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Removal of Lead Ion from Aqueous Solutions Using Sawdust Coated by Polyaniline

R. ANSARI * and F. RAOFIE

Chemistry Department,
Guilan University,
Rasht, Iran, POB: 41335-1914
E-mail: *ransari@guilan.ac.ir*

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Abstract: **P**olyaniline was synthesized chemically, coated on sawdust via cast method in the form of emeraldine base (EB) from formic acid as solvent, and used as an adsorbent for removal of lead ion or from aqueous solution. The effects of some important chemical and physical factors in removal efficiency have also been investigated. Among the different parameters, the effect of pH was the most prominent. It was found that metal uptake is occurred under neutral or slightly alkaline conditions, while under relatively strong acidic media, the sorption of the investigated metal ions was negligible and desorption is a predominant process. It was found that undoped PANi (EB form) coated on polar substrates such as sawdust (SD) can be used as an effective adsorbent for removal of heavy metal ions in water and wastewater treatments. All the previous investigations and applications take advantage of the electrical conductivity (metallic), electrochemical (redox activity) and electrochromic properties of the polyaniline. While; in this research, we have taken advantage of the chelating properties of PANi for metal sorption.

Key words: Adsorption, polyaniline, sawdust, lead ion, desorption

Introduction

Heavy metal ions are highly toxic for animals and human beings. Environmental contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities. These metals are of significant importance as they are non-biodegradable and once released into the environment, they can only be diluted or transformed, not destroyed [1].

Heavy metal ions pose a series risk to the environment and endanger public health and the environment. Therefore, they should be removed from water and wastewaters before discharge. The origin of the heavy metal contamination of waters lies in the illegal disposal of industrial effluents, corrosion of the metal pipes used to carry water. Adsorption by activated carbons and ion exchange resins has been widely studied as an effective technique for removing toxic heavy metals such as Hg^{+2}, Cd^{+2}, and Pb^{+2} from aqueous solutions[2-4]. However; these methods suffer from the complete elimination of heavy metals at very low concentrations. So, many investigators are directed towards chemical modifying activated carbon (AC), or other adsorbent surfaces (synthetic or biomaterials), synthesis cation exchanger resins with a chelating group such as iminodiacetic acid and microbial methods to increase removal efficiency of heavy metals ions from aqueous solutions [5, 6]. Adsorption of metals by modified AC can be correlated to its both physical and chemical nature and metal sorption by AC is mostly due to the surface complex formation between the metal ions and the acidic surface functional groups [7,8]. The removal efficiency is influenced by many parameters such as surface area and other physical properties of the adsorbent, adsorbate concentration, solution pH, sorbent dosage and its modification procedure. Polyaniline is a well-known conducting/electroactive polymer. It is one of the most potentially useful conducting polymers and has received considerable attention in recent years by many investigators [9-16].

Recently some investigators directed their research toward application of conducting polymers (e.g. polypyrrole, polyaniline) for water softening and removal of heavy metal ions from aqueous solutions [7]. The principle is based on the switchable ion exchange properties of conducting polymers. The application of electrochemically controlled ion-exchange for water and wastewater treatment in order to removing of heavy metals offers certain ecological and economic advantages because its electrochemical regeneration is accompanied by without any chemical additives.

The unique electrical/electrochemical properties of PANi, have led to use this polymer in various applications such as sensors, rechargeable batteries, light emitting diodes, smart windows, non linear optical and energy storage devices, anti-static and anti-corrosion coating materials[16,18]. Polyaniline can be easily synthesised either chemically or electrochemically from acidic aqueous solutions. Chemical polymerisation of aniline in aqueous acidic media (bronsted acid) can be simply performed using of oxidising agents such as $(NH)_4S_2O_8$, KIO_3 and $K_2Cr_2O_7$. Chemical structure of PANi can be shown as in Figure 1.

