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# POLYPYRROLE CONDUCTING POLYMER: A NOVEL ADSORBENT FOR ARSENIC IONS FROM AQUEOUS SOLUTION

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**Abstract.** In this study, a novel conducting polypyrrole (Ppy) fine powder has been prepared as a new adsorbent to remove heavy metal ions like arsenic ions from an aqueous solution. Polypyrrole was chemically synthesized by using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as an oxidant at various mole ratios. Various ion concentrations of arsenic were treated by Ppy adsorbent, and the concentrations of arsenic were measured by inductively coupled plasma mass spectroscopy (ICP-MS). The efficiency of the adsorbent was evaluated by calculating the difference in arsenic concentrations before and after adsorption. The results show that Ppy acts as an effective adsorbent to remove arsenic ions from an aqueous solution. In addition, the surface morphology and functional groups were analyzed by Field Emission Scanning Electron Microscopy (FE-SEM), and Attenuated Total Reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, respectively before and after treatment. This study shows that certain preparation conditions of Ppy could remove arsenic ions from an aqueous solution effectively, which may encourage further application in true solution as it involves low cost and is easy to prepare.

## INTRODUCTION

Demand of potable water is increasing due to increasing population but unfortunately contamination of natural and waste water by different pollutants is generated due to industrialization or urbanization. Industrial waste waters 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 [1-6]. Also, soils in surrounding military bases are offering potential risk of certain heavy metals which can be a threat to ground water and surface water [5, 7]. Exposure of these heavy metal ions even in trace levels causes short term and long term effect on the body [8]. Usually, heavy metals cannot be decomposed or biodegraded<sup>4</sup>. Thus, how to remove these undesirable heavy metals from water bodies effectively is remaining a great task for the environmental scientists.

Categorized as the first priority toxic element by World Health Organization (WHO) and United States Environmental Protection Agency (US EPA), arsenic (As) is a type of contaminant commonly found in the ground and surface waters

[9-12]. A massive epidemic of arsenic poisoning such as skin or lung cancer and even bladder cancer has been reported in Asia and America, especially in India, Bangladesh, Vietnam, Cambodia, Thailand, Chile, southwest USA and Canada [10]. The predominant species of arsenic being inorganic forms of arsenate [As(V)] and arsenite [As(III)], are highly toxic compared to organo-arsenates [10,12]. WHO and various environmental protection agencies have set the permissible limits of As as 0.01 mg/L in drinking water [11, 12] since a very low level of chronic exposure may cause As poisoning [17].

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 waste water or aqueous solution [2-6]. Among them adsorption is widely used because of low costs, simple design and easy operation [6].

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 [2-6].

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Polypyrrole-based adsorbents play a major role in removing various heavy metal ions due to their ease of synthesis, biocompatibility and redox properties [6]. Since the adsorption efficiency largely depends on the preparation conditions of Ppy, a lot of effort has been made to remove heavy metal ions by polypyrrole conducting polymer prepared by chemical oxidative polymerization of pyrrole in the presence of different oxidants and dopants at different conditions [18-24]. However, no reports are available on the higher efficiency of arsenic ions by polypyrrole conducting polymer. Thus, 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 ions from aqueous solution. The effects of different parameters such as adsorbent dosage, contact time, initial pH and concentration of arsenic ions have been investigated as a function of operating conditions of adsorption.

## METHOD AND MATERIALS

This study was carried out in three phases. In the first phase, sufficient amount of conducting polypyrrole-based adsorbents were synthesized at various mole ratios of monomer to oxidant. In the second phase, batch adsorption treatment was carried out at different operating conditions and the adsorption efficiency (AE) was measured by Inductively Couple Plasma–Mass Spectroscopy (ICP-MS); and in the third phase, characterization of the products was done both before and after adsorption. 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.

### 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 each time, 1.342 g of pyrrole monomer was taken in 100 ml distilled water. Based on the mole ratios, required amount of oxidant (e.g. 5.406 g in

case of 1:1) was completely dissolved in another 100ml of distilled water. Later, both solutions were simultaneously mixed in a big beaker and allowed to stand for 3 hours at ambient temperature 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.

