BIOSORPTION OF TOXIC METALS: THE POTENTIAL USE OF MAIZE TASSEL FOR THE REMOVAL OF Pb (II) FROM AQUEOUS SOLUTIONS

Caliphs M. Zvinowanda[1*], Jonathan O. Okonkwo[1], Victoria Mpangela[1], Josephine Phaleng[1], Pride N. Shabalala[1], Teresa Dennis[1], Patricia Forbes[2], Nana M. Agyei[3] and Kenneth I. Ozoemena[4]

[1]Department of Environmental, Water & Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa.
[2]Air Quality and Climate Change, NRE, CSIR, Pretoria, South Africa.
[3]Department of Chemistry, University of Limpopo, PO Box 235, Medunsa, 0204, Pretoria, South Africa.
[4]Molecular and Nanomaterials Electrochemistry Laboratory, Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.

ABSTRACT

In this study, we show for the first time the removal of Pb(II) from aqueous solutions by tassel powder. Batch experiments were conducted on tassel powder, and the effects of contact time, pH, temperature and concentration on the extent of Pb(II) removal studied. The highest adsorption (about 80 %) was at pH 7, and equilibrium was established between contact times 4-24 h. Adsorption of 5 mg/L Pb(II) standard concentration was rapid suggesting that adsorption may have been controlled by external diffusion. When increasing the concentration from 10-20 mg/L, the controlling step of adsorption was suggested to be that of internal diffusion.

KEYWORDS: Diffusion, batch adsorption procedure, influence of pH, contact time.

INTRODUCTION

Pb(II) is a well-known toxic metal that poses a serious threat to the fauna and flora of receiving water-bodies. In spite of strict regulations on the disposal of Pb(II) in most countries, the metal can still be found in a variety of wastewaters originating from catalysts, extractive metallurgy, smelting, metal electroplating, mining, and building construction, piping, cable covering and battery industries [1-5], as well as sewage sludge [6]. Pb(II) has been linked with poor mental development in children [7].

Various treatment technologies have been developed for Pb(II) removal from water. The hydrometallurgical technology extracts and concentrates Pb(II) from liquid waste using any of the variety of the processes, such as ion exchange, reverse osmosis, membrane filtration, sludge leaching, solvent stripping, precipitation and adsorption [8-10]. However, all these processes are expensive. Consequently, there has been a search for cheaper processes.

Hydrous oxides, such as iron oxides [11, 12], manganese oxide [13], titanium oxide [14] and fly ash [15, 16], have been used for the adsorption of the indicated metals and phosphates. A variety of naturally occurring materials, readily available in quantity and at a low cost, have been tried as adsorbents for metal removal from aqueous environment. The categories include peat moss [17], straw [18], banana pith [19], and rice husk [20, 21]. Also included are other corn starch, coconut shell, chelest fibre iry [22, 23], tea waste [24], olive cake [25], sunflower seed peel [26], antep pistachio shells [27], and micro-particles of dried plants [28]. Not all of these materials have been successful. However, the cost of the adsorptive metal removal process is relatively high when pure adsorbents are used. Also strains are placed on those agricultural products that are already in use for other purposes. Therefore, there is an increasing trend for substituting pure adsorbents using natural by-products or stabilized solid waste materials for the development of cost-effective adsorbents.

Maize is one of the major agricultural crops in many developing countries. Once the useful nutrient rich portions of maize plants have been harvested, the remaining portion of the plant is usually discarded as waste. Available information indicates that tassel (the male flower, found at the top of the plant) may contain some cellulosic hydroxyl groups which can easily bind with positively charged metal ions. Maize tassel, therefore, appears to be a good candidate for the adsorption of heavy metals from aqueous solutions. The utilization of tassels for the removal of Pb(II), and probably other metals, from aqueous solution would, however, attach some economic value to this waste material.

In this study, we demonstrate the removal of Pb(II) from aqueous solutions by means of tassel powder using batch adsorption procedures. The authors are not aware of any account in the literature of previous studies of Pb(II) removal from aqueous solution using tassel powder. So, the present study is the first report on tassel.

MATERIALS AND METHODS

All chemicals used were of analytical grade. Acids were obtained from Associated Chemicals Enterprise (ACE) Pty Ltd, South Africa. Tassel flowers were collected, separated, dried under ambient conditions, crushed by hand and, finally, reduced to smaller particles by milling. Using batch experiments, the effects of contact time, pH of the metal effluent solution, and concentration on the extent of metal

to provide a stable temperature and sufficient contact be-

ble hand-held combo pH and EC-meter (HI 98830) from Hanna Inc. was used for pH adjustments.