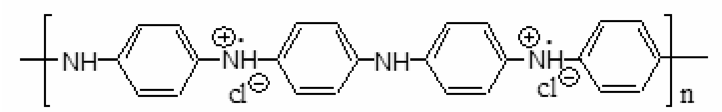

Figure 1 Chemical structure of polyaniline as synthesized and acid doped(PANi/HCl)

All of the previously reported of polyaniline conducting polymers are based on its interesting and unique electrical conductivity (metallic) and electoactivity. However; this paper deals with the new potential application of polyaniline as a cation exchanger material useable for environmental protection in water and wastewater treatment technology. Based on the polymer structure and its dependence on the nature of dopant acid and pH, a range of chemical processes such as ion exchange, complex formation, precipitation and even enzyme reactions can be carried out on polymer surface. This finding should be very important and promising for application of polyaniline in future water and wastewater treatment technology.

Experimental

Reagents

The entire chemicals used were of analytical reagents (AR grade). All solutions were prepared in Milli-Q water. Aniline (Merck) was purified by vacuum distillation and stored in freeze before polymerization.

Adsorption experiment and preparation of PANi/SD adsorbent

Polyaniline was synthesized chemically as described previously using potassium dichromate as oxidant. After purification and changing it into emeraldine base (EB) by treatment with a dilute ammonia solution (0.5M) or NaOH 0.2 M, it was dried and then dissolved in concentrated formic acid (%88). A layer of PANi coated on sawdust (SD) via cast method. The detailed procedure of preparation polyaniline, and adsorbent can be found in our previous report that we employed this adsorbent for removal of Cr(VI) ion from aqueous solutions[19]. The sawdust coated by PANi filtered and then dried at ~60 ^{o}C in an oven for removing the remained solvent. Sawdust coated by polyaniline (PANi/SD) used for sorption of lead ion.

A glass column with dimensions of 1cm diameter and 10cm length equipped with a glass frit was employed as fixed packed bed for column adsorption experiments. A solution of 100 ppm of lead ion in distilled water obtained from $Pb(NO_3)_2$ salt was used as synthetic polluted test solution. Lead ion solution for adsorption experiments and calibration curve preparation was prepared from a $Pb(NO_3)_2$. Quantitative determination of lead was carried out using atomic absorption spectroscopy (AAS). For concentrations below 10 ppm wavelength of 217 nm and slit 10mm, for concentrations of 10-100 ppm the wavelength of 261.4 nm and slit 0.5 mm were used. The evaluation of the metal uptake was performed according to: $X = V (C_i – C_e)w^{-1}$, where V is the volume of inlet solution, C_i and C_e are the inlet (initial) and outlet (unadsorbed) concentration respectively, and w is the dry weight of adsorbent.

Results and Discussion

(I) Adsorption studies using PANi (Batch system)

(i) Effect of initial concentration

For performing this experiment, 50 mg polymer (PANi powder) was treated with 5 mL of 10 ppm Pb^{2+} for 30 minutes accompanied by shaking (200rpm). Unadsorbed lead was analyzed after separation the sorbent by centrifuge. The results obtained are shown in Figure 2.

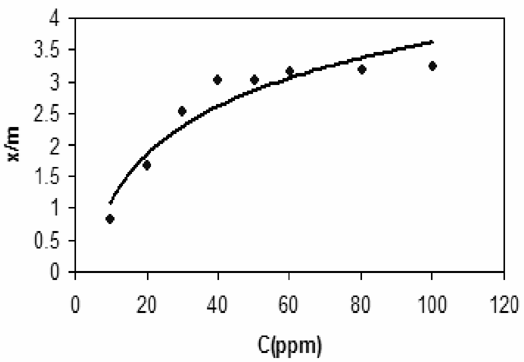

Figure 2. Effect of initial concentration on the removal of lead ion by PANi

As the results show, increasing initial concentration of adsorbate (Pb^{2+}) leads to an increase in adsorption percent.

(ii) Effect of sorbent dosage

In this experiment different weights of adsorbent PANi (EB form) (0.10-1.0 g) were treated with 5.0 mL lead solutions with constant concentration of 100 ppm. All the other conditions were the same as used for Figure 2. The results obtained are shown in Figure 3.

