Development of bi-metal doped micro- and nano multi-functional polymeric adsorbents for the removal of fluoride and arsenic(V) from wastewater

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The contamination of ground water by fluoride and arsenic has recently considerably increased, especially in some regions of India. In this context, the development of efficient adsorbents for the control of fluoride and arsenic, which are the common pollutants in wastewater, assumes significance. Herein, we describe the synthesis, characterization, and application of bi-metals (Fe and Al) doped micro- and nanoparticles based adsorbents for the removal of fluoride and arsenic(V) ions from water. The adsorbents were prepared by suspension polymerization. Fe and Al were incorporated during a polymerization step. The bi-metals doped beads (0.8 mm) thus prepared were carbonized and activated to create porous structure inside the materials. Nanoparticles (~100 nm) were produced by milling of the beads, which were carbonized and activated. The adsorption tests carried out on Al/Fe-doped adsorbents revealed significant loading of those ions. The equilibrium loading of fluoride on nanoparticles based adsorbents was determined as ~100 mg/g corresponding to the aqueous phase concentration range of 0–90 ppm, whereas that of arsenic(V) was determined as 40 mg/g corresponding to the range of 0–70 ppm. The methodology adopted in this study is a step towards developing multi-functional adsorbents for the removal of different types of solutes from wastewater.

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1. Introduction

Over the past decade, significant increase in the concentration levels of arsenic and fluoride in surface water has been reported from several regions of India and its neighboring country, Bangladesh [1–4]. The primary reason is the rapid decline in the water table as increasingly more surface water is exploited for irrigated agriculture, and rural and urban water supply. Needless to add, risk to the human health has increased with increased concentration levels of these solutes in potable water. Adsorption has shown considerable potential in removing arsenic and fluoride from water. While many technologies such as precipitation and coagulation, chemical oxidation, membrane, ion exchange, and biological treatment are also in place for the removal of arsenic and fluoride from wastewater, adsorption offers some strategic advantages. (1) The amount of water required in the treatment is relatively much less. Therefore, the technology suits the regions where water is scarce. (2) The process is relatively less energy intensive. Therefore, the technology may be affordable by the developing countries where power situation may be grim. (3) No additional chemicals are required for treating wastewater, nor does the method involve any post-treatment step. Therefore, the operation is simple [5].

Development of efficient adsorbents is vital to the successful application of adsorption in water remediation. In this context, a variety of adsorbents have been developed for the removal of fluoride and arsenic from wastewater. Activated alumina and alumina supported metal oxides are the common adsorbents extensively studied for defluoridation applications [6–11]. Activated carbon or metals impregnated activated carbon has achieved limited success [12–14]. Nonetheless, a hierarchal web of activated carbon micro- and nanofibers dispersed with Al was synthesized in a recent study, and found effective in removing fluoride from wastewater [15]. With regard to the remediation of arsenic laden wastewater, literature may be considered extensively replete with studies on the development of Fe-modified activated carbon in the form of either powders or granules or fibers [16–21]. With Fe possessing large and selective affinity towards arsenic because of the formation of strong surface complexes, and activated carbon providing a large surface area for impregnation, a variety of Fe-doped carbon based adsorbents have been synthesized for the removal of arsenic.

More recently, Fe-doped activated micro/nano carbon particles were developed as efficient adsorbents for arsenic removal [22]. The
incorporation of Fe within the polymeric beads during a polymerization step was the novelty of the study. In view of its encouraging performance for arsenic removal, bi-metals doped micro/nano-adsorbent is potentially an attractive multi-functional generic platform for water remediation. Herein, we explore the possibility of synthesizing activated micro/nano carbon particles as adsorbent by incorporating simultaneously both Al and Fe in the polymeric beads and evaluate its performance for the removal of fluoride and arsenic (V) from water.