### Batch Adsorption

The batch adsorption was carried out for known concentration of arsenic ions with the prepared Ppy adsorbents at various mole ratios and doses. The adsorbent doses used were from 0.05 g to 0.35 g for 50 ml known concentration of arsenic. A pH of 6.5 was maintained at room temperature. The initial and final concentrations of the arsenic ions in aqueous solution were determined by ICP-MS and the adsorption efficiency (AE) was calculated as:

AE Percentage =  $(c_i - c_f / c_i) \times 100$ ; where  $c_i$  is the initial concentration (mg/L) and  $c_f$  is the final concentration (mg/L).

### Characterization

The surface morphology was observed by Field Emission-Scanning Electron Microscopy (FE-SEM) [Hitachi Brand, Model SU 8220] and functional groups were observed by Attenuated Total Reflectance–Fourier Transform Infrared Spectrophotometer (ATR-FTIR) [Perkin-Elmer, FTIR- Spectrum 400].

## 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 by increasing the amount of oxidant at the same preparation conditions. The adsorption efficiency of the prepared Ppy was found to be highly dependent on the specific mole ratios of monomer to oxidant (Table 1). The higher monomer:oxidant ratio (1:3 and 1:2) gives the higher amount of yield but the monomer:oxidant ratio 1:1 shows the maximum adsorption efficiency of the arsenic ions. Polymerization with higher oxidant ratios produces a very hard and compact polymer with less active sites available for the binding interactions with arsenic ions.

TABLE 1  
MONOMER TO OXIDANT RATIO VERSUS ADSORPTION EFFICIENCY

| Monomer:oxidant | Yield (g) | Physical Appearance                         | Adsorption Efficiency,% |
|-----------------|-----------|---|-------------------------|
| 1:0.25          | 0.1247    | Very thin layer, glazy                      | 85.4                    |
| 1:0.50          | 0.2986    | Irregular thin leaves like, glazy and shiny | 89.7                    |
| 1: 1            | 0.6549    | Irregular flakes, glazy, shiny, fine powder | 99.8                    |
| 1:2             | 1.2172    | Thick, muddy like, not shiny                | 88.3                    |

|     |        |                                |      |
|-----|--------|--------------------------------|------|
| 1:3 | 1.6831 | Very thick, coarse and compact | 78.9 |
|-----|--------|--------------------------------|------|

On the other hand, polymerization with lower oxidant ratio (1:0.5) and very low oxidant ratio (1:0.25) produces very thin and soft layer powder due to incomplete polymerization. Polymerization with same ratio (1:1) produces an irregular flaky, shiny and stable fine powder with balanced amount of oxidant. Thus, it provides more active sites availability (nitrogen in amine functional groups of Ppy) and forms ionic adsorption of arsenic ions.

#### Effect of Adsorbent Dosage

Fig. 1 shows the effect of adsorbent dosage on the removal of arsenic ions and indicated that the maximum efficiency (99.8%) was found using 0.2 g of the prepared adsorbent. After that with the increase in Ppy dosage, the adsorption efficiency remained almost unaltered. More adsorbent dosage inhibits further the arsenic ions adsorption due to the burial of the active sites.

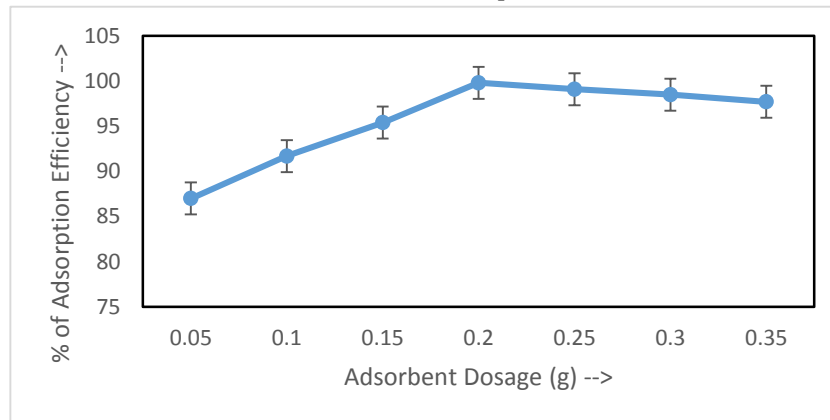


Fig. 1. Effect of adsorbent dosage on the removal of arsenic ions from aqueous solution.