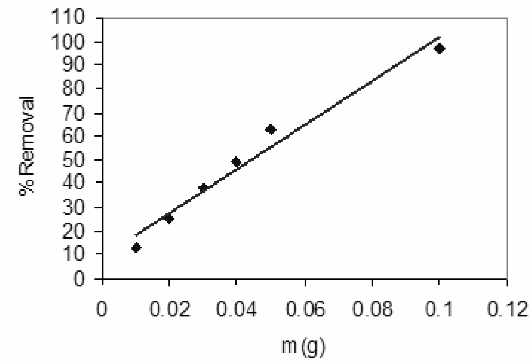

Figure 3. The effect of sorbent dosage (PANi) on Pb^{2+} sorption

As our results show, with increasing sorbent dosage (PANi), sorption percent increases. According to the results shown in Figure 3, 0.10 g of PANi/SD can completely clean 5 mL 100 ppm aqueous solution contaminated by lead ion.

(iii) Effect of pH

For this investigation, 50 mg of sorbent (PANi) were treated with 5 mL of Pb^{2+} ion (50 ppm) at different pH values (0 - 6). The pH of solutions was adjusted using dilute HNO_3 solution (0.1M). The results obtained are shown in Figure 4.

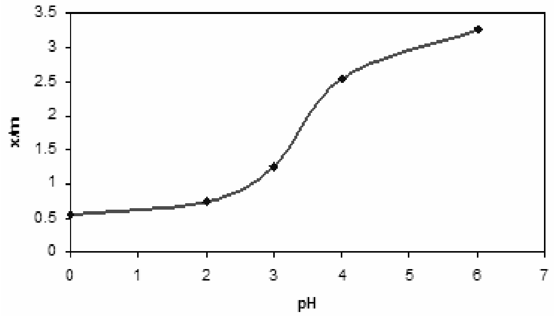

Figure 4. The effect of pH on Pb^{2+} sorption by PANi

As our results show, with increasing the pH of metal solution, sorption of lead ion is increased and in acidic media (pH < 4) the sorption of metal ions is very poor. With increasing the pH of treated solution, the polymer is changed into undoped form, then free amine or imine groups in the polymer will be available for metal chelating, so the sorption of Pb^{2+} ion is increased considerably. At acidic pH values, polyaniline is changed into acid doped state (-N groups are protonated), so the polymer can not function as a ligand or chelating agent, therefore, the metal uptake is not occurred.

(II) Adsorption Studies using PANi/SD sorbent (batch system)

(i) Effect of initial concentration

For performing this experiment, 100 mg adsorbent (PANi/SD) were treated with 10-100ppm lead ion solutions and the results are shown in Figure 5.

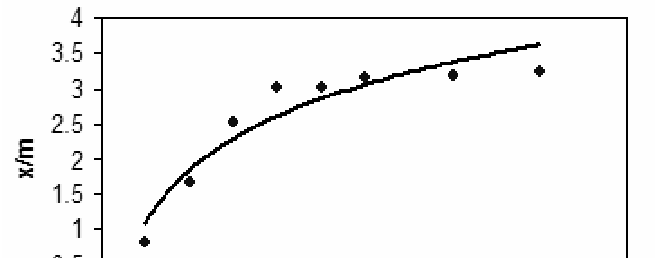

Figure 5. Effect of initial concentration on the removal of lead ion by PANi/SD. The adsorption experimental conditions and calculations were as described in Figure 2.

In order to have a better comparison, uncoated SD was also used for adsorption of lead ion and the results obtained were shown in Figure 6.

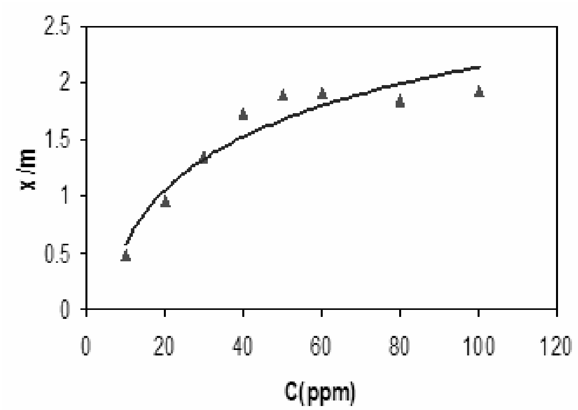

Figure 6. Effect of initial concentration on the removal of lead ion using sawdust (SD) as sorbent.

Our results indicate that the sorption of lead ion by both PANi/SD increases with increasing the initial concentration of metal ion. The lead ion can also be sorbed by SD but the sorption percent is much lower than PANi/SD.