Herein, it may be mentioned that there are a few studies reported in literature on the synthesis of polymeric beads by suspension polymerization. For example, Maria et al. [23] have prepared styrene/Divinylbenzene based composite materials containing iron. The prepared materials were gel-like resins and the average size of such materials was ~150 μm. In addition, the iron particles were found to be agglomerated only on the surface of the polymeric beads. No iron particles were detected inside the particles. The application of such materials was in cell labeling or cell separation because of their magnetic behavior. Zhang and Pang [24] have used suspension polymerization to prepare magnetic chelating resins incorporating, albeit amino and mercapto groups. The resins were in the powdered form, with the average size less than 45 μm. Rana et al. [25] also synthesized the iron incorporated polystyrene based beads by suspension polymerization. The synthesized magnetic beads of size varying between 45 μm–125 μm exhibited potential applications in the area of scavenger resins. The similar micron size styrene based magnetic particles (~7 μm) were synthesized by suspension polymerization by Ding et al. [26] possibly in the bio-applications such as protein purification and recovery of enzymes.

From the overview of the above referred studies, it is clear that most of the polymeric materials prepared by suspension polymerization were of micron size and incorporated with Fe-magnetic particles mostly on their external surface. The incorporation of Fe and Al particles within the micro-/meso pores of the prepared beads having the average size of ~0.8 mm and significantly large BET area is the novelty of the present study.

In the present study, the polymeric beads were prepared by suspension polymerization. The salts of Al and Fe were incorporated during a polymerization step. The bi-metals doped spherical beads (average size: ~0.8 mm) thus prepared were carbonized and activated at high temperature to create porous structure inside the materials with significant BET area. Nanoparticles (~80–130 nm) were produced by milling of the beads, which were subsequently also carbonized and activated. The adsorption tests carried out under batch conditions on the metals doped beads and nano sized particles as adsorbents revealed significant loading of F and As(V) ions. The methodology adopted in this study is a step towards developing multi-functional adsorbents useful for the removal of different types of solutes from wastewater.

2. Materials and methods

2.1. Chemicals

All reagents used in the experiment were high purity grade. The phenol, hexamethylene tetraamine (HMTA), formaldehyde, triethylamine (TEA), 95% hydrolyzed poly vinyl-alcohol (PVA, avg. MW = 95000), ferric chloride, aluminum nitrate (Al(NO3)3), sodium fluoride (NaF) and sodium arsenate hepta (Na2HAsO4) were purchased from Merck (Germany). All solutions were prepared in water obtained from a Milli-Q system (Millipore, Bedford, MA).

2.2. Preparation of polymeric beads

The Al and Fe-doped polymeric beads were prepared by suspension polymerization. The polymerization reaction was performed in a 2-L three-neck glass vessel mounted over a heating mantle and equipped with a reflux water condenser, thermometer and continuous stirrer. The detailed description of the equipment used for the polymerization reaction is available [21]. Phenol (50 g of the monomer) was heated to the molten stage before mixing it with 63 ml of formaldehyde (solvent) and 1.5 ml of TEA (basic catalyst). At room temperature (~30 °C) while stirring at 370–410 rpm, the solution became homogenous in 6–8 h. Subsequently, 200 ml of distilled water was added to the reaction vessel. After 30 min, 3.5 g of HMTA (cross linking agent) was added, and the vessel was heated at a rate of 3 °C/min until the temperature reached 100 °C. Approximately 45 min after the addition of hexamine, 3 g of PVA (suspension stabilizing agent) was added. The time when the PVA was added was found to be critical to the quality of the beads produced. Approximately 35 min after the PVA was added, aluminum nitrate and ferric chloride were simultaneously added to the reaction mixture. The metallic salts were added in five different proportions (4:0, 3:1, 2:2, 1:3, and 0:4) to the reaction mixture, keeping the total amounts of the salts constant at 4 g. Therefore, five different adsorbents with different Al and Fe loadings were prepared in this study.

There is a clarification in order for the total amount of inorganic salts used for the synthesis. In the present study, we also used different total amounts of inorganic (Fe and Al) salts during the suspension polymerization. However, we first synthesized the polymeric beads without incorporating metals, and optimized the operating conditions of polymerization (the amount of monomer and other reagents, temperature, stirring speed, etc) for producing the uniform spherical phenolic beads of relative large size (~1 mm), with maximum product-yield. The optimized amount of monomer (50 g in the present case) used for the polymerization reaction was, therefore, limited by the volume (2 L) of the existing reaction vessel used in the experiment. It was also observed that increasing the total amount of the inorganic salts in excess of 4 g relative to 50 g of phenol used as a monomer, the shapes of the products (beads) formed after curing were irregular (non-spherical), often resulting into undesirable flakes-like products. In addition, the yield after the carbonization and activation of the polymeric beads was relatively small (~30%). The combined weight of the inorganic salts was, therefore, optimized at 4 g, with different amounts (4:0, 2:2, and 0:4) of individual salts.

