INTERNATIONAL JOURNAL
FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Removal and Recovery of Hazardous Metal Ions from the Industrial Effluent using Waste Fish Scale Impregnated Polyurethane Foam: Voltametric Method

Vijay L. Gurav[1], Rajesh A. Samant[2]

[1, 2]Department of Chemistry, K. C. College, D. W. Road, Charchgate, Mumbai, (Maharashtra) India- 400020

Abstract: Waste fish scale powder shows Chitosan properties to adsorb hazardous metals of contaminated waste water or effluent. As the waste fish scale was crushed and dried to fine powder, it was coated on non reactive polyurethane foam. The objective of this study was to understand removal of hazardous metals using waste fish scale impregnated on polyurethane foam and quantify with voltametric method. Various parameters such as pH, amount of adsorbent, contact time etc. are studied. The best removal and recovery was found at pH- 5 to 6, 300 mg amount of adsorbent (for 50 ml sample solution) and contact time of 90 min. This procedure was applied for determination of Zn (II), Cu (II), Cd(II), Pb(II), Fe(II) and Mn(II) in industrial effluent. The results indicated that waste fish scale impregnated on polyurethane foam is a promising adsorbent for removal of hazardous metals from industrial effluent.
Keywords: Hazardous metals; Polyurethane foam; Chitosan:

I. INTRODUCTION

India is among top ten industrialized countries in the world. Pollution is a main problem of industrial civilization. The pollutants are the outcome of various chemical industries like Pesticides, detergents, plastics, petrochemicals, paints, dyes, food additives etc.[1-3]. Besides these, there are a number of effluents and emissions in the atmosphere. Mining activities also add to this problem particularly dusting and particulate matter thus, pollution is a gift of industrial civilization [4-7]. Among the many other low cost absorbents identified, chitosan has the highest absorption capacity for several metals. Chitosan chelates five to six times[8-12] greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin [13-15]. The waste fish scale in dry and fine powder form, shows the property of adsorbent exactly like chitosan. As the fish scale was dried and ground to fine powder it was necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. The adsorption capacity of chitosan was increased by impregnated on polyurethane foam [16-23], hence the similar base material was tested here for the dry powder of waste fish scale. In this work removal and recovery of hazardous metals such as Zn (II), Cu (II), Cd(II), Pb(II), Fe(II) and Mn(II) in industrial effluent using waste fish scale powder impregnated polyurethane foam was studied.

II. MATERIALS AND METHODS

A. Instrument Specification

Differential pulse Voltammetric analysis experiments were performed with a Metrohm 797 VA Computerized (Switzerland) equipment with three electrode system consisting Hanging mercury drop electrode (HMDE) as working electrode, Platinum as auxiliary electrode and Ag / AgCl / KCl as reference electrode. Elico LI-127 digital pH meter (Elico India Ltd., Hyderabad, India) with a combined glass electrode was used for measurement of pH.

B. Chemicals Preparation

All chemicals used were of analytical reagent grade. The 1000 mg/L stock solution of Zn (II), Cu(II), Cd(II), Pb(II), Fe(II) and Mn(II) heavy metals were prepared by dissolving appropriate amount of $ZnCl_2$, $CuCl_2.2H_2O$, $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, $FeCl_3$, and $Mn(NO_3)_2$ metal ions in slightly acidic double-distilled water [24-26]. The solutions prepared were then standardized using volumetric method and then appropriate quantities were diluted to get 50 mg/L concentrations. An effluent sample was synthetically mixing appropriate volume of each standard to get 50 mg/L of each metal. Polyurethane foam was purchased from local ijarket. All volumetric Glassware's used were of A-grade (Borosil India Ltd. make).