(ii) Effect of sorbent dosage

For performing this research, 5.0 mL of 100 ppm lead ion was treated with different weights of SD and PANi/SD sorbents with the same particle size (35-50 mesh). The results obtained are shown in Figure 7**.** As our results show (Figure 7), increasing sorbent dosage leads to complete elimination of lead ion from treated solution.

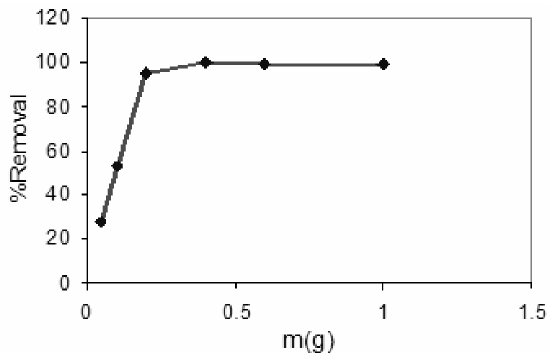

Figure 7 Effect of sorbent dosage on sorption of lead ion

(iii) Effect of contact time

For this investigation 0.10 g of PANiEB/SD or SD were mixed with 5 mL of 100 ppm lead ion at different exposure times(5-120 min). The samples after filtration were analyzed for unadsorbed lead ion. The results are summarized in Figure 8. As it is indicated, sorption of metal ion is increased by increasing exposure time.

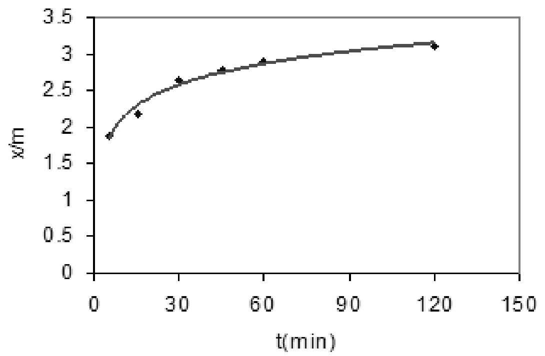

Figure 8. Effect of exposure time on lead sorption or removal by SD and PANiEB/SD

(iii) Effect of agitation

For this investigation 0.10 g of PANiEB/SD or SD were mixed with 5 mL of 100 ppm lead ion for constant exposure time (30 min) at different rates of shaking (0-250 rpm). The samples after filtration were analysed for unadsorbed lead ion. The results are summarized in Figure 9.

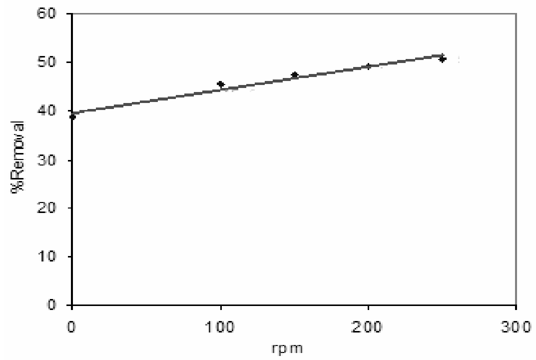

Figure 9. Effect of agitation rate on Pb^{2+} sorption PANi/SD

As it is demonstrated, lead ion uptake by PANi/SD is improved by increasing the rate of agitation.

(v) Effect of pH

For this investigation 0.10 g of PANi/SD or SD were mixed with 5 mL of 50 ppm lead ion for 30 min at different pH values using dilute HNO_3. The samples were also agitated with the rate of 200rpm during exposure. Then, the samples were filtered and analysed for unadsorbed lead ion. The results are summarized in Figure 10.

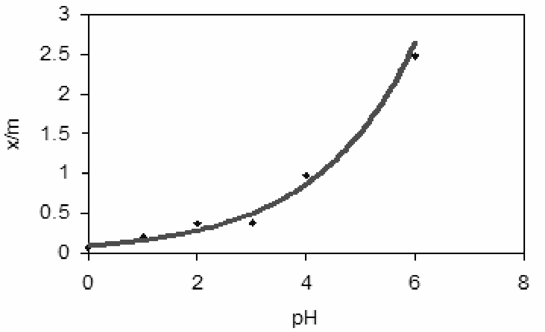

Figure 10. Effect of pH on lead sorption by PANi/SD

As we have already observed in the case of pure PANi, higher lead ion sorption is observed for PANi/SD at higher pH values too.