To this end, after the addition of the salts, the reaction mixture continued to be heated. During the reaction, the speed of the stirrer was never allowed to fluctuate from the initially fixed set value to avoid solidification of the product. After 3 h, the heating was stopped, and the reactor was allowed to cool in the still air. When the temperature of the reaction products reached room temperature, the products were filtered to separate the solids from the residual liquid. The filtered product (spherical beads of an average size of ~0.8 mm) was washed three times with distilled water, then by methanol, followed by acetone. Finally, the prepared beads were sieved. In a typical experiment, the yield was approximately 30 g (15–16% w/w).

In this paper, the different phenolic beads are labeled as PH_40, PH_31, PH_22, PH_13, and PH_04, depending on the relative amounts of Al and Fe added to the reaction mixture. For example, PH_40 represents the polymeric beads doped with 4 g of Al-salts, whereas PH_04 represents the polymeric beads doped with 4 g of Fe-salts, and PH_22 represents the polymeric beads doped with 2 g each of Al- and Fe-salts, and so forth.

2.3. Preparation of the activated micro and nano sized particles

The prepared polymeric beads were carbonized then physically activated using steam in a horizontal tubular furnace. The beads were carbonized in a ceramic boat at 1050 °C for 1 h under a N2 atmosphere. Prior to the carbonization, the beads were pre-heated from room temperature to the carbonization temperature at a heating rate of 5 °C/min. Subsequent to the carbonization, the activation was
performed for 1 h by steam at 900 °C in the same tubular furnace. The yield of the carbonized and activated beads typically varied between 42% and 45% of the initial weight of the polymeric beads. The prepared carbonized/activated beads are labeled as APH_40, APH_31, APH_22, APH_13 and APH_04, with the prefix A to denote activated samples. The carbonization and activation caused an approximately 60% reduction in the particle size, with the average size of the carbonized/activated beads measured as ~0.50 mm. Some samples of the PH_22 beads were crushed by ball-milling to the nano-size (~200 nm). These particles (labeled as PH22_BM) were also carbonized and activated in the same tubular furnace to create activated nano particles containing Al and Fe. The activation and carbonization conditions were the same as those used for preparing the activated beads, except that the carbonization and activation temperatures were set to 1000 °C and 850 °C, respectively, which were slightly lower than the previous conditions. The lower temperatures were found to be the most superior adsorbent in the study. The average particle size of the remaining three types of beads (APH_04, APH_22, APH_40) having different metals ratio was found to be approximately the same (~0.8 mm) after sieving.

2.4. Adsorption tests

Stock solutions of fluoride and arsenic(V), each with a concentration level of 500 ppm, were prepared from the salts of sodium fluoride (NaF) and disodium hydrogen arsenate (NaH2AsO4·7H2O), respectively, in ultrapure water. From the stock solutions, various test solutions were prepared in conical flasks, each containing 50 cc of the test solution but different concentrations of the solute (fluoride at 10–100 ppm or arsenic(V) at 1–50 ppm). A definite amount (~0.05 g) of the prepared adsorbents was transferred to the conical flasks. The flasks containing the test solutions and adsorbents were sealed with parafilm and then kept in a mechanical shaker (125 rpm) at a temperature of 30 °C with a variation of ±1 °C. All the test samples were prepared in triplicate for reproducibility.