C. Preparation Of Adsorbent From Waste Prawns Scale

The waste Fish (prawn) scales were collected from local fish market of Ratnagiri (Maharashtra) India. The cleaned waste prawns scale was dried in the sunlight for two days, then kept oven at $60^{o}C$ temperature till it becomes crispy. Using Mechanical grinder, it was ground to fine powder of particle size less than 50 mesh. In 50 gm powdered prawn scale was mixed with 200 ml of 10% HCl then 10% NaOH, 10% NaOH solution was added for de-protination. After 24 Hrs. it was washed 4-5 times by distilled water. In that solution 50 % NaOH solution was added for deacetylation. After 24 Hrs. it was washed by distilled water till all traces of acid or base present are removed. Solution was filtered by using whatman filter paper no 1. The residue was kept in oven at $60^{o}C$ temperature for 8 hrs. The dried prawn scales powdered chitosan was stored in air tight polythene bottle for further analysis [11].

D. Preparation Of Fish Scale Impregnated Polyurethane Foam

20 gms of fish scale powder was slowly added to 500 ml of 10% acetic acid with constant stirring. The mixture was heated to get a whitish viscous adsorbent gel. The polyurethane foam cubes (0.5 x 0.5 x 0.5 cm in size) used for the coating of adsorbent gel had an average pore size of 0.6 X 0.8 mm. About 200 ml of adsorbent gel was diluted with water (400 ml) and heated to $40 – 50^{o}C$. About 40 gms of polyurethane foam (PUF) was slowly added and mechanically agitated using a rotary shaker at 200 rpm for 24 hours. This gel-impregnated PUF was washed with deionised water and dried. This process was repeated twice more to get a thick coating of adsorbent on PUF [16].

E. Preparation Of Adsorbent Column For Recovery And Its Optimization

A glass column (300 mm x 20 mm) having a stop cock and with glass wool as a support at the bottom was packed with 300 mg of the fish scale impregnated on polyurethane foam. The column bed was washed with distilled water prior to use.

F. Procedure of Metal Removal by Adsorption

A known amount (200 mg to 400 mg) of fish scale impregnated on polyurethane foam was mixed with 50 ml of the 50 mg/L (mixed ion solution or synthetic effluent) metal ion solution with adjusted acidic pH (Between 2 to 7) was mixed and kept with occasional shaking for fixed time (30 min. to 150 min). The solution was then filtered and the fish scale impregnated on polyurethane foam was separated. The filtrate was analyzed for the amount of metals ions unadsorbed.

G. Procedure of Metal Recovery (stripping) From Adsorbent

The metal ions adsorbed fish scale impregnated on polyurethane foam separated from the adsorption process was then filled in the separation column and then the metal ions were stripped back using 10 ml 1M HCl at 1 ml per minute flow rate. The concentration of stripped metals was also checked for verification of adsorption efficiency [27-29].

H. Differential Pulse Voltammetric Measurements

10 ml ultra pure water, 5 ml of 0.1M of KCl and 1ml of acetate buffer (pH 4.6) was taken in polarographic vessel and then the measurement was started for blank under the given parameters Table-1. 1 ml of sample (metal solutions 50 mg/L before adsorption, after adsorption and stripped back solution after adsorption) was added to polarographic vessel and then voltamogram was recorded. Then to this solution the standard metal ion solution was added (three additions of 0.1ml) under the same conditions.

Table: 1 Operating parameters for Cyclic Voltmeter Instrument:-

Parameters	Description
Working electrode	Hanging Mercury Dropping Electrode (HMDE)
Calibration	Standard addition method
Mode	Differential pulse
Initial purge time	300 s
Addition purge time	10 s
Pulse amplitude	0.05 V
Start potential	-1.3 V
End potential	0.05 V
Voltage step	0.006 V
Voltage step time	0.1 s

Sweep rate 0.06 V/s	0.06 V/s
Peak Potential (Zn)	-9.80V
Peak Potential (Cu)	-0.10V
Peak Potential (Cd)	-0.56V
Peak Potential (Pb)	-0.38V
Peak Potential (Fe)	-0.46V
Peak Potential (Mn)	-1.2V

III. RESULT & DISCUSSION

The results of various process optimization measurements are as follows:

A. Effect of pH

The pH of the sample solution taken for adsorption was adjusted to pH 2, 3, 4, 5, 6 and 7 before adsorption. The % recovery (the ratio of recovered metal after adsorption from fish scale impregnated on polyurethane foam to input concentration) of the metals from the adsorption media showed the optimum adsorption at pH 6 for Zn (II), Cu (II), Fe (II), Mn(II) and pH 5for Cd (II) and Pb (II). Figure 1 indicates the graphical representation of the results, where it is clear that the adsorption is less than 30% at pH 2, between 50 to 55% at pH 3, about 80% at pH 4 but exceed 90% at pH 5 in almost all cases.
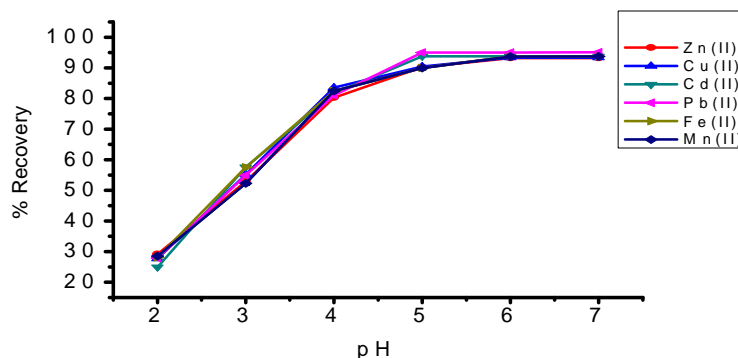

Fig. 1: % recovery of metals at different pH after recovery from adsorption media

B. Effect Of Amount Of Fish Scale Impregnated On Polyurethane Foam

The amount fish scale impregnated on polyurethane foam used for adsorption was varied from 200 mg to 400 mg for 50 ml sample. The maximum % recovery (the ratio of recovered metal after adsorption from fish scale impregnated on polyurethane foam to input concentration) as optimum at 300 mg. For 200 mg and 250 mg the recovery was less than 60% and around 80% respectively, while from 300 mg and above the recovery is almost constant at 90.5% to 92.5%. The fig 2 indicates the optimization of % recovery against amount of adsorbent taken for adsorption of 50 mg/L metal ion solution at pH 6 for Zn (II), Cu (II), Fe (II), Mn(II) and pH 5 for Cd (II) and Pb (II).
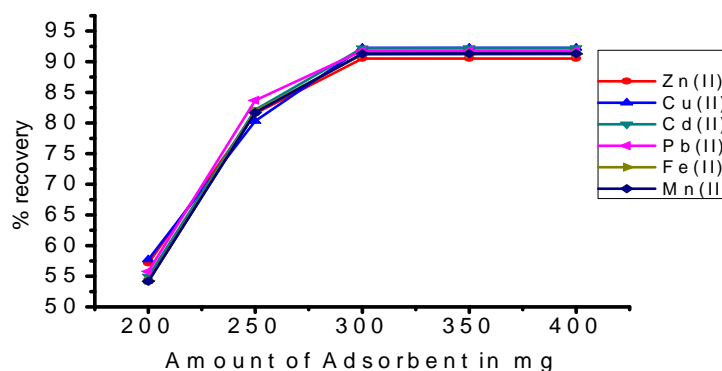

Fig. 2: % recovery of metals at different amount of fish scale impregnated on polyurethane foam.