A flame atomic absorption spectrometer (FAAS) Perkin Elmer AA 3030, equipped with automatic background corrector, was used for all determinations.

One gram (1.0 g) tassel powder was added into 50 ml of reaction mixture containing 5 mg/L of Pb(II) standard in a 250-mL Erlenmeyer flask, and pH was adjusted to about 1 with 1.0 M HCl. The mixture was placed in a shaking water-bath at 25 ^{o}C. The above procedure was repeated for reaction mixtures containing 10, 15 and 20 mg/L of Pb(II) standard. After equilibration for 1 h, the mixture was centrifuged at 3,000 rpm for 3 min, and the supernatant filtered with 0.45-µm membrane filter. Pb(II) concentration in the filtrate was subsequently determined by FAAS analysis. Percentage of Pb(II) extracted was calculated from the difference between the concentration of lead in aqueous solution before and after equilibration.

To study the effect of pH on adsorption, the above batch experiment was repeated adjusting the pH of Pb(II) ion solution to 3, 5, 7, 9, 10 and 12 with 0.02 M NaOH. Time course experiments were carried out by shaking the adsorption mixture at various predetermined intervals of 1, 4, 8, 12, 15 and 24 h, and the rest of the procedure described above was then repeated.

RESULTS AND DISCUSSION

Good linearity of the calibration equation ($y = 0.0028x + 0.0008$) with R^2 of 0.9953 was obtained and determination was by reference to the standard curve.

Influence of pH on adsorption

The influence of pH on the adsorption of Pb(II) ions over a range of concentration is illustrated in Fig. 1. Pb(II) adsorption increased from pH 1 to 7; thereafter remained relatively constant, except for 5 mg/L. At pH 7, the four concentrations registered between 50-80 % adsorption. As can be seen from Fig. 1, quantitative adsorption was at the peak at pH 7. The trend observed in the present study agrees with that reported on Pb(II) and Cu(II) removal using rice husk [21].

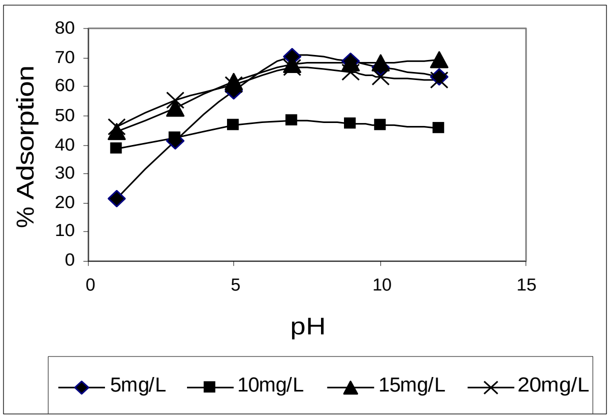

FIGURE 1 - Influence of pH on adsorption at different concentrations with 1 g of tassel flowers, at 25 ^{o}C.

Influence of contact time on adsorption

For a given substance to be effective as an adsorbent of metallic species, its adsorption rate must be fast and quantitative. Adsorption periods of 1, 4, 8, 12, 15 and 24 h were evaluated at different concentrations of Pb(II) standard solutions at different pH levels. Figs. 2-3 show the percent adsorption of Pb(II) ions by powdered maize tassel at pH 1 and 7. Less than 20% adsorption was exhibited by 5 mg/L within 1 h; while at the other concentrations more than 20% adsorption was achieved. Increased adsorption was observed at all concentrations within 4 h, as can be seen in Fig. 2. Again 5 mg/L showed the lowest percent adsorption, compared to the other concentrations. This pattern is also evident at 24 h, where 10-20 mg/L levels showed more than 50% adsorption. A similar pattern as observed in the present study has been reported, although the study was on phosphate removal using fly-ash and ordinary Portland cement [15]. Such a trend has been reported also on the removal of Pb(II) and Cu(II), and Cd(II) with rice husk and coconut shell, respectively [6, 21].