From the intermediate samplings and analysis of the solutions in the shaker, the adsorption equilibrium was found to be attained in approximately 6–8 h. After equilibrium, the flasks were released from the shaker, and the solutions were filtered by Whatman filter paper to separate the liquid from the adsorbents. The liquid was then centrifuged at a high speed (1000 rpm) for 30 min to induce the precipitation of the suspended particles out of the solution. The centrifuged solutions were again filtered through the 0.22 μm size filter paper. The solution was analyzed for ion-concentrations by an ion chromatograph (Metrohm IC 861) equipped with a guard column (IC SEP AN2 GUARD) and a main anion column (Metrosep A Supp 5, 250/4.0 mm). The calibration of the instrument was performed every time with and prior to the sample analysis. The instrument was calibrated with the standard solutions of arsenic(V) and fluoride purchased from Merck. The lower limit of detection for the instrument was 0.1 mg/L, and the variation in the analysis was less than ±1.0 mg/L for both salts. The retention times for As(V) and fluoride were observed to be approximately 28 min and 12 min, respectively, following the sample injection. Samples of both solutes were also periodically analyzed during the adsorption tests to ascertain variations in pH during the adsorption.

The adsorbed amounts of F and As ions by the prepared adsorbents were calculated from the species balance equation of $q = V(C_0 - C_e)/w$, where $q$ is the amount (mg/g) of ions adsorbed, $C_0$ is the initial ion concentration (mg/L) and $C_e$ is the equilibrium ion concentration (mg/L) in the solution, $V$ is the volume (L) of the solution, and $w$ is the weight (g) of the adsorbent.

3. Characterization

3.1. Surface area, pore volume and pore size distribution (PSD)

The surface characteristics such as the specific surface area, pore volume and PSD of the different adsorbents prepared in this study were determined by an Autosorb 1C (Quantachrome, USA) instrument. The multipoint Brunauer, Emmett, and Teller (BET) surface area was measured using the nitrogen adsorption/desorption isotherm. The isotherm data were experimentally obtained using $N_2$ as an adsorbent gaseous molecule at 77 K. Prior to the measurements, the samples were degassed at 200 °C for 8 h to remove any adsorbed water or trapped gases in the samples. The total pore volume was...
measured from the amount of N\textsubscript{2} adsorbed at the relative pressure close to unity (0.9994). The PSD was calculated from the desorption isotherms by the Barrett, Joyner, and Halenda (BJH) method for mesopores (2–40 nm) and the density functional theory (DFT) for micropores (<2 nm).

Fig. 3 shows the adsorption isotherms of the different adsorbents prepared in this study. For all samples, the volume of adsorbed gas (i.e. N\textsubscript{2}) steeply increased below P/P\textsubscript{o} ≈ 0.05, before gradually leveling off. As shown in the plots, the adsorption equilibrium was established at a low relative pressure (<0.4). The samples exhibited the adsorption isotherm of type I, which is a characteristic of materials predominantly having micropores. For PH\textsubscript{22}_BM_A nanoparticles, a steep increase in the adsorbed volume was observed beyond P/P\textsubscript{o} ≈ 0.9. This is a common characteristic of N\textsubscript{2}-adsorption isotherms and is observed in most of the nano-structured materials [27,28].

Table 1 presents the data for the BET area, total pore volume and micropore and mesopore volumes calculated as per the IUPAC norms from the isotherms. There are four salient observations to make. (1) Milling followed by carbonization and activation significantly increased the BET area of the prepared materials. The BET area (~750 m\textsuperscript{2}/g) of the PH22_BM_A nanoparticles was nearly twice that of the activated metals doped beads. (2) All adsorbents were mostly microporous having micropore volumes 60–80% of the total pore volume. (3) The maximum variation in the BET area of the prepared beads (APH_40, APH_31, APH_22, APH_13 and APH_04) was small (~80 m\textsuperscript{2}/g) in comparison to their average BET area (~330 m\textsuperscript{2}/g), which suggests that the bi-metal (Al/Fe) doped beads prepared in this study may be considered to possess approximately the same specific area. In general, the Fe-doped beads had a larger BET area than the Al-doped beads. We will re-visit this aspect of the surface characteristics of the materials in relationship to their adsorption capacity later in the paper.

3.2. Scanning electron microscopy (SEM) and electron dispersive X-ray (EDX) analysis

The SEM and EDX analysis were conducted on various samples of the prepared adsorbents by a Field Emission SEM (Supra VP40, Zeiss) instrument. The surface morphologies and elemental distribution of the pre- and post-adsorbed specimens were investigated by SEM imaging and EDX mapping of several locations on the samples. The
representative images and maps are presented and described herein for each adsorbent.