(vi) Desorption study

When a solid sorbent is applied for sorption of pollutants (organics or inorganics), the possibility of regeneration of the sorbent is a great importance from the point of application view in industries. However; complete regeneration is not always possible. In this research for desorption study, 0.10 g of PANi/SD was first treated with 5.0 mL of 100 ppm lead ion in distilled water for 30 min. For regeneration of the sorbent or recovery of lead ion, sorbent containing lead ion were treated with 5 mL of HNO_3 0.5 M at RT. The results obtained (sorption and desorption) are shown in Table 1.

Table 1 Regeneration of exhausted PANi/SD sorbent

PANi/SD g (weight)	%Regenration with 5 mL H_2O	%Removal	%Regenration With 5 mL HNO_3
0.10	~ 0	52	68
0.10	~ 0	50	73
0.10	~ 0	50.5	84.5
0.10	~ 0	49	82.5
0.10	~ 0	51	74.0

Simple washing with distilled water can not remove the sorbed metal ions. Employing HNO_3 as a regenerant solution, it is possible to regenerate the used adsorbent up to 70-75 percent.

(vii) Sorption of lead ion using Regenerated PANi/SD

In order to performing this experiment, 0.10 g of regenerated PANi/SD was treated with 5 mL of 50 ppm lead ion prepared in distilled water and then agitated with 200rpm for 30 minutes. It was observed that the regenerated sorbent can effectively adsorb lead ion without any important loss in its sorption capacity compared to unused state (Table 2). The loss in sorption capacity was about 2%.

Table 2 Sorption of lead ion by regenerated PANi/SD sorbent.

PANiEB/SD g	C(ppm)	V(ml)	rpm	Time (min)	%Removal
0.1	50	5	200	30	%97.5
0.1	50	5	200	30	%96.4
0.1	50	5	200	30	%98.2

0.1	50	5	200	30	%97.8

(III) Adsorption studies using PANi/SD sorbent (Column systems)

Parameters obtained in batch processes are useful in providing information for continuous or column systems that are more practical in industries for treatment systems. However the data obtained in batch experiments are generally not valid for continuous flow systems. It is therefore, necessary to perform flow test using column in the assessment of the usefulness of a system in real applications. It is also needed to mention that polyaniline is finely divided or powdered form and can not be used in column system because of resulting important pressure drop of the liquid passed through the column. Therefore, column system was used for PANi/SD as sorbent, but for batch investigation both PANi or EB and PANi/SD was employed.

(i) Effect of initial concentration of Pb^{2+} ion

In this experiment, 1.0 g of sorbent (PANi/SD) packed in a glass column (1cm × 10 cm dimensions). The column was first washed with 0.1 M HCl and 0.5 M ammonia solutions separately. The column was finally washed with distilled water. Then, 10 mL of lead ion solution with different initial concentrations (10-100 ppm) passed through the column with flow rate of 3 mL/min at room temperature. The results obtained are shown in Figure 11.

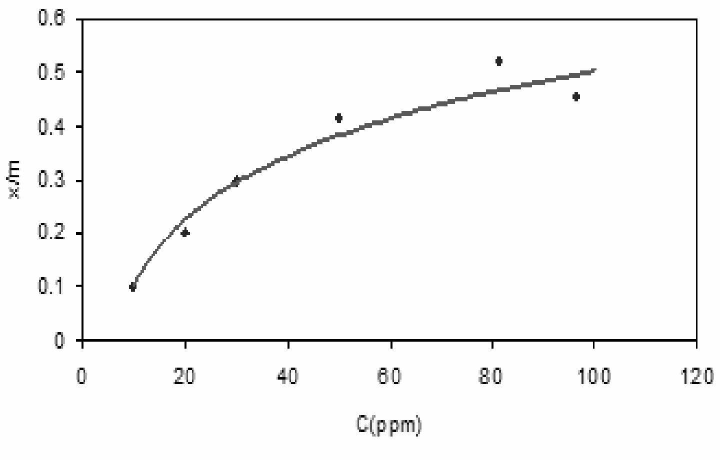

Figure 11. Effect of initial Pb^{2+} ion concentration on sorption by PANi/SD column.

