and easily available materials, which can adsorb these cations.

Montmorillonite clay was obtained from R.A. Davis Co. (Ltd.) in Bulawayo, Zimbabwe. Soft pine wood shavings were used as they contain a greater percentage of cellulose and were easily obtained from local carpenters. The wood shavings were processed into flour by pulverizing and the flour and activated bentonite were mixed in varying ratios to form wood-bentonite composite (WBC). Synthetic solutions of the metal ions were diluted to the required concentration and used for the study of pH and effect of initial concentration of  $Pb^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions. 0.1 M HCl or 0.1 M NaOH was used for pH adjustment. Varying amounts of adsorbent were mixed with metal solutions and agitated at 1000 rpm. After adsorption samples were separated by centrifugation and the liquid analyzed spectrophotometrically. All the chemicals used were of analytical reagent grade. All the solutions were made with double distilled water.

$Pb^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions were examined within a range of pH 1.0-12.0. As the pH increased from 2 to 6, there was a gradual increase in the adsorption of ions by the WBC. No significant change in adsorption was observed above pH 6. The data obtained from the results reveals maximum values of  $Q_e$  and % adsorptions at around pH 6.0 for  $Pb^{2+}$  and 6.0 for  $Mg^{2+}$  and  $Ca^{2+}$ . The adsorption of  $Pb^{2+}$  on WBC mainly occurs at  $5.5 < pH < 6.5$ . The adsorption of  $Pb^{2+}$  increases rapidly at  $pH < 4.0$ . The adsorption phenomenon of  $Pb^{2+}$  has been explained by several researchers who noted that the surface of the clays contains a large number of active sites. Consequently, it may become positively charged at low pH, leading to increased competition between  $H^+$  and the metal ions for available adsor-

ption sites. Therefore, the net interaction is that of electrostatic repulsion, which means that higher acid concentration suppresses hydrolysis of cations. Thus at low pH,  $H^+$  ions compete effectively with the  $Pb^{2+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$  ions to occupy sorption sites on the adsorbent surface resulting in minimum sorption of  $Pb^{2+}$  ion. However, as pH increased to 6, this competition decreased as the number of negatively charged sites on adsorbent surface increased and the number of positively charged sites decreased. This resulted in greater electrostatic attraction of the cations ions by the WBC adsorbent surface. Hsu [12] and Bishnoi *et al.* [13] attributed the increase in cationic uptake by WBC to the increase in negative charge on the surface of the adsorbent that promotes ionic interaction between adsorbate and the sorbate. These findings have also been confirmed by Nharingo *et al.* [14] Ibrahim *et al.* [15] Chen and Wang [16] Jiang *et al.* [17] Chaari *et al.* [18] and Unuabonah *et al.* [19].

Percentage adsorption decreased after pH 7 to pH 12. The reason for low adsorption capacity in high pH is the competition between the excess of  $OH^-$  species in the solutions [20]. In addition, the adsorption of  $Pb^{2+}$  ions on surface material types is principally dominated by ion-exchange or outer-sphere complexation at low pH values and by inner-sphere complexation at high pH [21]. Consequently the number of moles of  $Pb^{2+}$  removal may decrease at low pH.

Effect of initial concentration of Pb(II) Mg(II) and Ca(II) on adsorption capacity of WBC was investigated by varying initial concentration of the synthetic water from 10 to 100 mg/L to achieve saturation of all sites so that sorption capacity could be determined while keeping all other parameters constant at optimum conditions. For this study, pH, adsorbent dosage and contact time were fixed as pH 6, 0.8 g/100 mL and 90 min for  $Pb^{2+}$ , 1 g/100 mL and 30 min for  $Mg^{2+}$  and 0.2 g/100 mL and 30 min for  $Ca^{2+}$  as shown in Tables 1-3.

The percentage of removal decreased with the increasing concentration of  $Pb^{2+}$ ,  $Mg^{2+}$  and  $Ca^{2+}$  ions. The removal increases as dilution of ions in solution proceeds as shown in Tables 1-3. This indicates that energetically less-favourable sites become

TABLE-1  
EFFECT OF INITIAL CONCENTRATION OF  $Pb^{2+}$

Initial concentration	Final concentration	Adsorption (%)	Qe
20.0	16.0	20.0	0.5
35.0	19.0	45.7	2.0
46.0	24.0	47.8	2.7
61.0	26.0	57.4	4.4
85.0	29.0	65.9	7.0
106.0	35.0	67.0	8.9
141.0	41.0	70.9	12.5

TABLE-2  
EFFECT OF INITIAL CONCENTRATION  
ON ADSORPTION OF  $Mg^{2+}$

Initial concentration	Final concentration	Adsorption (%)	Qe
25.6	0.3	98.7	2.5
53.4	1.1	97.9	5.2
75.8	11.8	84.5	6.4
124.2	94.9	23.6	2.9
181.7	152.8	15.9	2.9
193.5	166.3	14.1	2.7

TABLE-3  
EFFECT OF INITIAL CONCENTRATION  
ON ADSORPTION OF  $Ca^{2+}$

Initial concentration	Final concentration	Adsorption (%)	Qe
18.4	4.50	75.4	6.9
30.2	21.5	28.8	4.4
47.4	38.8	18.1	4.3
64.6	55.9	13.5	4.0
92.0	85.2	7.4	3.1

involved with increasing ion concentration in the aqueous solutions.