The trend observed in Fig. 2 is repeated in Fig. 3, i.e., increased adsorption with increase in contact time. However, percent adsorption at 5 mg/L is significantly higher than the adsorption exhibited by the other concentrations at 1 h contact time, as well as 10 mg/L at all the contact times. At contact times of 4 h, 8h, 12h, 15h and 24 h, the percent adsorption (>80%) rates of 5 mg/L, 15 mg/L and 20 mg/L are approximately the same. The adsorption at pH 7 (Fig. 3) is higher than that observed at pH 1 in Fig. 2.

The observed increase in adsorption at these concentration levels can be attributed to the availability of the active sites within the tassel adsorbent which were not

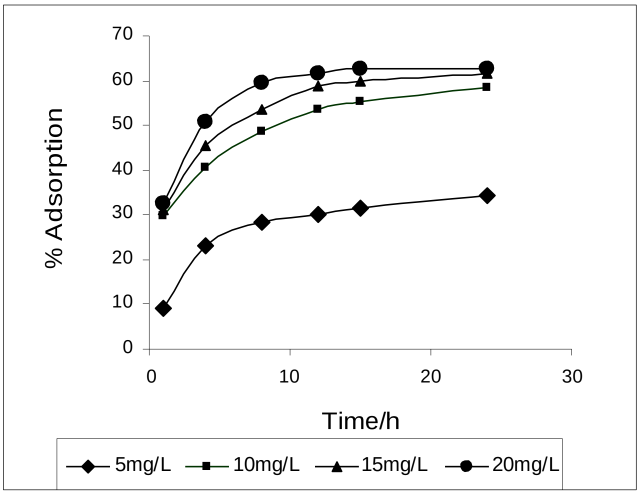

FIGURE 2 - Influence of contact time on adsorption (pH 1) with 1 g tassel flower at 25 ^{o}C.

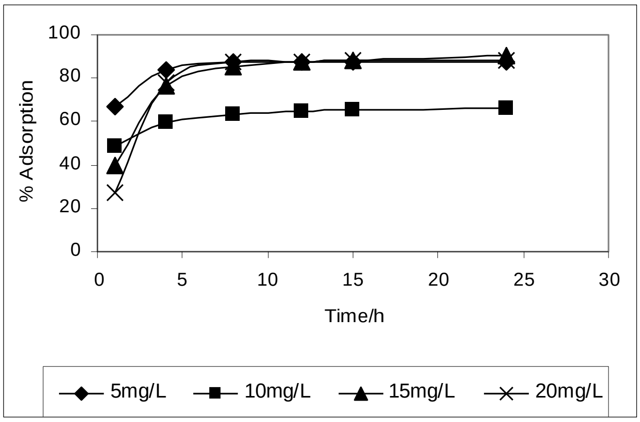

FIGURE 3 - Influence of contact time on adsorption (pH 7) with 1 g tassel flower at 25 ^{o}C.

fully occupied at short time intervals. That 5 mg/L showed the highest adsorption with increase in contact time, is a strong evidence of the availability of the active sites for binding. As the concentration of solution increased, the active sites were becoming fully occupied such that the adsorbent was getting to its saturation point with increase in contact time. It can also be observed that the adsorption of Pb(II) ions by maize tassel was very rapid within the first h, followed by a gradual process. Equilibrium was attained between 4-24 h. This behaviour suggests the occurrence of a rapid external mass transfer, followed by a slower internal diffusion process which may be the rate determining step.

Influence of temperature on adsorption

The effect of solution temperature was investigated using 20mg/L lead solutions with pH of 1, 7 and 12, respectively, as shown in Fig. 4. All the 3 curves obtained, show a decrease in adsorption of lead ions as the temperature is increased to about 65 ^{o}C. Thereafter, adsorption increases slightly and then remains almost invariant at the 3 different pH. The adsorption process is seen to be more pH-dependent than temperature. pH 7 gave the highest adsorption (87.6%), followed by pH 12 (63%), and lastly pH 1 exhibiting adsorption of 38%. Generally, from the principles of thermodynamics, one would expect the adsorption to decrease with increase in solution temperature. However, hydrolysis of the adsorbent surface at temperatures above

formation. These groups would further improve the activity of the adsorbent such that the desorption process become

process, regardless of increased kinetic energy of adsorbate to leave the surface.