(iii) Effect of flow rate

In this part of investigation, 50 mL of lead ion with concentration of 100 ppm passed through the column containing 1.0 g PANi/SD sorbent with different flow rates (1-5 mL min^{-1}). The results are summarized in Figure 12.

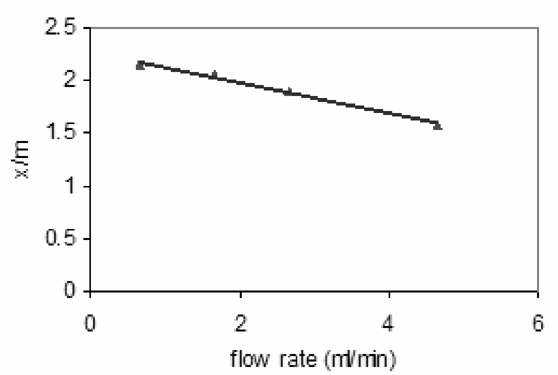

Figure 12. Effect of flow rate on sorption of lead ion by PANi/SD column

According to the results obtained, it can be concluded that increasing flow rate of liquid through the column, % sorption decreases. Efficient removal of lead ion can be achieved at low flow rates of solutions in column system.

(iv) Effect of pH

In order to investigate the effect of pH on sorption of Pb^{2+} ion by PANi/SD column, 1.0 g of sorbent packed in glass column as described before. 50 mL of Pb^{2+} solution (100 ppm) at different pH (from 0 to 6 using HCl) passed through the column with flow rate of 3ml/min at RT. The results obtained are shown in Figure 13.

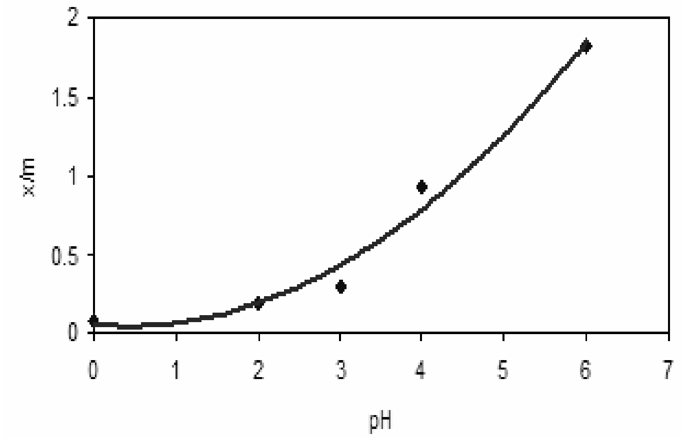

Figure 13. Effect of pH on Pb^{2+} sorption by PANi/SD column

As our results show, sorption of Pb^{2+} ion increases as pH of treated solution increases. However at higher pH values (alkaline), precipitation of Pb^{2+} ions may occur as well. The same finding was obtained in our batch system investigation.

(v) Breakthrough curves for SD and PANi/SD sorbents

In this experiment, 1.0 g of PANi/SD packed in a glass column, and then Pb^{2+} solution with concentration of 50 ppm passed through the column with constant flow rate (3 mL min^{-1}). Each time 10 ml was poured into the column. The outlet solution was analyzed for unadsorbed Pb^{2+} ion in order to obtain the break through curve. The results obtained are shown in Figure 14.

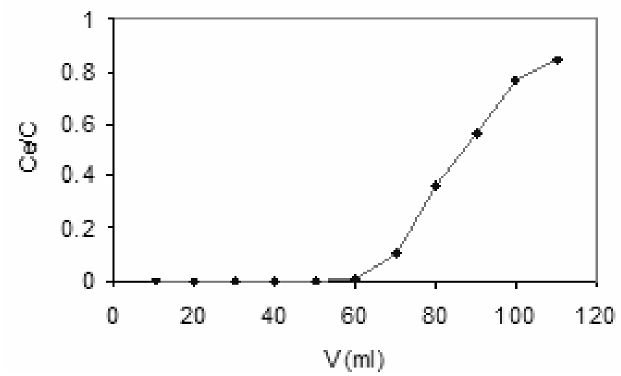

Figure 14. Breakthrough curves obtained for adsorption of lead ion by PANi/SD column.

