



Removal of Mercuric 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

Received 12 October 2005; Accepted 23 January 2006

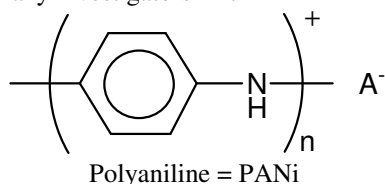
Abstract: This paper deals with a new application of polyaniline synthesized chemically, coated on sawdust via cast method in the form of emeraldine base (EB) from formic acid as solvent, and used as an effective adsorbent for removal of mercuric ion or other heavy metals from aqueous solution. Among the different parameters investigated, the effect of pH was found to be 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.

Key words: Adsorption, polyaniline, sawdust, mercuric ions, desorption

Introduction

Heavy metal ions such as mercuric, lead and cadmium 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 destroyed¹. They 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 solutions²⁻⁴. 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 (shown below) 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 investigators⁹⁻¹⁷.



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, 12}. The principle is based on the switchable ion exchange properties of conducting polymers. We have already shown that polyaniline in acid doped state (PANi/HCl) can be used as anion exchanger for removal of toxic anions such dichromate¹².

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 PAN, have led to use this polymer in various applications such as sensors, rechargeable batteries, light emitting diodes(LED), smart windows, non linear optical and energy storage devices, anti-static and anti-corrosion coating materials^{17, 19}. 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 easily performed using of oxidising agents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KIO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ (**Figure 1**).

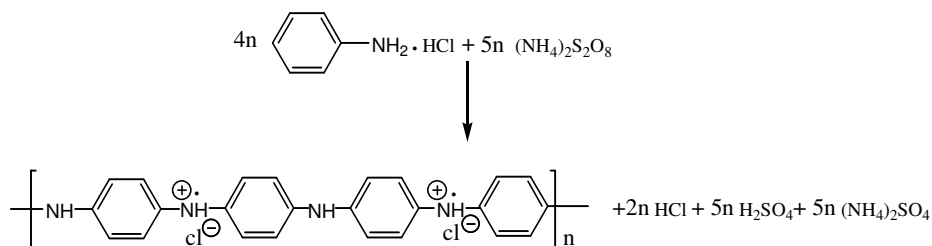


Figure 1. Chemical polymerization of polyaniline (PANi)

Polyaniline can exist in various oxidation states characterized by the ratio of imine to amine nitrogen¹¹. Upon simple treatment of polymer with dilute alkaline solutions (e.g. NH_3 or NaOH) or it changes into a material called emeraldine base (EB) consists of equal numbers of reduced and oxidised repeat units (**Figure 2**).

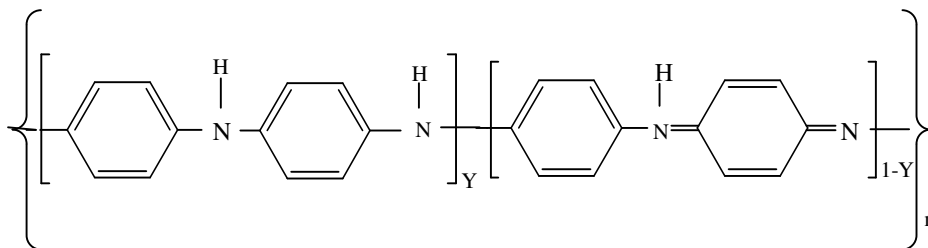


Figure 2. Emeraldine form of polyaniline (EB)

