Polymer-based adsorbent for heavy metals removal from aqueous solution

H N M E Mahmud1*, A K O Huq1,2 and R Yahya1
1Department of Chemistry, University of Malaya, 50603, Kuala Lumpur, Malaysia
2Department of Food Technology and Nutritional Science, Mawlana Bhashani Science and Technology, University, Santosh, Tangail-1902, Bangladesh

E-mail: ekramul@um.edu.my

Abstract. A novel conducting polymer-based adsorbent, polypyrrole (PPy) fine powder has successfully been prepared as a new adsorbent and utilized in the adsorption of heavy metal ions like arsenic, zinc and cadmium ions from aqueous solution. PPy was chemically synthesized by using FeCl3.6H2O as an oxidant. The prepared PPy adsorbent was characterized by Brunauer-Emmet-Teller (BET) surface analysis, field emission scanning electron microscopy (FESEM) and attenuated total reflectance fourier transform infrared ATR-(FTIR) spectroscopy. The adsorption was conducted by varying different parameters such as, contact time, pH and adsorbent dosage. The concentrations of metal ions were measured by inductively coupled plasma mass spectroscopy (ICP-MS). The results show that PPy acts as an effective sorbent for the removal of arsenic, zinc and cadmium ions from aqueous solution. The as-prepared PPy fine powder is easy to prepare and appeared as an effective adsorbent for heavy metal ions particularly arsenic in wastewater treatment.

1. Introduction
Industrial wastewaters containing heavy metal ions such as As(III)/As(V), Pb(II), Cd(II), Ni(I), Cr(III)/Cr(VI), Zn(II), Cu(II), Hg(I)/Hg(II), Co(II) etc. are directly or indirectly discharged into the streams, lakes, rivers or oceans [1]. Usually, heavy metals cannot be decomposed or biodegraded. Various methods such as chemical precipitation, ion-exchange, membrane filtration, adsorption, electrochemical technologies etc. are applied for the removal of various heavy metal ions from wastewater or aqueous solution [2]. Among them, adsorption is widely used because of low cost, simple design and ease of operation [3].

Some conducting polymer based-adsorbents like polyaniline, polypyrrole (PPy) and their composites have received considerable attention due to their potential application as adsorbents of heavy metal ions such as chromium, lead, zinc, copper, nickel etc. from aqueous solution [2,3]. Polypyrrole based-adsorbents play a major role in removing heavy metal ions due to their ease of synthesis, biocompatibility and redox properties. Since the adsorption efficiency largely depends on the preparation conditions of PPy, a lot of efforts have been made to remove heavy metal ions by polypyrrole conducting polymer prepared by chemical oxidative polymerization of pyrrole in presence of various oxidants at different conditions [4,5].

In this present effort, polypyrrole fine powder, a novel conducting polymer, has been chemically synthesized paying attention to the monomer to oxidant ratios for the removal of arsenic, zinc and cadmium ions from aqueous solution. The effects of different parameters such as adsorbent dosage, contact time and initial pH on the uptake of arsenic, zinc and cadmium ions have been investigated.

2. Materials and methods
2.1. Materials
High purity chemicals were used in all reagents and the stock solution was prepared using deionized water. Freshly distilled pyrrole (Sigma-Aldrich) was used as monomer and ferric chloride hexahydrate (Sigma-Aldrich) was used as an oxidant. HCl and NaOH (Analytical Grade) were used to control the pH of the stock solution.
2.2. Characterization
The surface morphology was observed by a Field Emission-Scanning Electron Microscope (FE-SEM) [Hitachi, SU 8220] and functional groups were observed by Attenuated Total Reflectance–Fourier Transform Infrared Spectrophotometer (ATR-FTIR) [Perkin-Elmer].

2.3. Polypyrrole synthesis
Polypyrrole adsorbent was prepared by chemical oxidative polymerization of pyrrole monomer using iron (III) chloride hexahydrate as an oxidant. The different mole ratios of monomer to oxidant (1: 0.25, 1: 0.5, 1: 1, 1: 2 and 1: 3) were followed in aqueous solution for complete polymerization. The change of the initial color from green to finally black indicated the formation of PPy. The black mixture was then filtered and washed several times with distilled water to remove excess reactants before drying at 65 °C for 24h.

2.4. Batch adsorption
The batch adsorption was carried out for known concentration of arsenic, zinc and cadmium ions with the prepared Ppy adsorbents prepared from using 1:1 mole ratio of monomer to oxidant.