#### Effect of Contact Time

The adsorption efficiency of arsenic ions on certain dosage (0.2g) was measured at contact times of 1, 2, 4, 6, 8 and 10 hours keeping all other parameters constant. Fig. 2 shows the effect of these contact times and indicated that maximum efficiency was found at a contact time of 6 hours. It was observed that the

adsorption efficiency increased first in first few hours and then slowly increased over the time up to 6 hours and beyond that time adsorption efficiency was steady. This is due to equilibrium that has been achieved at that time. The contact time was selected as 6 hours for further experiments.

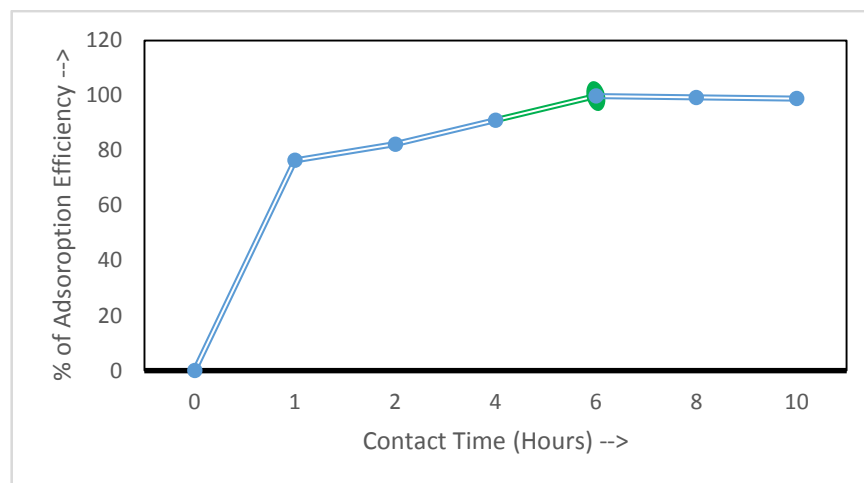


Fig. 2. Effect of contact time on the removal of arsenic ions from aqueous solution

#### Effect of pH

All heavy metal ions are pH sensitive. In case of arsenic adsorption by several polymeric and non-polymeric adsorbents, the optimum pH range is 5-7 [9, 25, 26].

In this study it was observed that the optimum pH was 6.5 at certain dosage and constant conditions (Fig.3).



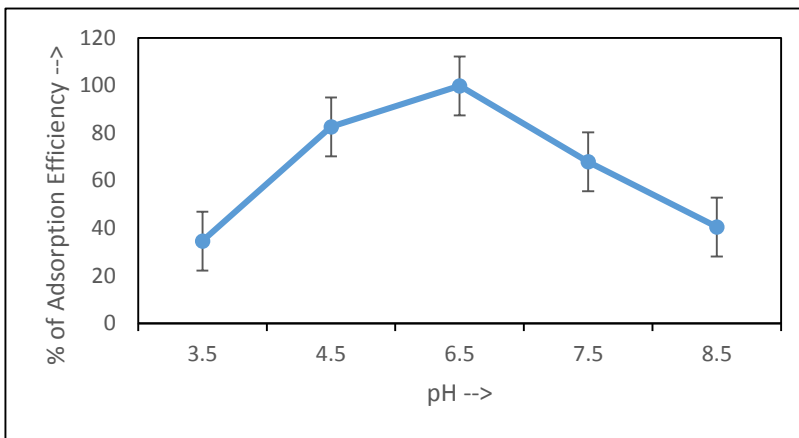


Fig. 3. Effect of pH on the removal of arsenic ions from aqueous solution

**Effect of Initial Concentration**

The effect of initial arsenic ion concentration in aqueous solution was investigated on certain dosage (0.2g) and contact time (6 hours) keeping all other parameters constant. Table 2 shows that with the increase in the initial arsenic ion concentration from

1000 ppb to 5000 ppb, the efficiency of arsenic ion removal gradually decreased from 99.8% to 84.7%. This is probably due to the higher number of arsenic ions per unit mass of adsorbent.

