World Applied Sciences Journal 12 (3): 358-363, 2011
ISSN 1818-4952

Studies on the Removal of Heavy Metal Ions from Industrial Effluents Using Ammonium Pyrrolidine Dithio Carbamate (APDC) Loaded Polyurethane Foams (PUF)

[1]K.S.R. Murthy and [2]R. Marayya

[1]Bharat PG College, Mangalpally, Ibrahimpatnam, Rangareddy District, 501510,
[2]Head, Corporate Quality Assurance and Regulatory Affairs, NATCO Pharma, Hyderabad, India

Abstract: Open cell polyurethanes (PUF) find wide range of applications as good column materials for the concentration and removal of both organic and inorganic pollutants because of their high efficiency for sorption of various ionic and neutral materials. Ammonium pyrrolidine (APDC) loaded PUF were found to ct as good sorption materials which can be applied to develop commercially viable and highly efficient separation processes for the removal of heavy metals like Pb, Hg. Cd, Ni, Cu and Cr and these results are presented in this paper. The optimum conditions like flow rate, pH, plasticizer concentration were established for the removal of these toxic heavy metals individually and when present in mixture with APDC loaded PUF (2.5 g PUF-2.0 g 10% APDC). These studies revealed that a combination of modular columns in series will remove completely all these toxic heavy metals when present together even at 100-1000 ppm. An experimental design is worked out to treat 10 litres volume of waste water containing 100-10000 ppm each of this heavy metal. The extraction efficiency and the process cost analysis were determined. The application of this new media for the removal of heavy metals from municipal sewage and the chloro-alkali industrial wastes was demonstrated.

Key words: Industrial Effluents · Heavy Metal Removal · Chloro-alkali Industrial Waste · Recovery of Wastes · Polyurethane Foams

INTRODUCTION

High loads of heavy toxic metal ions discharged from various industrial operations in electroplating industries, metallurgical industries, mining operations etc cause serious environmental problems due to their non-degradability. Polyurethane foams with their high surface area and cellular structure offer as good column materials for sorption of various ionic materials even from dilute solutions. The thermodynamic properties of foam-filled columns are known to be very favourable for the treatment of effluents with high flow-rates simply by gravitation flow, particularly when they are loaded with chelating agents [1].

The design and synthesis of polyurethane foams with anchored chelating functions groups is till an open and promising field for the development of highly efficient, low cost sorption materials tailor made with specific properties suitable for the treatment of large volumes of industrial waste for the removal and recovery of toxic pollutants under varied experimental conditions. The large choice of chelating agents together with the high possible selectivity, which can be achieved by careful control of the experimental conditions, has allowed the application of chelating agent loaded PU foam as very effective and low cost sorbent materials for the removal of toxic pollutants [2-8]. The application of PU foams and Thio-polyurethane foams (T-PUF) for the selective removal of phenols [7] and mercury [8] from industrial effluents was reposed earlier.

In the present study, the authors report their data on the adsorption efficiency of APDC loaded PUF for the removal and recovery of Pb(II), Hg(II), Cd(II), Ni(II), Cu(II) and Cr(VI) when present individually and in mixture and their application for the removal of toxic metals from industrial wastes/effluents.

MATERIALS AND METHODS

Experimental: The flexible polyurethane foam was obtained from U-Foam Pvt Ltd., Hyderabad, with bulk density 29.6 kg/m^3, surface area of 31.5 m^2/kg and density of 16 kg/m^3). All of the chemicals used were of analytical grade.

Corresponding Author: K.S.R. Murthy, Professor of Chemistry, Bharat PG College, Mangalpally, Ibrahimpatnam, Rangareddy District, 501510, India. Mob: +91 9000527886, E-mail: ksrmurthy1969@yahoo.com.

Preparation of APDC Coupled Polyurethane Foam: The flexible polyurethane foam was cut into small cubes of about 5 mm edge, soaked in 2M hydrochloric acid, washed with distilled water and acetone and then dried in an oven at 80°C. To 10 g of this foam, 10 ml of 2% APDC (Loba-Chemie GR) in chloroform and 2% TBP (BDH) in chloroform were slowly added. Stirring the foam into the solution and the chloroform was finally evaporated off.

Batch Studies: In a series of flasks containing 0.1g of PUF/APDC-TBP-PUF, 50 ml of metal ion solutions of concentrations varying from 0 to 100 ppm were added and shake for two hours at 30°C and the amount adsorbed on the PUF was determined by analyzing the clear aqueous solutions by AAS (Shimadzu AA 6200) Method.

Preparation of Column: About 0.5 g of APDC-TBP-PUF foam material is put into a 150 mm (length) and 10 mm (id) glass column with sinter disc and Teflon stopcock. The column was packed by gently pressing with a glass rod until a uniform consolidation was noticed, 10 ml of petroleum ether was passed through the column to remove air bubbles and then the column was allowed to dry to be free from solvent contamination and this column was used for all dynamic equilibrium experiments.