C. Effect Of Contact Time Of Adsorbent

The optimized adsorption condition i.e. pH and Amount of adsorbent for metal ions were set externally before the adsorbent was added. The contact time was varied from 30 min. to 150 min. The results show 90 min. was sufficient contact time for adsorption. The results are summarized in Fig 3.
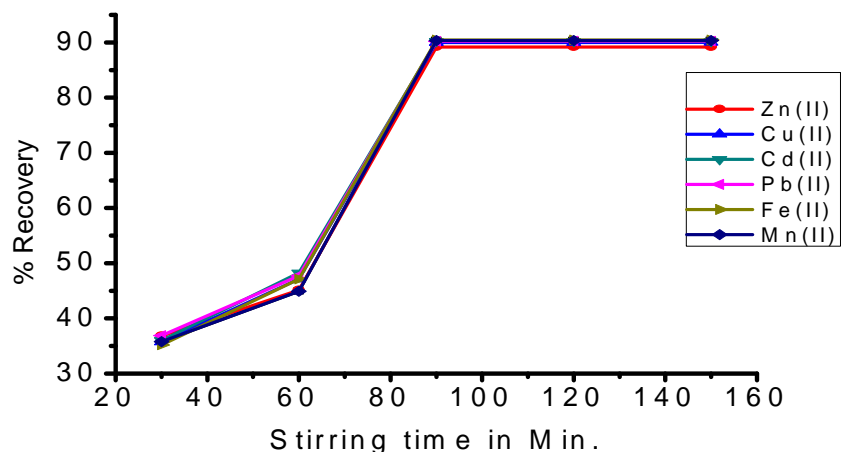

Fig. – 3: % recovery of Heavy metals at different contact time between metal ion and fish scale impregnated on polyurethane foam. (Other parameters as per optimized conditions).

D. Results Of Adsorbing Capacity Of Fish Scale

The results of various metals present in the sample before and after adsorption with fish scale impregnated on polyurethane foam at optimized conditions (mentioned above) are reported in table 2.

Table 2: Results of metal present in sample before and after adsorption with fish scale impregnated on polyurethane foam:-

metal	Amount of metal in mg per 50 ml sample		
	Before in sample	After in filtrate	Recovery
Zinc (II)	303±0.3	9±0.3	293±0.3
Copper (II)	405±0.3	13±0.3	392±0.3
Cadmium (II)	158±0.3	6±0.3	152±0.3
Lead (II)	185±0.3	6±0.3	178±0.3
Iron (II)	605±0.3	19±0.3	585±0.3
Manganese (II)	358±0.3	12±0.3	345±0.3

It was considered of interest and to support the adsorption is due to fish scale and not only because of the polyurethane. The results of various metals present in the sample before and after adsorption at optimized conditions (mentioned above) with only using polyurethane are reported in table 3.

Table: 3 Results of metal present in sample before and after adsorption with pure polyurethane foam:-

metal	Amount of metal in mg per 50 ml sample		
	Before in sample	After in filtrate	Recovery
Zinc (II)	325	242	81.6
Copper (II)	428	335	89.9
Cadmium (II)	151	109	34.7
Lead (II)	203	158	41.2
Iron (II)	585	435	140.4
Manganese (II)	320	238	75.8

IV. CONCLUSION

Fish scale impregnated on polyurethane foam as solid phase offers a simple, efficient and cost- effective method for removal of Zn (II), Cu (II), Cd(II), Pb(II), Fe(II) and Mn(II). Under the optimised conditions, these metals were quantitatively adsorbed at pH 5.0 for Cd(II) and Pb(II), pH 6 for Zn(II) , Cu(II), Fe(II) and Mn(II). 300 mg of adsorbent and 90 min, contact time was sufficient for efficient adsorption of these heavy metals. Considering the costal border of India the dry fish scale is available in plenty and the same can be used as low cost hazardous metal removal material.

V. ACKNOWLEDGEMENTS

REFERENCES

[1] Akpor OB, Ohiobor GO, Olaolu TD. Heavy metal pollutants in wastewater effluents : Sources , effects and remediation 2 . Sources of Heavy Metals in. 2014;2(4):37–43.

[2] Sweileh WM, Al-Jabi SW, Zyoud SH, Sawalha AF. Outdoor air pollution and respiratory health: A bibliometric analysis of publications in peer-reviewed journals (1900 - 2017). Multidiscip Respir Med. 2018;13(1):1–12.