Figs. 4–6 contain the SEM images of the APH_40, APH_22, and APH_04 samples, before and after adsorption. Each figure contains an image of the prepared bead at 150× magnification, followed by images of the surface at 100 KX, before and after the adsorption of fluoride and arsenic. Fig. 7 contains the SEM images of the PH22_BM_A nanoparticles, before and after adsorption. The corresponding EDX elemental maps are shown on the right-hand-side of the figures.

From the comparative examination of the images (Figs. 4–6a) of the adsorbents, APH_40, APH_22, and APH_04, distinct differences between the morphologies of their external surfaces may be observed.

1. The surface of the Al-doped beads was smoother than the Fe-doped beads. (2) The latter adsorbents were relatively more porous.

3. The surface of the Al/Fe-doped beads was also porous, although to a relatively lesser extent. The images (Figs. 4–6b) taken at the larger magnification (100 KX) confirm the increasing porosity in the external surface of the beads with the increasing Fe-content. As observed in Figs. 4–6(c–d), the surface morphology of the prepared beads also changed following the adsorption of fluoride or arsenic. By comparing the respective images of the fluoride and arsenic adsorbed surfaces, the agglomeration of the adsorbed phase on the latter can be observed.

As shown in Fig. 7a, the surface morphology of the PH22_BM_A nanoparticles was distinctively different from the millimeter sized beads. (Ball) Milling caused breakage of the beads, originally sized at ~0.8 mm, to nanoparticles of the average size of ~200 nm. Most of the breakage or rupturing occurred in the macro-pores of the beads, resulting in the creation of nonporous nanoparticles. Similar to the surface changes of the beads after adsorption, the nanoparticle surfaces also changed following the adsorption of fluoride or arsenic, as observed from the SEM images presented in Figs. 7b and c, respectively. In addition, particle agglomeration was observed on the surface of the adsorbents treated with arsenic (Fig. 7c).

The corresponding EDX maps for three adsorbents, APH_40, APH_22, and APH_04, discussed above are shown in Figs. 4–6(b’–d’). The maps for PH22_BM_A (nanoparticles) are shown in Fig. 7a’–c’). The mapping confirmed the presence of Al (shown in green dots) in APH_40, APH_22, and PH22_BM_A, and Fe (shown in red dots) in APH_04, APH_22, and PH22_BM_A. The elemental mapping also confirmed the presence of arsenic and fluoride (shown in different colored dots defined in the figure-captions) in all four adsorbents, suggesting that both fluoride and arsenic may be adsorbed by the beads doped with Al or Fe alone, although to different extents. If the number-density of the different elements shown on the maps is used as the qualitative indicator of their incorporation extent in the beads, the amount of fluoride adsorbed by the different adsorbents may be considered to be in the following order: PH22_BM_A > APH_40 > APH_22 > APH_04. Alternatively, the amount of arsenic adsorbed by the different adsorbents may be considered to be in the following order: PH22_BM_A > APH_04 > APH_22 > APH_40. The quantitative descriptions of the relative adsorption capacities of the prepared adsorbents are described and discussed in the following section. The elemental carbon and oxygen were also detected by the EDX analysis. No other impurities were detected. The SEM and EDX results of the other adsorbents, namely APH_31 and APH_13, are not included here for brevity.

3.3. Atomic absorption analysis (AAS) measurements

The iron and aluminum contents of the various prepared adsorbent samples were determined by AAS. The samples were first added to an aqua regia solution in a beaker. The beakers were then placed on a shaker. The metal-leaching was performed for 6 h. After leaching, the metals contents of the treated solutions were measured using a Varian (model: Carry 100) AAS. The data obtained from the AAS analysis are reported in Table 1. As shown, the iron content in APH_04 was ~35 mg/g, which significantly increased to 103 mg/g in the PH22_BM_A nanoparticles. On the other hand, the aluminum content in APH_40 was ~8.4 mg/g, which also increased to ~18 mg/g in the nanoparticles. As also observed from the table, the mass ratio of Al and Fe is approximately 1:4.1 in APH_22 and 1:5.6 in the nanoparticles (PH22_BM_A). These data may be compared to 1:4.7 as the stoichiometric ratio of Al and Fe used in the reaction mixture. The difference between the elemental ratios for APH_22 and PH22_BM_A is attributed to the different extent of leaching for Al and Fe. Based on the AAS data, the extent of Fe-leaching may be considered to be larger than that of Al from the nanoparticles.