Procedure for Treating Chloro-alkali Industry Waste: The sample of wet sludge waste supplied by M/s. National Rayon Corporation Ltd., Mumbai has the following composition.

(i) % Moisture – 37.50
(ii) Ca (CO_3^{-2}, Cl^{-2}, SO_4^{-2}) 46.40
(iii) $Mg(OH)_2$ – 13.00
(iv) % $Fe(OH)_3$ – 3.10
(v) %Hg - 0.056.

0.1 kg of the above wet sludge was extracted with 0.5 liters of 2N sulphuric acid for 3-5 hours at 80°C. Besides mercury, only magnesium was extracted to an appreciable extent. The sulphuric acid extract was filtered and neutralized with sodium hydroxide to pH 3-4 and made up to 1 litre with distilled water. 0.1 litre of this extract was then passed through PUF-APDC-TBP foam columns under dynamic conditions keeping two foam columns in series. The mercury free effluents were then discharged into the drain. The mercury sorbed on the foam column can be recovered quantitatively using either acetone or alcohol.

RESULTS AND DISCUSSION

The absorption efficiencies of unloaded PUF and APDC-TBP loaded PU form for different toxic heavy metal ions are likely to vary based on their absorption efficiency and metal-ligand formation constants with active sites of the foam or loading agent. The medium may exhibit specificity for certain metals under certain experimental conditions. Therefore to examine the efficiency and specificity of reagent loaded PU foam media for the removal and recovery of toxic heavy metals from the industrial waste water when they are present together, systematic investigations were carried out varying different experimental parameters.

Percent Recovery of Metal Ions: It is well known that PU foams supports take up plasticizers and chelating agents more efficiently than other conventional granular supports that are available today and almost this intake increases by 2-3 times. This high uptake of the stationary phase on the PU foam (which acts as an inert support in reagent loaded forms), results in relatively high breakthrough capacities of these foam columns and the results are presented in Table 2.

Batch Studies: The removal and recovery efficiency of heavy metal ions by APDC-TBP-PUF was studied by batch studies. In addition with this the various optimum conditions to achieve maximum recovery of this heavy metal ions were established which are as below.

Effect of Solution Ph on the Sorption of Metal Ions: The effect of pH on the sorption process indicates that the nature of interaction governs the distribution of solute between liquid and solid phases. Batch studies were carried out by taking 50 ml of metal ion solution with the sorbents of polyurethane foam, APDC loaded polyurethane foam and exhibited quantitative sorption of these metals ions was observed in the pH range of 3-5, above pH 5.0 the percent extraction gradually decreased and precipitation of the metal ions was observed at above pH 8.0. The pH sorption data can be explained by a cation chelation mechanism by which anionic metal complexed may be sorbed and which does not necessarily require protonation polyurethane sites but is nevertheless closely related to the weak-base anion-exchange concept.

Table 1: Effect of foam quantity on the absorption of various metal ions Conditions: Volume of the solution: 100ml(10ppm); Temperature: 30±0.5°C

		Percent extraction of metal (%E)											
		Hg(II)		Pb(II)		Cd(II)		Cu(II)		Ni(II)		Cr(VI)	
S. No.	Foam Qty (mg)	A	B	A	B	A	B	A	B	A	B	A	B
1	100	46.0	45.0	15.0	45.0	18.0	32.0	14.0	45.0	14.0	37.0	13.0	37.0
2	200	46.0	60.0	31.0	50.0	22.0	45.0	23.0	58.0	16.0	65.0	16.0	44.0
3	400	47.0	85.0	42.0	72.0	37.0	61.0	36.0	86.0	22.0	78.0	21.0	52.0
4	500	58.0	98.0	55.0	90.0	45.0	80.0	45.0	98.0	38.0	98.0	36.0	65.0

A: Unloaded foams (PUF) * values are an average of three determination

B: APDC-TBP-PUF

Table 2: Breakthrough capacity and Total column Capacity of the metal ions

S.No.	Metal ion	Breakthrough Volume (ml/g)	Breakthrough Capacity (mg/g)	Total column Capacity (mg/g)
1	Hg(II)	100	18.2	37.8
2	Pb(II)	50	9.6	38.6
3	Cd(II)	30	5.9	34.6
4	Cu(II)	50	9.9	30.1
5	Ni(II)	50	9.8	32.5
6	Cr(VI)	20	3.8	26.5

Table 3: Effect of chloride ion on the absorption of various metal ions using PUF-APDC-TBP foam conditions: Volume of the solution: 100ml (10ppm); Temperature: 30±0.5°C