[3] Matsuura KCKT, Ethylenediamine EDA. Removal of heavy metals and pollutants by membrane adsorption techniques. Appl Water Sci [Internet]. 2018;8(1):1–30. Available from: https://doi.org/10.1007/s13201-018-0661-6

[4] Kumar GVSRP, Avinash K, Bharath M, Srinivasa YK. Removal of Cu (II) using three low - cost adsorbents and prediction of adsorption using artificial neural networks. Appl Water Sci [Internet]. 2019;9(3):1–9. Available from: https://doi.org/10.1007/s13201-019-0924-x

[5] Jain DSMCK, Yadav AK. Removal of heavy metals from emerging cellulosic low-cost adsorbents : a review. Appl Water Sci. 2017;7(5):2113–36.

[6] Bohli T, Ouederni A, Villaescusa I. Simultaneous adsorption behavior of heavy metals onto microporous olive stones activated carbon: analysis of metal interactions. Euro-Mediterranean J Environ Integr. 2017;2(1):1–15.

[7] Barakat MA. New trends in removing heavy metals from industrial wastewater. Arab J Chem [Internet]. 2011;4(4):361–77. Available from: http://dx.doi.org/10.1016/j.arabjc.2010.07.019

[8] Boudouaia N, Bengharez Z, Jellali S. Preparation and characterization of chitosan extracted from shrimp scales waste and chitosan film: application for Eriochrome black T removal from aqueous solutions. Appl Water Sci [Internet]. 2019;9(4):1–12. Available from: https://doi.org/10.1007/s13201-019-0967-z

[9] Vijay L. Gurav, Rajesh A. Samant 'Chitosan on immobilized silica: Differential pulse Voltametric determination of heavy metal ions from industrial effluent' Water Conservation Science and Engineering. DOI: 10.1007/s41101-019-00080-7 (Accepted Manuscript)

[10] De Castro Dantas TN, Neto AAD, Moura MCPDA, Neto ELB, De Paiva Telemaco E. Chromium adsorption by chitosan impregnated with microemulsion. Langmuir. 2001;17(14):4256–60.

[11] Liu C, Wang G, Sui W, An L, Si C. Preparation and Characterization of Chitosan by a Novel Deacetylation Approach Using Glycerol as Green Reaction Solvent. ACS Sustain Chem Eng. 2017;5(6):4690–8.

[12] Singh P, Nagendran R. A comparative study of sorption of chromium (III) onto chitin and chitosan. Appl Water Sci [Internet]. 2016;6(2):199–204. Available from: http://dx.doi.org/10.1007/s13201-014-0218-2

[13] Rajesh. A. Samant*, Vijay. L. Gurav 'A Biosorption of Heavy Metal Ions from effluent using Waste Fish Scale' Asian J. Research Chem. 11(5): September-October 2018

[14] Zhang C, Zhang H, Li R, Xing Y. Morphology and adsorption properties of chitosan sulfate salt microspheres prepared by a microwave-assisted method. RSC Adv [Internet]. 2017;7(76):48189–98. Available from: http://dx.doi.org/10.1039/C7RA09867G

[15] Teimouri A, Ghanavati Nasab S, Habibollahi S, Fazel-Najafabadi M, Chermahini AN. Synthesis and characterization of a chitosan/montmorillonite/ZrO2 nanocomposite and its application as an adsorbent for removal of fluoride. RSC Adv. 2015;5(9):6771–81.

[16] Keshavarz A, Zilouei H, Abdolmaleki A, Asadinezhad A, Nikkhah AA. Impregnation of polyurethane foam with activated carbon for enhancing oil removal from water. Int J Environ Sci Technol. 2016;13(2):699–710.

[17] Marlina, Iqhrammullah M, Darmadi, Mustafa I, Rahmi. The application of chitosan modified polyurethane foam adsorbent. Rasayan J Chem. 2019;12(2):494–501.

[18] Bodnar M, Hartmann JF, Borbely J. Preparation and characterization of chitosan-based nanoparticles. Biomacromolecules. 2005;6(5):2521–7.

[19] Khalid A, Zubair M, Ihsanullah. A Comparative Study on the Adsorption of Eriochrome Black T Dye from Aqueous Solution on Graphene and Acid-Modified Graphene. Arab J Sci Eng. 2018;43(5):2167–79.