Where, the values for Y can be between 0 (completely oxidized state) to 1 (completely reduced state). PAN can exist in four different oxidation states: leucoemeraldine; pernigraniline, emeraldine base (intermediate form) and emeraldine salt (conductive form). Emeraldine base (EB) is an important form of polyaniline which has an ideal structure with the Y value of 0.5 (50% oxidized). It is insoluble in water and common organic solvents. It is soluble in few solvents such as formic acid (88%), and 1-methyl 2-pyrrolidinone (NMP). This permits it to be solution processed to produce large, flexible, free standing films or coating the solid supports through casting. Emeraldine base (insulator state of PANi) then can be protonated (doped) with a non-oxidising protonic acid such as HCl , H_2SO_4 or *p*-toluene sulfonic acid. 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, complexation, precipitation and even enzyme reactions can be carried out on polymer surface. All of the previously reported of polyaniline conducting polymers are based on its interesting and unique electrical conductivity (metallic) and electroactivity. 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. This finding should be very important and promising for application of polyaniline in future water and wastewater treatment technology.

Due to the strong adsorption of mercuric ion to polyaniline film, it has been recently reported that polyaniline coated mercury thin film electrodes have been successfully used for determination of heavy metal ions (e.g. Zn , Pb , Cd) in water samples with anodic stripping voltammetry (ASV) technique²⁰.

Experimental

Sawdust (35–50 mesh size) was used as solid support for coating of polyaniline. Polyaniline (PANi) was synthesized chemically using potassium dichromate as oxidant, and then changed into emeraldine from (EB) by treatment with a dilute alkaline solution (0.2M NaOH). Sawdust coated by polyaniline (EB form) prepared through cast method from formic acid. The detailed procedure for preparation of polyaniline coated on sawdust (PANi/SD) can be found in our previous publication.

Sorption experiments of mercuric ion by our recently developed adsorbent were carried out using both batch and column systems at room temperature. A glass column with dimensions of 1cm diameter and 15cm length was employed as fixed packed bed for adsorption experiments. A solution of 100 ppm of mercuric ion in distilled water (pH= 5-6) obtained from HgCl_2 salt was used as synthetic polluted test solution.

Determination of mercuric ion was carried out spectrophotometrically and a calibration curve obtained from standard solutions of mercuric ion (0-10ppm). Mercuric ion makes a very stable chelate with dithizone ($K_f = 10^{27}$) and is readily extracted into an organic solvent such as chloroform or CCl_4 with high efficiency even in acidic media. Spectrophotometric determination of mercuric ion as dithizonate in chloroform was performed at 485nm (λ_{max} obtained from absorption spectrum). 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) Investigation of removal of mercuric ion by PANi/SD using batch system

• Effect of initial Hg^{+2} concentration

In this experiment, 50 mg pure adsorbent (PANi) was treated with 5 mL of mercuric ion at different initial concentrations (1-100 ppm) for 30 minutes accompanied by stirring (200 rpm). For performing the experiment with PANi/SD, 10 mg adsorbent was treated with 10-100 ppm mercuric ion solution. The results are shown in **Figures 3a** and **3b**.

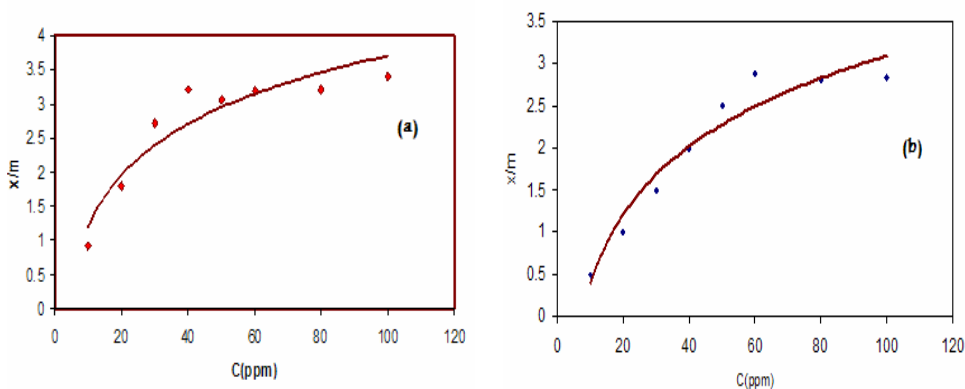


Figure 3. Effect of initial concentration on the removal of mercuric ion by: (a) pure PANi powder, (b) PANi/SD

Our results indicate that the sorption of mercuric ion by both PANi and PANi/SD sorbents increases with increasing the initial concentration of the mercuric ion.