		Percentage Extraction (%E)				
		Concentration of chloride ion (M)				
Sno.	Metal ion	0.01	0.05	0.2	0.5	1.0
1	Hg(II)	98	98	97	8598	65
2	Pb(II)	98	98	98	98	96
3	Cd(II)	98	98	98	97	96
4	Cu(II)	98	98	97	97	96
5	Ni(II)	97	97	97	97	95
6	Cr(VI)	98	98	98	98	98

Effect of Plasticizers: Different plasticizers like dibutyl phthalate, diallyl phthalate, alpha-dinonyl phthalate, tri-n-butyl phosphate loaded on PUF were tested for the extraction efficiency of the metals at pH 4.0 under optimized conditions. The experimental data indicate that the plasticized foam materials will always give higher percentage of extraction than the unplasticized foam. The effect of plasticizers on the extraction efficiency decreased in the following order.

Tri-n-butyl phosphate > dibutyl phthalate > diallyl phthalate >alpha-dinonyl phthalate

Effect of APDC Concentration: The experimental results for the treatment of heavy metal ions indicate that the extraction efficiency of APDC-TBP-PUF vary in the order Hg > Pb > Cd > Cu > Ni > Cr which is also the order of their stability constants with APDC [9, 10].

The amount of metal absorbed also increased with increasing foam quantity (Table 1) and for the same quantity of foam with different bed heights in column studies it was observed that the longer the bed height the higher will be the percent extraction.

Effect of Concentration of Metal Ions: The uptake of metal was determined by taking 500 mg of the foam containing APDC and polyurethane foam in the column by passing 100 ml of the metal ion solution each time with the feed concentrations ranging from 10 to 50 microgram/ml at a flow rate of 1 ml/min.. These results indicated that with increase in the concentration of metal ion the percentage extraction decreased while the mg of metal absorbed

Table 4: Application of PUF-APDC-TBP for the treatment of Raw Sewage Conditions: Column 300 X 200 mm; foam: 3.0 g; volume of the sewage 1000 ml; Flow Rate: 1 ml/min, pH 4.0; Recovery of solvent: acetone; Temperature: 30±0.5°C

Composition of the sewage	Recovery of metal ions (%)	Quantity of metal ion recovered (mg)
Raw Sewage + 1 ml of 10 mg of each of Pb, Hg, Cd, Ni, Cu and Cr	70	417
Raw Sewage + 1 ml of 50 mg of each of Pb, Hg, Cd, Ni, Cu and Cr	82	495

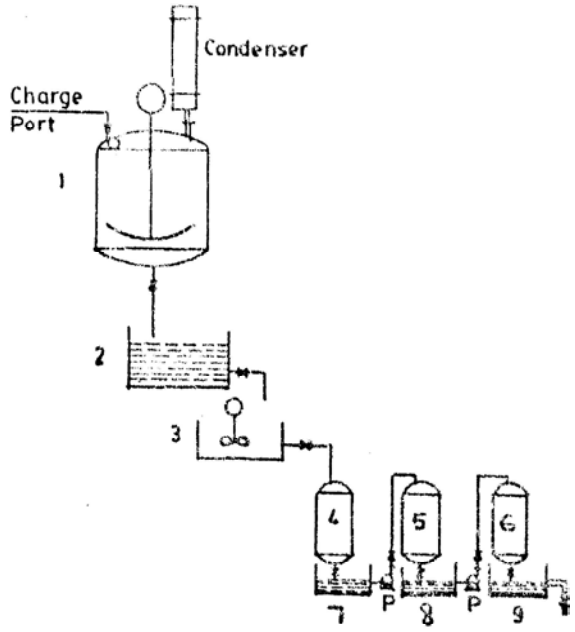

Fig. 1: Flow Chart for Industrial Effluent Treatment and Chloro-alkali solid sludge treatment
1. Reaction Vessel (750 L);
2. Filtration Tank (500 L);
3. Neutralisation Tank (500 L)
4,5,6: Foam columns (2.0 m X 0.5 m)
7,8,9: Collection tanks
P: Transfer Pumps

per g of foam increased. Upto a concentration of 500 mg/L the percentage sorption of mercury is ranging from 58.0 to 98.0% whereas in the case of chromium the percentage sorption from 36 to 65%. Though the sorption percentage decreases as the concentration of metal ion increases ultimately it reaches a constant value.

Effect of Chloride Ion: The effect of chloride ion (which is likely to be associated with these metal ions in the industrial effluents) on the absorption efficiency of APDC-TBP-PUF for various metal ions was tested at different concentrations ranging from 0.01 to 1.0 M and these results are presented in Table 3. The data reveal that chloride ion as NaCl even up to 1.0 M has a negligible effect on the absorption efficiency of the foam for different metal ions except for Hg. However, for Hg above 0.1 M there is a definite decrease in the absorption efficiency and this decreasing tendency increases with the increasing concentration of chloride ion.