3. Results and discussion
Different physical appearances of PPy were observed with different amounts of yields during the synthesis of polypyrrole using different monomer to oxidant ratios. It was observed that the formation of PPy (yield) was increased with increasing the amount of oxidant at the same preparation conditions (Table 1). The higher monomer:oxidant ratio (1:3 and 1:2) gives the higher amount of yield but the monomer:oxidant ratio of 1:1 shows the maximum adsorption efficiency for all the heavy metal ions. Polymerization with higher oxidant ratios produces a very hard and compact polymer with less active site available for the binding interactions with metal ions.

| Monomer:oxidant ratio | Yield (g) | Physical Appearance                  |
|-----------------------|-----------|-------------------------------------|
| 1:0.25                | 0.1247    | Very thin layer, glazy              |
| 1:0.50                | 0.2986    | Irregular thin leaves likes, glazy and shiny |
| 1: 1                  | 0.6549    | Irregular flakes, glazy, shiny, fine powder |
| 1:2                   | 1.2172    | Thick, muddy likes, not shiny        |
| 1:3                   | 1.6831    | Very thick, coarse and compact      |

On the other hand, polymerization with lower monomer to oxidant ratio (1:0.5) and (1:0.25) produces very thin and soft layer powder which appears very difficult to handle. Polymerization with 1:1 ratio produces an irregular flaky, shiny and stable fine powder with balanced amount of oxidant. It provides more active sites availability (nitrogen in amine functional groups of PPY) and therefore, the adsorption of heavy metal ions by polypyrrole adsorbent prepared from 1:1 mole ratio of monomer to oxidant has been reported.

3.1 Effect of adsorbent dosage
Figures 1-3 show the effect of adsorbent dosage on the adsorption of metal ions. It shows that the maximum efficiency of metal adsorption was exhibited by using 0.2-0.25 g of the prepared adsorbent. With the increase in PPY dosage beyond 0.2-0.25 g, the adsorption efficiency remained almost unaltered. More adsorbent dosage inhibits further adsorption of metal ions due to the saturation of the active sites.
3.2. Effect of contact time

The adsorption efficiency of arsenic ions on certain dosage (0.2g) was measured as a contact time of 1, 2, 4, 6, 8 and 10 hours keeping all other parameters constant. Figure 4 shows the effect of these contact time and indicated that maximum efficiency was found at a contact time of 6 hours. It was observed...
that the adsorption efficiency increased very first in first few hours and then slowly increased over the
time upto 6 hours and beyond that time adsorption efficiency was steady. This is due to equilibrium
that has been achieved at that time.

![Figure 4](image)

**Figure 4.** Effect of contact time on the adsorption of arsenic ions from aqueous solution.

The adsorption efficiency of zinc ions on certain dosage (0.25g) of PPy adsorbent was measured at
a contact time of 15 minutes interval keeping all other parameters constant. The adsorption of zinc ion
is dependent on contact time and the maximum efficiency (45.1%) was found at a contact time of 75
minutes (Figure 5).

![Figure 5](image)

**Figure 5.** Effect of contact time on the adsorption of zinc ions from aqueous solution.

Figure 6 showed that the adsorption efficiency of cadmium ions was rapid at first 30 minutes and
then slowly increased over the time up to 150 minutes and beyond that time adsorption efficiency was
steady.
3.3. Effect of pH
All heavy metal ions are pH sensitive. In case of arsenic ion adsorption by several polymeric and non-polymeric adsorbents, the optimum pH range is 5-7 [6]. In this study, it was observed that the optimum pH was 6.5 at certain dosage and constant conditions for the removal of arsenic ions from aqueous solution (Figure 7).

3.4. Effect of pH on zinc ion adsorption
In the case of zinc ion adsorption from aqueous solution, the optimum range of pH was found 3-7 using several adsorbents [7]. Figure 8 shows the effect of pH on zinc ion sorption by PPy adsorbent.
The adsorption of zinc ions onto PPy was highly pH dependent and the optimum pH was found to be 4.5. The effect of initial pH on cadmium sorption onto PPy adsorbent was studied at pH 2.5-10.5. The adsorption of cadmium ions onto PPy was highly pH dependent and the pH 5.5 has been found as the optimum pH for cadmium ion adsorption (Figure 9). Several researchers showed the optimum range of pH of cadmium ions adsorption was found between 4-7 [8,9].