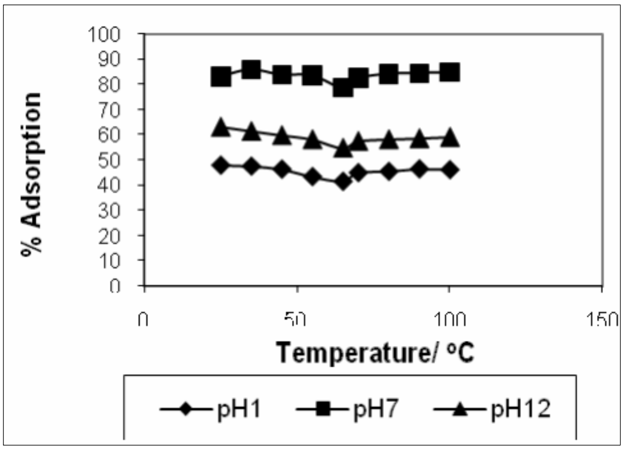

FIGURE 4 - Influence of solution temperature on adsorption (pHs 1, 7 and 12) with 1 g of tassel flower.

Influence of concentration on adsorption

A plot of average adsorption shown by maize tassel adsorbent against concentration of lead is illustrated in Fig. 5. It can be observed that the adsorption of lead at low concentration was rapid suggesting that it was controlled by external diffusion. By increasing the concentration, the controlling step of adsorption became internal diffusion within adsorbent pores, and, thus, the process of adsorption was observed to be slow with increasing concentrations.

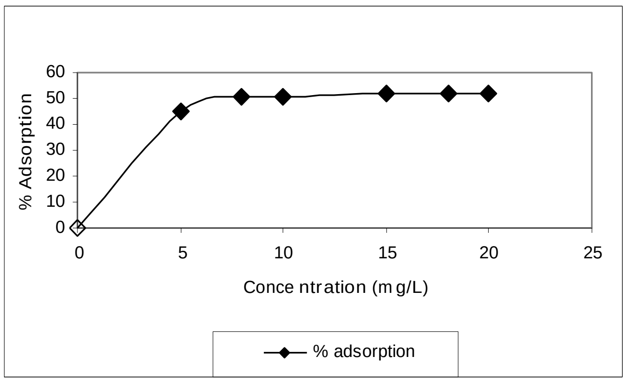

FIGURE 5 - Influence of concentration of Pb(II) on adsorption (pH 7, 24 h) with 1 g tassel at 25 ^{o}C.

Average values need a number of experiments. The ability of tassel flower to adsorb heavy metals, such as lead, has been demonstrated. However, more work needs to be done to demonstrate its capacity to adsorb lead in the presence of other heavy metals, such as Cr, Fe, Zn, Mn, Cd, etc. The effect of ionic strength on adsorption of toxic metals, such as lead, is another factor which needs further research.

CONCLUSIONS

The ability of maize tassel to remove varied concentrations of Pb(II) through batch experiments was demonstrated. Quantitative adsorption within pH 1, 3, 5, 7, 9, 10 and 12, good sorption capacity with an average of 55% adsorption, and a high sorption rate (4-24 h) of the adsorbent, demonstrate its potential application for the removal of trace metals from aqueous solutions, and, particularly, environmental waters. Furthermore, as little as 1.0 g of ad-sorbent gave above 75 % adsorption. The application of the adsorbent to the removal of heavy metals from wastewater and river water will show the full potential of maize tassel as a useful and cost-effective adsorbent.

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REFERENCES

[1] Bachauer, M.J. (1973) Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper and lead. Environ. Sci. Technol.7: 131-135.

[2] Periasamy K. and Namavayam C. (1994) Process development for removal and recovery of cadmium from wastewater by low cost adsorbent: adsorption rates and equilibrium studies. Ind. Eng. Chem. Res. 33: 317-320.

[3] Low K.S., Lee C.K. and Leo A.C. (1995) Removal of metals from electroplating wastes using banana pith. Biores. Technol. 51 (2-3): 227-231.

[4] Singh C.K., Sahu J.N., Mahalik K.K., Mohanty C.R., Mohan B. Raj. and Meikap B.C. (2007) Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid. J. Hazard. Mater., doi: 10.1016/j.jhazmat.2007.08.043.

[5] Pehlivan E., Yanik B.H., Ahmettli G. and Pehlivan M. (2007) Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Bioresour. Technol., doi: 10.1016/j.biortech.2007.07.052.

[6] Bhattacharya K. and Venkobachar C. (1984) Removal of cadmium (II) by low cost adsorbents. J. Environ. Eng. Div ASCE 104: 110-112.

[7] Riley J.P. and Skirrow G. (1975) Chemical Oceanography, vol. 3, 2nd edn. Academic Press, London. 85 - 86.