As the results show (Figure 14), our recent developed adsorbent can be used effectively in contineous or column systems. 60 mL of meccuric solution with concentration of 50ppm can be completely purified by the column containing 1.0 g PANi/SD sorbent.

(vi) Desorption study

For performing this investigation, 10 mg of adsorbent (PANi /SD) was first treated with 5 ml of Pb^{2+} with concentration 100 ppm (sorption was %50). The exhausted column was then treated with 0.5 M HCl solution for 5 minutes for regeneration. The analysis showed that 60 - % 65 of the sorbed metal (lead ion) could be recovered. Increasing exposure time or concentration of regenerant (HCl), recovery percent might be improved. It should also be remembered that biomaterials (e.g. SD) are not very stable in strong acidic or basic conditions. Therefore; application strong acidic or basic media should be avoided when we work with biomaterials.

Conclusion

Polyaniline can be easily synthesized chemically directly on sawdust or coated via cast method. Sawdust which is a very cheap and environmental friendly material was found to be a suitable substrate for coating of PANi in order to be used in water and wastewater treatments for removal of heavy metal ions from solutions both for batch and column systems. Sorption or metal uptake by our recently developed sorbent seems to be occurred mostly via complex formation reaction or chelating between metal ion and amine groups in polymer (PANi). In acidic media the amine groups are protonated, so desorption of metal ion is occurred. Under neutral conditions, PANi exists in deprotonated form, so the free -N groups will be available for metal chelating. Sorption/desorption of lead ions by PANi, is mostly reversible and the processes can be simply controlled by *pH* of solution. The finding in this paper is very important from application point of view for water and wastewater treatments in order to remove toxic heavy metal ions.

References

1. Tramontina J, Marchado G, Azambuja D S, Piatnicki C M S and Samios D, *Material Research*, 2001,**4**, 195.
2. Rengaraj S, Kyeong-Ho Yeon, Seung-Hyeon Moon, *Journal of hazard. Mat*er., 2001, **B87**, 273.
3. Gomez Serrano V, Garcia A M and Mansilla A E, *Journal of Water Res.*,1998, **32** 1.

4. Bansode R, Losso J N, Marshall W E and Rao R M, *Biosource technology*, 2003, **89**, 115.
5. Kadirvelu K, Thamaraiselvi K and Namasivayam C, *Biosource Technology*, 2001,**76**, 63.
6. Anoop Kapoor, Viraraghavan T and Roy Cullimore D, *Biosource Technology*, 1999,**70**, 95.
7. Weidlich C, Mangold K M and Juttner K, *Electrochimica Acta*, 2001, **47**, 741.
8. Ansari R and Omidvari R, *Polish Journal of Environmental Studies*, 2005,**14** ,191.
9. Zeng X. R. and Man Ko T., *Polymer*, 1998, **39** , 1187.
10. Gospondinova N and Terlemezyan, *Prog. Polym. Science*, 1998, **23**,1443.
11. Kang E T, Neoh K G and Tan K L*, Prog. Polym. Science*, 1998,**23**, 277.
12. Negi Y S and Adhyapak, *J. Macromol. Sci. Polym. Rev*., 2002,**C 42**, 35.
13. Hung W S, Humphrey B D and Mac Diarmid A G, *Chem. Soc. Farad. Trans.*, 1986, **82**, 2385.
14. Cao Y, Andreatta A, Heeger A J and Smith P, *Polymer*, 1989, **30**, 2305.
15. Chiang J C and MacDiarmid A G, *Synthetic Metals*, 1989, **13**, 193.
16. Focke W W, Wnek G E, and Wei Y, *J. of Physical Chemistry* and references therein, 1987, **91,** 5813.
17. Gurunathan K, Murugan A. V, Marimuthu R, Mulik U P and Amalnerkar D P, *Material Chemistry and Physics*, 1999, **61**, 173.
18. Foot P J and Simon R, J. Phys. D: *Appl. Phys*., 1989, **22**, 1598.
19. Ansari R, Aliakbar A and Masoudi M, *Journal Polymer Materials*, 2005, **2**, 75.