• Effect of sorbent dosage on adsorption of mercuric ion by PANi/SD

In this experiment different weights of adsorbent (PANi/SD) (0.05-1.0 g) were treated with 5 mL mercuric ion solutions with constant concentration of 100 ppm. As our results show (**Figure 4**), with increasing sorbent dosage up to 0.30g, sorption percentage is increased.

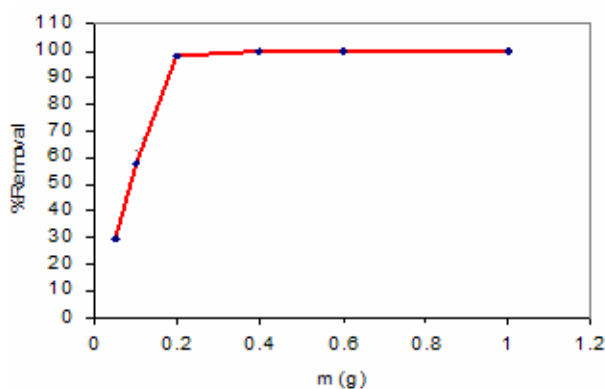


Figure 4. The effect of sorbent dosage on Hg^{2+} sorption

- **Effect of pH**

For this investigation, 10 mg of sorbent (PANi /SD) were treated with 5 mL of Hg^{2+} ion (50 ppm). The pH of solutions was adjusted using dilute nitric acid solution (0.1M). The results obtained are shown in **Figure 5**.

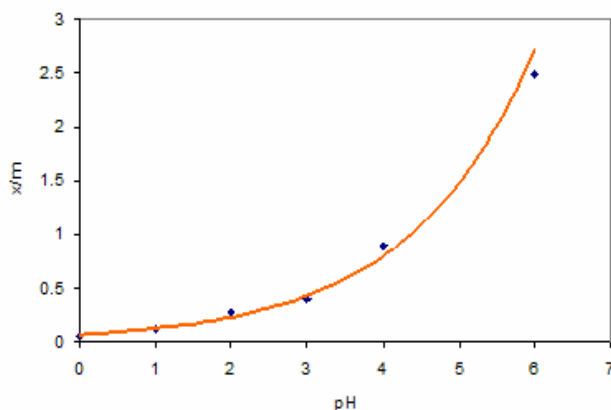


Figure 5. The effect of pH on Hg^{2+} sorption by PANi /SD

As our results show, with increasing the pH of solution, sorption of mercuric ion is increased and in acidic media ($\text{pH} < 4$) the sorption of metal ions is decreased substantially. 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 Hg^{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.

- **Effect of exposure time**

For performing this experiment, 10 mg of adsorbents (PANi/SD), were treated with 5 mL of 100 ppm mercuric ion for different periods (5- 120 minutes) accompanied by stirring at RT. The results of adsorption obtained from the analysis of unadsorbed Hg^{2+} ion in solution are shown in **Figure 6**.

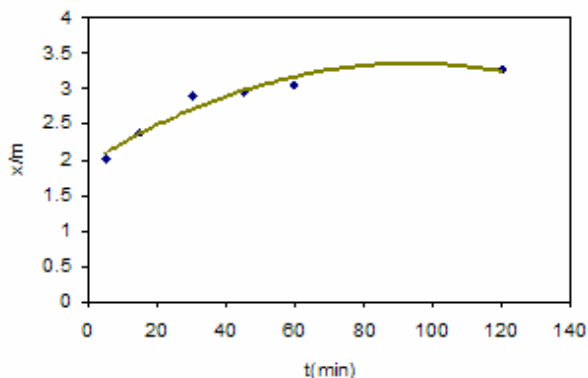


Figure 6. The effect of agitation time in sorption of Hg^{2+} ion by PANi/SD

As our results shown in Fig. 6 show, metal uptake by PANi/SD sorbents is increased with increasing exposure time within 60 minutes, and then it is become nearly constant.