[20] Lee HC, Jeong YG, Min BG, Lyoo WS, Lee SC. Preparation and acid dye adsorption behavior of polyurethane/chitosan composite foams. Fibers Polym. 2009;10(5):636–42.

[21] Li N, Bai R, Liu C. Enhanced and selective adsorption of mercury ions on chitosan beads grafted with polyacrylamide via surface-initiated atom transfer radical polymerization. Langmuir. 2005;21(25):11780–7.

[22] Machado Centenaro GSN, Facin BR, Valério A, de Souza AAU, da Silva A, de Oliveira JV, et al. Application of polyurethane foam chitosan-coated as a low-cost adsorbent in the effluent treatment. J Water Process Eng [Internet]. 2017;20(November):201–6. Available from: http://dx.doi.org/10.1016/j.jwpe.2017.11.008

[23] Ghosh SB, Bhaumik R, Mondal NK. Optimization study of adsorption parameters for removal of fluoride using aluminium-impregnated potato plant ash by response surface methodology. Clean Technol Environ Policy. 2016;18(4):1069–83.

[24] El-Said AG, Badawy NA, Abdel-Aal AY, Garamon SE. Optimization parameters for adsorption and desorption of Zn(II) and Se(IV) using rice husk ash: Kinetics and equilibrium. Ionics (Kiel). 2011;17(3):263–70.

[25] Yusuff AS. Optimization of adsorption of Cr(VI) from aqueous solution by Leucaena leucocephala seed scale activated carbon using design of experiment.

Appl Water Sci [Internet]. 2018;8(8):1–11. Available from: https://doi.org/10.1007/s13201-018-0850-3

[26] Palisoc ST, Estioko LCD, Natividad MT. Voltammetric determination of lead and cadmium in vegetables by graphene paste electrode modified with activated carbon from coconut husk. Mater Res Express. 2018;5(8).

[27] Chattoraj S, Mondal NK, Sadhukhan B, Roy P, Roy TK. Optimization of Adsorption Parameters for Removal of Carbaryl Insecticide Using Neem Bark Dust by Response Surface Methodology. Water Conserv Sci Eng [Internet]. 2016;1(2):127–41. Available from: http://dx.doi.org/10.1007/s41101-016-0008-9

[28] Gupta A, Balomajumder C. Statistical optimization of process parameters for the simultaneous adsorption of Cr(VI) and phenol onto Fe-treated tea waste biomass. Appl Water Sci. 2017;7(8):4361–74.

[29] Turkyilmaz H, Kartal T, Yildiz SY. Optimization of lead adsorption of mordenite by response surface methodology: Characterization and modification. J Environ Heal Sci Eng. 2014;12(1):1–9.

[30] Li Y, Wahdat F, Neeb R. Digestion-free determination of heavy metals (Pb, Cd, Cu) in honey using anodic stripping differential pulse voltammetry and potentiometric stripping analysis. Fresenius J Anal Chem. 1995;351(7):678–82.

[31] Qneirolo F, Valenta P. Trace determination of Cd, Cu, Pb and Zn in annual growth rings by differential pulse anodic stripping voltammetry. Fresenius' Zeitschrift für Anal Chemie. 1987;328(1–2):93–8.

[32] Locatelli C, Astara A, Vasca E. Voltammetric and Spectroscopic Determination of. Environ Monit Assess. 1998;23–37.

[33] Golimowski J, Valenta P, Nürnberg HW. Trace determination of chromium in various water types by adsorption differential pulse voltammetry. Fresenius' Zeitschrift für Anal Chemie. 1985;322(3):315–22.

[34] Adamczyk M, Grabarczyk M. Simple, insensitive to environmental matrix interferences method of trace cadmium determination in natural water samples. Ionics (Kiel). 2019;25(5):1959–66.

[35] Monticelli D, Psaro R, Pozzi A, Dossi C, Recchia S. Differential pulse voltammetric determination of tin in the presence of noble metals. Anal Bioanal Chem. 2005;383(1):115–21.

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 (24*7 Support on Whatsapp)