4. Results and discussion

4.1. Adsorption data

Fig. 8(a) and (b) presents the equilibrium concentrations of the fluoride and arsenic(V) ions, respectively, in the solid phase as a function of the aqueous phase concentrations, for samples APH_40, APH_22, APH_04, and PH22_BM_A. Each plot essentially represents the equilibrium isotherm of the solutes for the different adsorbents at 30 °C over the aqueous phase concentration range of ~0.1–85 mg/L or ppm. As shown, the solid phase concentrations monotonically increased with the increasing aqueous phase fluoride or arsenic(V) concentrations and asymptotically reached a maximum value for each adsorbent. This maximum value corresponded to the saturation capacity of the adsorbent.

In general, the Fe-doped micro sized beads were observed to have a larger arsenic adsorption capacity than the Al-doped beads. Alternatively, the Al-doped beads had a larger fluoride adsorption capacity than the Fe-doped beads. The results are not surprising because activated alumina and iron are known to specifically possess affinity for fluoride and arsenic ions, respectively. The salient result is the considerable fluoride adsorption efficiency observed for APH_04, suggesting that Fe may also be used for the removal of fluoride from water. Reviewing the literature, there are indeed a few Fe-modified adsorbents, which have been applied for the fluoride removal [29,30].

The more interesting result is the considerable adsorption efficiency observed for the combined Al- and Fe-doped adsorbents, mainly APH_22 that was tested for the remediation of water laden with either fluoride or arsenic. The APH_22 adsorption capacities for fluoride and arsenic(V) were ~45 mg/g and 20 mg/g, respectively, corresponding to the aqueous phase concentration of 60 ppm for the respective ions. The equilibrium ion loadings were much higher than the reported literature values in most cases and comparable in a few cases, for fluoride or arsenic [4–15]. Therefore, it is not surprising that the PH22_BM_A nanoparticles, which were synthesized by the milling of their parent micro sized beads followed by activation, have a much larger specific area (~750 m²/g) and therefore, have an even higher adsorption capacity than the micro sized adsorbents prepared in this study, for fluoride and arsenic(V) ions. As previously stated, the different adsorbents had nearly the same specific areas (avg. 330 m²/g with variation of ±50 m²/g). Therefore, the varying equilibrium loading extents of fluoride or arsenic(V) ions on the micro sized adsorbents (beads) may be attributed to the different amounts of metals (Al and Fe) incorporated into the beads. However, the superior performance of the nanoparticle based adsorbent (PH22_BM-A) is...
attributed predominantly to the relatively larger number of active sites available for adsorption, as reflected by its significantly large BET area (~750 m²/g). However, it is important to note that the nanosized adsorbent particles of PH22_BM-A, when used in a commercial packed bed adsorber, would require a suitable binder phase to avoid entrainment of the nanoparticles in the flow of the water to be treated. The synthesis of an appropriate binder phase for the nanoparticles is currently being pursued. It is also important to mention that the WHO guidelines are prescribed for the total arsenic, As(III) and As(V), in potable water. In that context, the removal of As(V) is relatively easy. We plan to address the application of the prepared materials for the removal of As(III) in a separate study.

As also shown in Fig. 8 and (b), the Freundlich isotherm equation \( q = K C^n \), where \( C \) (mg/L) and \( q \) (mg/g) are the concentration in the solution and amount of solute adsorbed at equilibrium, was used to fit the equilibrium data of fluoride and As(V) ions in water. In general, the Freundlich isotherm describes the multilayer adsorption with heterogeneous surface energies. The equilibrium adsorption data...
were also fitted by the Langmuir isotherm, 

\[ q = \frac{Q \times k \times C}{1 + k \times C}, \]

where \( Q \) (mg/g) is the maximum solute loading (mg/g) and \( k \) (L/mg) is the Langmuir coefficient. However, the Langmuir isotherm equation could not explain the data, suggesting that the surface coverage with the solutes (F/As(V) ions) exceeded a monolayer. To this end, the values for Freundlich constants, \( K \) and the power of isotherm \( n \), measurement of the adsorption capacity and that of adsorption intensity, respectively, are reported in the figure.