- **Effect of agitation time**

In this experiment 0.10 g of adsorbents were treated with 5 mL of 100 ppm Hg^{2+} solutions for duration of 30 minutes at RT. The samples were stirred under different rates (0 – 250 rpm) using a shaker. The results obtained are summarized in **Figure 7**.

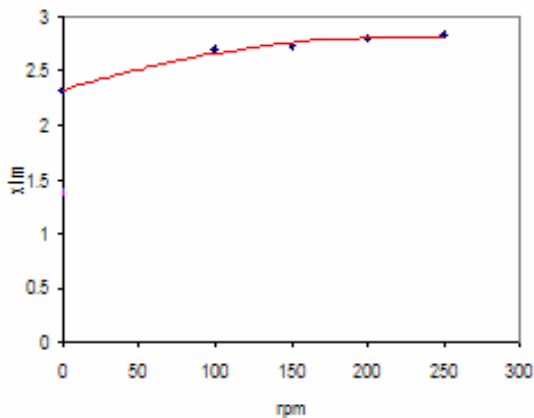


Figure 7. The effect of stirring rate on Hg^{2+} sorption by PANi/SD

As our data show, stirring rate does not affect sorption of mercuric ion substantially. It means that PANi/SD seems to be a very quick sorbent for mercuric ion from aqueous solutions.

- **Desorption studies**

For performing desorption studies, 10 mg of adsorbent (PANi /SD) was first treated with 5 ml of Hg^{2+} with concentration 100 ppm. The exhausted column was then treated with 0.1-0.5 M HCl solution for 5 minutes for regeneration. From results, it can be suggested that a change of pH could desorb the metal from PANi/SD, notably in acidic pH conditions. Under the specified conditions used in this experiment about %50 of metal was adsorbed under neutral conditions, when HCl from 0.1 to 0.5 M was used as regenerant, 60 - % 65 of metal was recovered.

(ii) Investigation of removal of mercuric ion by PANi/SD using column system

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.

•Effect of initial concentration of Hg^{2+}

In this experiment, 2.0 g of sorbent (PANi/SD) packed in a glass column (1cm \times 15 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 20 mL of mercuric 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 8**.

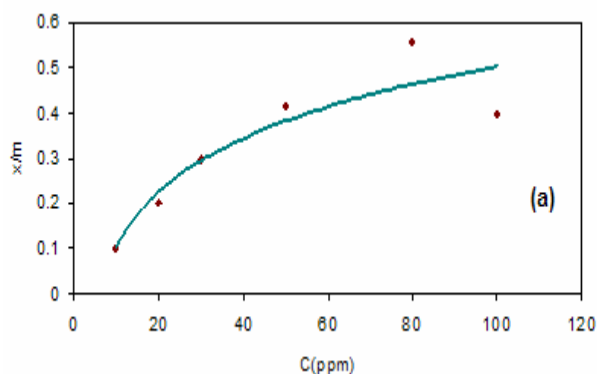


Figure 8 Effect of initial Hg^{2+} ion concentration on sorption by PANi/SD column

As our results indicate, with increasing the initial concentration of mercuric ion, sorption percentage of mercuric ion is increased.

•Effect of pH

In order to investigate the effect of pH on sorption of Hg^{2+} ion by PANi/SD column, 2.0 g of sorbent packed in glass column as described in Figure 8. 50 mL of Hg^{2+} solution (100 ppm) at different pH (from 0 to 6 using HCl) passed through the column with flow rate of 3 mL/min at RT. The results obtained are shown in **Figure 9**.