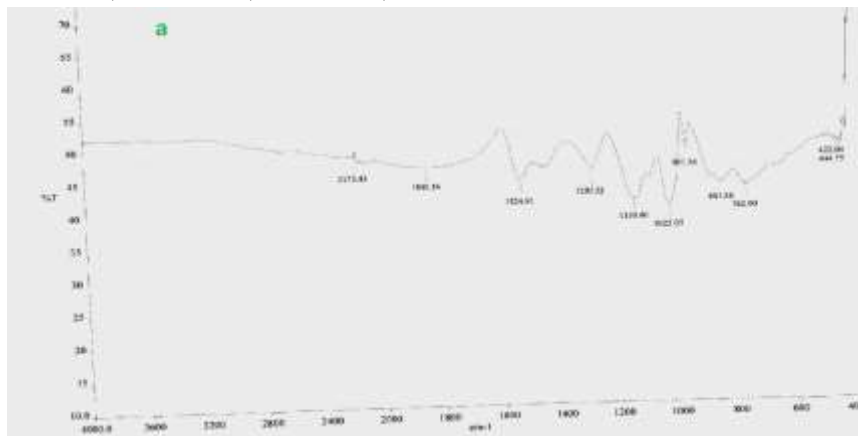
TABLE 2  
EFFECT OF INITIAL ION CONCENTRATION ON THE PERCENTAGE OF ARSENIC ION REMOVAL

| Initial arsenic ions concentration (ppb) | Adsorption Efficiency (%) |
|--|---------------------------|
| 1000                                     | 99.8                      |
| 2000                                     | 96.3                      |
| 5000                                     | 84.7                      |

**FTIR Spectroscopy**

The Fig.4 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 were shifted to higher wavelength after arsenic ions adsorption. The bands at 762.9 cm<sup>-1</sup>, 841.54 cm<sup>-1</sup>, 961.36 cm<sup>-1</sup>, 1022.05 cm<sup>-1</sup>, 1139.4 cm<sup>-1</sup>, 1285.32 cm<sup>-1</sup>, 1524.91cm<sup>-1</sup> and 2173.43cm<sup>-1</sup> observed in Ppy spectrum before adsorption have shifted to 782.17 cm<sup>-1</sup>, 887.29 cm<sup>-1</sup>, 964.94 cm<sup>-1</sup>, 1037.91 cm<sup>-1</sup>, 1158.42 cm<sup>-1</sup>,

1301.22 cm<sup>-1</sup>, 1537.02 cm<sup>-1</sup> and 2293.86 cm<sup>-1</sup>, respectively, after adsorption. All these shifts indicate the adsorption of arsenic ions by Ppy conducting polymer fine powder. The bands at 1037.91 cm due to N-H wagging and 1301.22 cm due to C-N in-plane deformation shifted to 1022.05 cm and 1285.32 cm, respectively, after arsenic ions adsorption that suggests the metallic bond formation with nitrogen for Ppy.



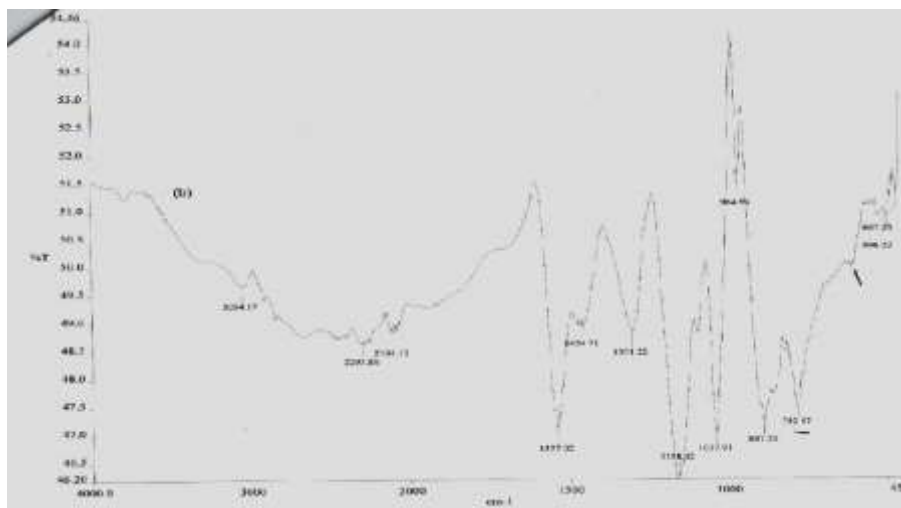


Fig. 4. FTIR- Spectra of Ppy before (a) and after adsorption (b)

Thus, from the FTIR spectrum, it can be evidenced that surface area of Ppy does not play major role but fine powder from balanced oxidation polymerization shows maximum adsorption due to the complexation ionic adsorption affinity between functionalized amine groups and arsenic ions.