4.2. pH variation during the adsorption and the proposed adsorption mechanism

The pH variation during the adsorption tests was monitored for both fluoride and arsenic ions by periodically taking samples from the test solutions. Fig. 9 shows the change in the solution pH before and after the adsorption of fluoride onto the four different adsorbents (APH_04, APH_22, APH_40, and PH22_BM_A). The initial pH values corresponded to the different initial concentrations (5–90 ppm) of the fluoride in the test solutions that were brought in contact with the four adsorbents. As shown, the pH of the test solutions was initially in the range of 7.1–7.6 and marginally decreased (maximum by ~0.6) following adsorption to the range of 6.8 and 7.0. A small decrease in the pH of the arsenic solutions was also observed. In this case, the pH values of the test solutions were initially in the range of 7.4–8.0 and decreased to the range of 6.7–7.4 (data not shown). The small pH variation during the adsorption suggests that post-treatment (after defluoridation or arsenic removal) of water treated by the adsorbents prepared in this study may not be required.

Fig. 10 describes a tentative molecular structure of aluminum and iron-doped synthesized polymeric adsorbents in this study. A step growth polymerization occurs between phenol and formaldehyde. Initially phenol reacts with formaldehyde to form hydroxymethyl phenol. The hydroxymethyl group then reacts with either free ortho or para site of the phenol or another hydroxymethyl group. This is followed by the incorporation of Fe/Al as shown in Fig. 10.

Fig. 11 depicts a probable molecular structure of the polymeric beads after adsorption with As(V) and fluoride ions. In the case of fluoride ions, under the present experimental conditions of pH varying between 6 and 7.5, fluoride ions are predominantly adsorbed by the following reaction:

\[ \equiv MOH + F^- \leftrightarrow \equiv MF + OH^- \]

where, \( M \) represents metal ion (Fe or Al), \( MOH \) represents the surface hydroxyl group, and \( MF \) the surface site occupied by a fluoride ion.

The above reaction represents the ligand exchange interactions between the fluoride ions and hydroxyl groups that are found to occur at or near the neutral pH region. A similar mechanism has been proposed earlier [31–33]. With regard to As(V), the species exist in several anionic forms (\( H_2AsO_4^- \), \( HAsO_4^{2-} \), and \( AsO_4^{3-} \)) in water above pH 3.0 [34]. Therefore, it could be removed by the cationic Fe/Al OH\(^2+\) by the following reaction:

\[ Fe/Al(OH)_2^+ + As(V) \rightarrow Fe/AlHAsO_4^- \]
Herein, it is important to mention that the pH variation was also determined apriori for the various samples of pure water containing different adsorbents, however, without containing solutes (arsenic or fluoride). Fig. 12 describes the data for such conditions. As observed, there is practically no variation in pH. The maximum variation (~0.7) was observed in the case of PH22_BM_A.

To further corroborate the proposed mechanism of ion exchange between the Fe or Al- particles and the adsorbate molecule (As/F ions), FT-IR spectra were taken for the various adsorbents before and after adsorption. Fig. 13 is the representative spectra of the nano-adsorbents (PH22_BM_A). It is evident from the spectrum that there is a change in the stretching vibration of phenolic O–H group before and after adsorption of fluoride as well as As(V) ions at 3700 cm\(^{-1}\), which further confirms the ion exchange mechanism.

**5. Conclusions**

Al and Fe were successfully incorporated into polymeric beads during an intermediate step of the synthesis by suspension polymerization. The synthesized Al- and Fe-doped, activated micron (~ 0.8 mm) and nano (~100 nm) sized porous adsorbents were shown to possess significant loadings of fluoride (~100 mg/g) and arsenic(V) (~40 mg/g) ions, which were larger than or comparable to the literature data. The various surface characterization analytical instruments used in the study confirmed the presence and dispersion of the incorporated metals onto the considerably large surface area (~760 m\(^2\)/g) of the prepared porous carbon based adsorbents. The methodology adopted in this study to prepare bi-metal doped carbon based porous adsorbents is a step toward developing multi-functional adsorbents for water remediation applications.

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