Column Studies: In column studies a flow rate of 1 mg/ml and pH 3-5 were found to be optimum for the removal of heavy metal ions. The breakthrough capacity values for various metals using APDC-TBP-PUF at pH 4.0 are shown in Table 2. The effective breakthrough of APDC-TBP-PUF was found to be in the order Hg (18.2) > Pb (9.6) > Cd (5.9) > Cu (9.9) > Ni (9.8) > Cr (3.8).

Applications: Municipal sewage and industrial wastewater containing mercury.

Raw sewage, secondary-treated sewage and waste water from industries and urban waste contain different salts of Ca, Mg, Zn, Al, Cr, Pb, cuy etc along with organic matter which may affect the pH and physical characteristics of the waste, necessitating some general pretreatment like neutralization and filtration etc.

Procedure for Treating Wastewater Containing Mercury: After removal of suspended particles through a filter or sedimentation in a sewage pit, the supernatant liquid was pumped into the pretreatment tank, neutralized and filtered. The clear filtrate was then passed through the APDC-TBP foam column under dynamic conditions for the removal of heavy metal ions before discharge into the drain. The corresponding flow-chart is shown in Fig. 1. the typical results obtained by adopting this procedure for the treatment of municipal sewage effluents are given in Table 4.

Chloro-Alkali Industrial Waste: The typical results for treatment of chlor-alkali industry waste are presented in Table 5. the same flow chart (Fig. 1) which is used for Municipal Sewage and Industrial waste water, is also used for the treatment of chloro-alkali sludge waste. Depending on the nature of the salt used and the method of purification adopted, the mercury content of mud from Indian chloro-alkali industry varies from 500-15600 mg/kg on dry basis, which is far more than in the case of

Table 5: Application of PUF-APDC-TBP for the treatment of Chloro-alkali Wet Sludge Conditions: Column 300 X 200 mm (2 Nos) Flow Rate: 100 ml/min, Recovery of solvent: acetone; Temperature: 30±0.5°C

Composition	Quantity of Hg* extracted (mg)	Volume of solvent (l)	Quantity of Hg* recovered (mg)	Hg Recovery (%)
Wet sludge extract 100 ml (56 ppm)	0.56	0.2	5.5	98
As abaove + $HgCl_2$	0.66	0.2	6.2	95

*Average of six determinations

developed countries like USA and Japan and thus pose a serious health hazard. For example M/s. National Rayon Corporation, Mumbai produced on an average of 3.5 tones/day of brine mud, which contains mercury to the extent of 100-1000 mg/kg of the wet sludge. Since APDC-TBP-PUF was found to be very efficient in the absorption of mercury even when present at low levels, its application for the removal of mercury from the brine mud and other solid wastes was tested as per the following procedure.

The Economic Feasibility: The working cost of the foam material to treat approximately 1000 liters of effluent with a concentration of 100-1000 ppm metal ions was found to be 8 USD. To remove 1 kg of metal ions from 20 KL of the effluent using APDC-TBP-PUF as an absorbing medium, USD 5000 will be sufficient towards the cost of plant machinery. These costs are calculated for one time use of absorbing medium only. Thus the operational costs for the removal of mercury using APDC-TBP-PUF as an absorbing medium are quite marginal taking into account the total cost of the industry and hazardous effects of these effluents on the environment. Further, these operational costs can still be reduced by increasing the number of recycles of the absorbing medium.

CONCLUSIONS

APDC coupled polyurethane foam exhibits a high sorption capacity for a wide range of pH between 3-10, making these sorbents is suitable for the treatment of acidic effluents. The process since is rapid for the uptake of the selected metals which facilitates the treatment of large volume of industrial effluents in short time comparing the process with other normally used sorbents like alumina and activated carbon. These new sorbents can successfully be over a wide range of concentrations which facilitates the direct treatment of metal bearing effluents. The metal ion sorbed can easily be desorbed by using hydrochloric acid. The sorbents does not lose its sorption capacities even a repeated use of 25 times without any recharge. Further it does not exhibit any leaching of chelating agents used in the experiments. The sorption of heavy metal ion is highly specific and quantitative even in the presence of associated ions. The versatility of these sorbents makes them more economically viable and cost benefit treatment. The direct application for the treatment of industrial waste was also demonstrated.

ACKNOWLEDGEMENT

The authors sincerely thank Prof. Y. Anjaneyulu, Retd Professor of JNT University, Hyderabad and Director TLGVRC, Jackson State University, Jackson, Mississippi -39217, USA for his support. One of the author (KSRM) heart fully acknowledge Mr. Ch. Venugopal Reddy, Secretary and Correspondent of Bharat Institutions, Hyderabad for his enormous support to carryout the research work.

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