[8] LaGrega M.D., Buckingham P.L. and Evans J.C. (1994a) Hazardous waste management, McGraw-Hill, New York. 859- 880.

[9] Gerth J. and Bruemmer G. (1983) Adsorption and immobilisation of nickel, zinc and cadmium by goethite (a-FeOOH). Fres. Z. Anal. Chem. 316: 616-620.

[10] Cowan C.E., Zachara J.M. and Resch C.T. (1991) Cadmium adsorption on iron oxides in the presence of alkaline-earth elements. Environ. Sci. Technol. 25: 437-446.

[11] Selek Murathan A. and Bütün, M. (2006) Removal of lead ions from dilute aqueous solution in packed columns by using natural fruit shells through adsorption. Fresen. Environ. Bull 15: 1491 – 1498.

[12] Prasad M. and Saxena S. (2007) Attenuation of divalent toxic metal ions using natural sericitic pyrophyllite. Journal of Environmental Management, doi:1016/j.jenvman.2007.07.013.

[13] Hasany S.M. and Chaudhary M.H. (1986) Investigation of adsorption behaviour of mercury in micro-amounts on manganese dioxide from aqueous solution. J. Radioanal. Nucl. Chem.100, 307-315.

[14] Koryukova V.P, Kovalchuk L.J. and Shabanov E.V. (1984) Sorption removal of heavy metal impurities from alkali metal carbonates and ammonia. Ionnyi Obmen Khromatogr, 62- 65.

[15] Agyei N.M., Strydom C.A. and Potgieter J.M. (2002) The Removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, Cement and Concrete Research 2134, 1-9.

[16] Ho Y.S. and McKay G. (1999) The sorption of lead (II) ions on peat. Water Res. 33 (2): 578-584.

[17] Bailey S.E., Olin T.J., Bricka R.M. and Adrian D.D. (1999) A review of potentially low cost sorbents for heavy metals. Water Res. 33 (11), 2469- 2479.

[18] Low K.S. and Lee C.K. (1997) Cadmium uptake by the Mass Calympers Deleserti. Besch. Biosensor. Technol. 38: 1- 6.

[19] Srinivason K. (1986) Evaluation of rice husk carbon for the removal of trace inorganics from water, PhD dissertation, Indian Inst. Technol. Madras.

[20] Roy D., Greenlav P.N. and Shane B.S. (1993) Adsorption of heavy metals by green algae and ground rice husks. J. Environ Health A. 28 (1): 37-50.

[21] Wong K.K., Lee C.K., Low K.S. and Haron M.J. (2003) Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. Chemosphere 50: 23-33.

[22] Wing R.E. and Sessa, D.J. (1998) Corn-based heavy metal extractants. Agricultural Research Magazine, July.

[23] Awofulu R.O. and Okonkwo O.J. (2005) Application of chelest fiber iry (aminopolycarboxylic acid- type cellulose) to the extraction of cadmium ions from aqueous solution. Fresen. Environ. Bull 14: 732-736.

[24] Amarasinghe B.M.W.P.K. and Williams R.A. (2007) Tea waste as a low adsorbent for the removal of Cu and Pb from wastewater. Chemical Eng. Journal 132: 299-309.

[25] Doyurum S. and Celik A. (2006) Pb(II) and Cd(II) removal from aqueous solutions by olive cake. J. Hazard. Mater. B138: 22-28.

[26] Özdemir M., Sahin Ö. and Güler, E. (2004) Removal of Pb (II) ions from water by sunflower seed peel. Fresen. Environ. Bull 13: 524 – 531.

[27] Sahin Ö., Demirel S. and Dilekoglu M.F. (2005) Removal of Pb(II) from aqueous solution by Antep pistachio shells. Fresen. Environ. Bull 14: 986 – 992.

[28] Benhima H., Chiban M., Sinan F., Seta P. and Persin M. (2007) Removal of lead and cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants. Colloids Surf. B: Biointerfaces, doi: 10.10.1016/j.colsurfb.2007.06.024.

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CORRESPONDING AUTHOR

Caliphs M. Zvinowanda
Department of Environmental,
Water & Earth Sciences
Faculty of Science
Tshwane University of Technology
Private Bag X680
Pretoria, 0001
SOUTH AFRICA

Phone: +27 12 382 6281
Fax: +27 12 382 6354
E-mail: zvinowandacm@tut.ac.za,

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