#### FE-SEM Micrographs

The morphology of prepared polypyrrole (Fig. 5a & 5b) was studied by using a field emission scanning electron microscope. In Figure 5(a), flower-like compact surface indicates the polypyrrole formation. There were very little visual changes observed in FE-SEM micrograph after adsorption of arsenic ions (Fig.5.b).

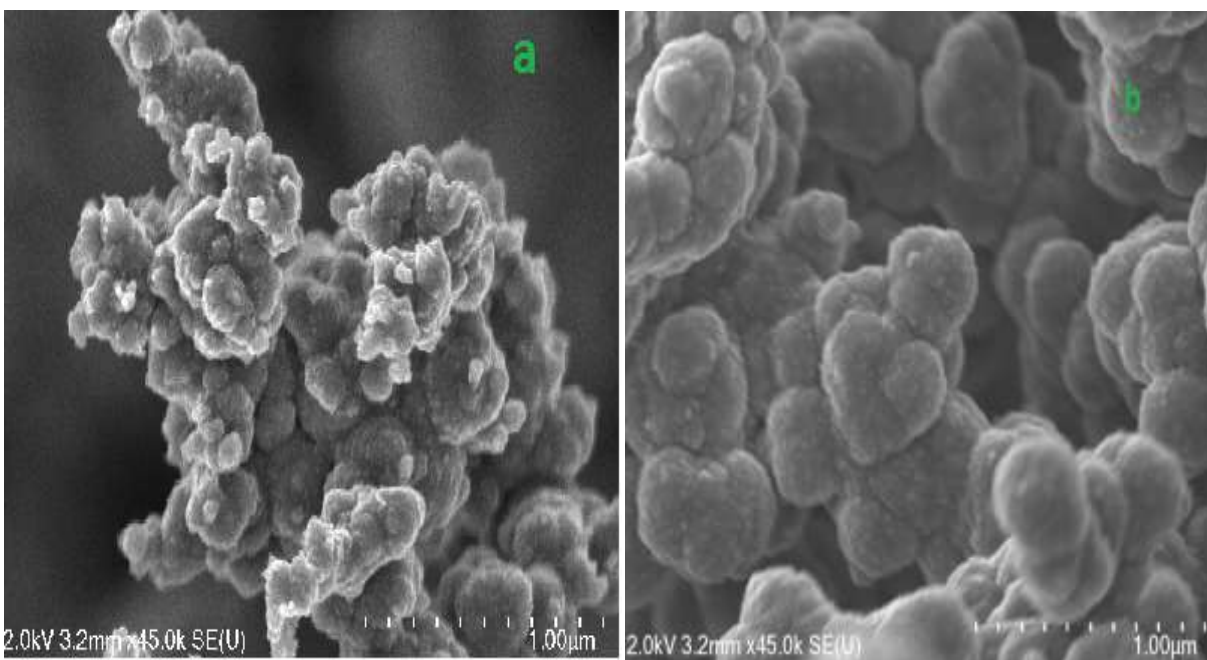


Fig. 5. FE-SEM of before (a) and after (b) adsorption of PPy-adsorbents.

In this study, the surface area does not play the main role in adsorption by Ppy but the nitrogen atoms in Ppy are mainly responsible for arsenic ions adsorption. Similar results were found in another study of cadmium adsorption [27].

#### CONCLUSION AND RECOMMENDATIONS

Ppy prepared by chemical oxidation using iron (III) chloride hexahydrate has exhibited almost 100% adsorption efficiency for the removal of arsenic ions from aqueous solution. It was indicated that monomer to oxidant ratios play a major role for

adsorption of arsenic ions and 1:1 shows the maximum adsorption. The maximum adsorption dosage was found as 0.20 g at pH 6.5 with a contact time of 6 hours at room temperature. This study shows that certain preparation conditions of Ppy were capable of removing arsenic ions from aqueous solution effectively which may encourage further to apply in true solution as it involves low cost and is easy to prepare.

#### Declaration of Conflicting Interests

No conflicts of interest.

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