#### ACKNOWLEDGEMENTS

One of the author (N.M.M.) is grateful to the management of Plus Five Pharmaceutical in Bulawayo, Zimbabwe for providing the necessary facilities and technical assistance to carry out the research work.

#### REFERENCES

- K. Kadirvelu, K. Thamaraiselvi and C. Namasivayam, *Bioresour. Technol.*, **76**, 63 (2001); [https://doi.org/10.1016/S0960-8524\(00\)00072-9](https://doi.org/10.1016/S0960-8524(00)00072-9).
- J.L. Huisman, G. Schouten and C. Schultz, *Hydrometallurgy*, **83**, 106 (2006); <https://doi.org/10.1016/j.hydromet.2006.03.017>.
- F. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011); <https://doi.org/10.1016/j.jenvman.2010.11.011>.
- Q. Li, J. Zhai, W. Zhang, M. Wang and J. Zhou, *J. Hazard. Mater.*, **141**, 163 (2007); <https://doi.org/10.1016/j.jhazmat.2006.06.109>.
- S.S. Gupta and K.G. Bhattacharyya, *J. Hazard. Mater.*, **128**, 247 (2006); <https://doi.org/10.1016/j.jhazmat.2005.08.008>.
- V.C. Taty-Costodes, H. Fauduet, C. Porte and A. Delacroix, *J. Hazard. Mater.*, **105**, 121 (2003); <https://doi.org/10.1016/j.jhazmat.2003.07.009>.
- A. Mudhoo, V.K. Garg and S. Wang, *Environ. Chem. Lett.*, **10**, 109 (2012); <https://doi.org/10.1007/s10311-011-0342-2>.
- I. Ali, M. Asim and T.A. Khan, *J. Environ. Manage.*, **113**, 170 (2012); <https://doi.org/10.1016/j.jenvman.2012.08.028>.
- M.T. Yagub, T.K. Sen, S. Afroze and H.M. Ang, *Adv. Colloid Interf. Sci.*, **209**, 172 (2014); <https://doi.org/10.1016/j.cis.2014.04.002>.
- S.S. Thavamani and R. Rajkumar, *Res. J. Chem. Sci.*, **3**, 44 (2013).
- J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla and M. Sánchez-Polo, *J. Environ. Manage.*, **85**, 833 (2007); <https://doi.org/10.1016/j.jenvman.2007.07.031>.
- T. Hsu, *Fuel*, **87**, 3040 (2008); <https://doi.org/10.1016/j.fuel.2008.03.026>.
- N.S. Bishnoi, A. Pant and Garima, *J. Sci. Ind. Res. (India)*, **63**, 813 (2004).
- N. Haringo and O. Hunga, *Int. J. Adv. Eng. Technol.*, **6**, 128 (2013).
- S.H. Ibrahim, A. El-Kady, N.S. Ammar, L. Meesuk, P. Wathanakul, M.A. Abdel-Wahhab, *J. Environ. Eng.*, **139**, 349 (2013).
- H. Chen and A. Wang, *J. Colloid Interface Sci.*, **307**, 309 (2007); <https://doi.org/10.1016/j.jcis.2006.10.054>.
- M.-Q. Jiang, X.-Y. Jin, X.-Q. Lu and Z.-L. Chen, *Desalination*, **252**, 33 (2010); <https://doi.org/10.1016/j.desal.2009.11.005>.
- I. Chaari, E. Fakhfakh, S. Chakroun, J. Bouzid, N. Boujelben, M. Feki, F. Rocha and F. Jamoussi, *J. Hazard. Mater.*, **156**, 545 (2008); <https://doi.org/10.1016/j.jhazmat.2007.12.080>.
- E.I. Unuabonah, K.O. Adebawale, B.I. Olu-Owolabi, L.Z. Yang and L.X. Kong, *Hydrometallurgy*, **93**, 1 (2008); <https://doi.org/10.1016/j.hydromet.2008.02.009>.
- O. Altin, O.H. Ozelge and T. Dogu, *J. Chem. Technol. Biotechnol.*, **74**, 1131 (1999); [https://doi.org/10.1002/\(SICI\)1097-4660\(199912\)74:12<1131::AID-JCTB158>3.0.CO;2-0](https://doi.org/10.1002/(SICI)1097-4660(199912)74:12<1131::AID-JCTB158>3.0.CO;2-0).
- Y. Aldegs, M. Elbarghouthi, A. Elsheikh and G. Walker, *Dyes Pigments*, **77**, 16 (2008); <https://doi.org/10.1016/j.dyepig.2007.03.001>.