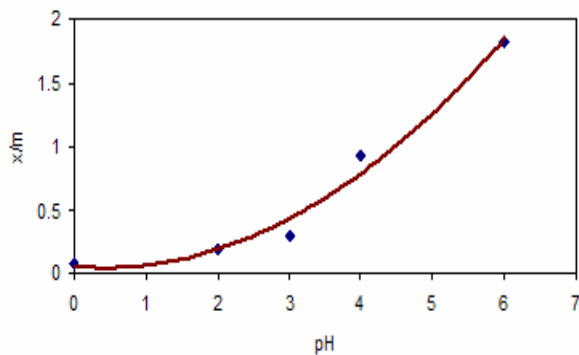


Figure 9. Effect of pH on Hg^{2+} sorption by PANi/SD column

As our results show, sorption of Hg^{2+} ion increases as pH of treated solution increases. However at higher pH values (alkaline), precipitation of Hg^{2+} ions may occur as well.

•Breakthrough curves for PANi/SD

A plot of effluent solute concentration vs. time usually yields as S- shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion. When working sorption experiments with columns, the breakthrough curves are very useful. In this experiment, 2.0 g of PANi/SD packed in a glass column, and then Hg^{2+} solution with concentration of 50 ppm passed through the column with constant flow rate (3ml/min). Each time 10 ml was poured into the column. The outlet solution was analyzed for unadsorbed Hg^{2+} ion in order to obtain the break through curve. The results obtained are shown in **Figure 10**.

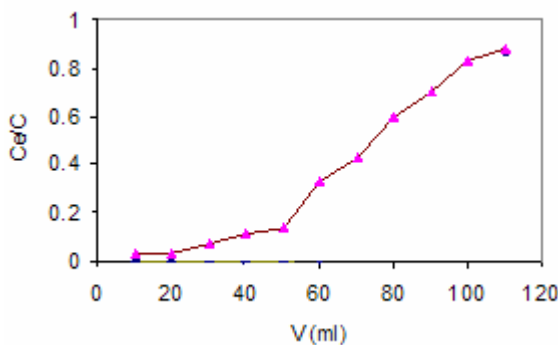


Figure 10. Breakthrough curves obtained for PANi/SD column

As the results show our recently developed adsorbent can be used effectively in continuous or column systems. 60 mL of mercuric solution with concentration of 50 ppm can be completely purified by the column containing 2.0 g PANi/SD sorbent.

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 in 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 Hg^{2+} ions by PANi, is mostly reversible and the processes can be controlled by simple pH of solution. The finding in this paper is very important from application point of view for water and waste water treatments in order to remove poisonous heavy metal ions.

References

1. Tramontina J, Machado 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. Mater.*, 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 D, Cullimore, *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** (2), 277.
12. Ansari R, Aliakbar A and Masoudi M, *Journal Polymer Materials*, 2005, **2**, 75
13. Negi Y S and Adhyapak, *J. Macromol. Sci. Polym. Rev.*, 2002, **C 42**, 35.
14. Hung, W S , Humphrey B D and MacDiarmid A G, *Chem. Soc. Farad. Trans.*, 1986, **82**, 2385.
15. Cao Y, Andreatta A, Heeger A J and Smith P, *Polymer*, 1989, **30**, 2305.
16. Chiang J C and MacDiarmid A G, *Synthetic Metals*, 1989, **13**, 193.
17. Focke W W, Wnek G E, and Wei Y, *J. Physical Chemistry* and references therein, 1987, **91**(No 22), 5813.
18. Gurunathan K, Murugan A V, Marimuthu R, Mulik U P and Amalnerkar D P, *Material Chemistry and Physics*, 1999, **61**, 173.
19. Foot P J and Simon R, *J. Phys. D: Appl. Phys.*, 1989, **22**, 1598.
20. Denise Alves Fungaro, *Sensors* , 2001, **1**, 206.