![Figure 9. Effect of pH on the removal of cadmium ions from aqueous solution.](image)

3.4. FTIR spectroscopy

Figure 10 shows the ATR-FTIR spectra of PPy (1:1) before adsorption (a) and after adsorption (b) of arsenic ions. All peak band positions of PPy before adsorption was shifted to higher wavelength after arsenic ions adsorption.

![Figure 10. FTIR- Spectra of PPy (a) before and (b) after adsorption.](image)

The bands at 762 cm\(^{-1}\), 841 cm\(^{-1}\), 961 cm\(^{-1}\), 1022 cm\(^{-1}\), 1139 cm\(^{-1}\), 1285 cm\(^{-1}\), 1524 cm\(^{-1}\) and 2173 cm\(^{-1}\) observed in PPy spectrum before the adsorption of metal ions have shifted to 782 cm\(^{-1}\), 887 cm\(^{-1}\), 964 cm\(^{-1}\), 1037 cm\(^{-1}\), 1158 cm\(^{-1}\), 1301 cm\(^{-1}\), 1537 cm\(^{-1}\) and 2293 cm\(^{-1}\), respectively, after adsorption. All these shifts indicate the adsorption of arsenic ions by PPy conducting polymer fine powder. The bands at 1037 cm\(^{-1}\) due to N-H wagging and 1301 cm\(^{-1}\) due to C-N in-plane deformation shifted to 1022 cm\(^{-1}\) and 1285 cm\(^{-1}\), respectively, after arsenic ions adsorption, suggests the metallic bond formation with nitrogen for PPy. Thus, from the FTIR spectrum, it can be evidenced that the fine powder from balanced oxidation polymerization shows maximum adsorption due to the complexation ionic adsorption affinity between the functionalized amine groups and arsenic ions.
The similar type of band shifts was observed for the adsorption of zinc and cadmium ions by the prepared polypyrrole adsorbent.

3.5. FE-SEM analysis
The morphology of prepared polypyrrole (Figure 11a and 11b) was studied by using a field emission scanning electron microscope. In Figure 11(a), flowery like compact surface indicates the polypyrrole formation. There was a very little visual changes observed in FE-SEM micrograph after the adsorption of metal ions (Figure 11.b). Similar micrographs have been observed for other heavy metal ions (zinc and cadmium). In this study, the surface area does not play the main role in adsorption by PPy like all other adsorbents but the nitrogen atoms in PPy are mainly responsible for arsenic ions adsorption. Similar results were found in another study of metal ions sorption [10].

![Figure 11. FE-SEM micrographs of PPy adsorbent (a) before and (b) after adsorption of metal ions (arsenic).](image)

4. Conclusions
Polypyrrole conducting polymer prepared by chemical oxidation using iron (III) chloride hexahydrate has exhibited complete adsorption efficiency for the removal of arsenic ions from aqueous solution. The fine polypyrrole powder prepared from using the monomer to oxidant ratio of 1:1 appeared to be a very efficient (100%) conducting polymer-based adsorbent for arsenic ions while a lower efficiency was observed for cadmium and zinc ions. The complete removal of arsenic ions by Ppy from aqueous solution encourages to study further for it to be used to treat wastewater. The low preparation cost and ease of preparation appear attractive for its commercialization particularly for heavy metal ions removal from aqueous solutions.

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References
[1] Nriagu J O and Pacyna J M 1988 *Nature* 333 134.
[2] Bernardo G R and Rene R M 2009 *J. Hazard. Mater.* 170 (2) 845.
[3] Javadian H 2014 *J. Ind. Eng. Chem.* 20 4233.
[4] Deng S and Bai R 2004 *Water Res.* 38 2424.
[5] Weidlich C Mangold K and Jüttner K 2001 *Electrochimica Acta* 47 741.
[6] Ioanis A K and Zouboulis A I 2002 *Water Res.* 36 5141.
[7] Bhattacharya A K, Mandal S N and Das S K 2006 *Chem. Eng.* 123 (1) 43.
[8] Mansour M S, Ossman M E and Farag H A 2011 *Desalination* 272 (1) 301.
[9] Hasani T and Eisaazdeh H 2013 *Synth. Metals* 175 15.
[10] Jia Y F, Xiao, B and Thomas K M 2002 *Langmuir* 18 470.