Research Article

Tannin-Aniline-Formaldehyde Resole Resins for Arsenic Removal from Contaminated Water

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Abstract: Tannin is the polyphenol reached substrate that has high affinity to bound metal ions. Tannin-formaldehyde resins were synthesized in the presence of aniline as a comonomer through a covalent bond and were studied to determine its efficiency for arsenic binding. The adsorption of metal ion on the resins was monitored by FTIR and EDX analysis. The metal ion adsorption parameters such as contact time and pH were studied to see effect on binding capacity. The metal ion adsorption capacity was measured by proton exchange method. The maximum adsorption capacity observed was around 90% for As(V) in the pH range of 4 - 8 and for As(III) in the pH range of 4 - 5. SEM study of resins was carried out to see the ligand formation with metal. The experimental results reveal that metal ions bind strongly to tannin resins. Adsorption/desorption behavior of metal ion on resins was studied for its reusability viewpoint. Nearly 95% of the adsorbed As(III) and As(V) ions were desorbed from tannin resins by using 1M nitric acid solution in the first step, which then decreased to 85% at the third step.

Keywords: Tannin-formaldehyde resins, Aniline, Adsorption, Desorption, Arsenic, Metal recovery/removal.

1. INTRODUCTION

The presence of toxic metals in ground water sources is a serious problem in water and wastewater management. Arsenic is a ubiquitous element widely distributed in the earth’s crust. It is released in drinking water supply by either natural sources or industrial processes [1]. Arsenic can cause serious health issues such as cancers of the skin, lungs and bladder. Epidemiological evidence indicates that arsenic concentration in drinking water exceeding 50 µgL⁻¹ is detrimental to public health. Toxicity of arsenic varies greatly according to its oxidation state. Naturally occurring inorganic arsenic generally exists in two oxidation states, arsenite [(As(III)] and arsenate [(As(V)]. Arsenic commonly present in water is a pH dependent species of arsenic (H₃AsO₃) and arsenate (H₃AsO₄) acid systems. In natural water and drinking water, it is mostly found as As(III) and As(V) [2,3]. As(III) is sixty times more toxic than As(V) [4, 5]. The maximum permissible concentration of arsenic, according to World Health
Organization (WHO), United States Environmental Protection Agency (US EPA), in drinking water is 10 µg/L [6]. However, arsenic concentrations, about hundred times more than the permissible limit, Several treatment methods have been investigated for arsenic contaminated drinking water and the main mechanism used for removal of arsenic from ground water are solvent extraction, chemical precipitation etc [7, 8]. Other techniques include reverse osmosis, adsorption, ion exchange methods and permeable reactive barriers [9, 10]. All methods and techniques are associated with disadvantages such as efficiency of metal removal, high cost of reagents and energy requirement [5-10]. Adsorption has emerged as an alternate to these traditional methods due to its simplicity and safety, ease of operation, maintenance and handling, sludge free operation, potential for regeneration and possibility of the use of low cost adsorbent. So far, various adsorbents for arsenic removal have been developed that include materials such as activated carbon, activated alumina, activated carbon impregnated with ferric hydroxide and tartaric acid, metal-loaded coral lime stone [11-14]. Most of these adsorbents however entail several problems in terms of efficiency and cost.

To improve adsorption capacity and to minimize the drawbacks, several organic and inorganic supporters have been applied such as cement, sand, slag, resin, cellulose bead and chitosan [15-21]. Anion exchange fibers were prepared from vinyl benzene chloride precursor for arsenate removal, but this adsorbent is costly and economically not viable [22]. Recently, Tripathy and coworkers reported granular activated alumina as a very effective adsorbent for removal of arsenic from aqueous solution [23]. However, it works only at lower pH range (5 - 6.5) and it has more affinity for competing ions such as fluoride, phosphate than arsenic. Activated alumina was used as adsorbent for the removal of arsenic, but is less effective adsorbent for As(III), and its efficiency decreases as pH increases [24]. Ion exchange resin was used as adsorbent but it is costly and economically not viable [25]. Zeolites were used as adsorbent for removal of arsenic but the adsorption capacity decreases with increases in pH [26]. However, above systems suffered from multiple preparation steps and time consuming processes.

The two main things considered while selecting adsorbent are cost of adsorbent and easy availability. Basically, low cost adsorbents used are originated from natural sources i.e. natural materials. Because of low cost and high availability of these natural materials, they receive much attention for use as adsorbent. Tannins (TA) are one of them and can be widely used as effective adsorbing agent for water treatment in developing countries. Tannin contains polyphenolic compounds which are more attractive towards heavy metal ions. Tannins extracted from the bark of the black wattle tree and available commercially containing multiple hydroxyl groups, exhibiting specific affinity to metal ions can probably be used as an alternative, effective and efficient adsorbent for the recovery of metal ions [27]. As tannins are water soluble compounds, when used directly, they are leached by water. To overcome this drawback, many researchers have been reported to immobilize tannins on to various matrices in order to solve the water-soluble problem [28]. In the immobilization reaction, the main role of formaldehyde is to react with phenolic moiety present in tannin and make a polymer which is insoluble in acidic as well as basic media. As a result, this tannin based adsorbent shows excellent adsorption capacity towards metal ions.

In the literature, adsorbents prepared from commercial condensed tannins are applied for the removal of heavy metal ions such as uranium, americium, copper, cadmium, chromium, vanadium and lead [29-34], but the studies of adsorption kinetics for the removal of arsenic metal ions from the effluents using tannin based sorbent have not been reported.

The main objective of the study was to develop the polymeric material synthesized from natural source of tannin for the removal of arsenic from waste water. In this paper we address the synthesis, characterization and arsenic ion adsorption kinetic studies using tannin-formaldehyde resins and tannin-aniline-formaldehyde resins.
2. EXPERIMENTAL

2.1 Materials

Tannin, sodium arsenate and sodium arsenite were procured from Loba chemie, Mumbai, India. Aniline and 25% ammonia solution were purchased from Merck, India. Formaldehyde (37% solution) was obtained from Qualigens, India. All chemicals were used without purification and distillation.

2.2 Preparation of Tannin-Formaldehyde Resins (TFA resins)

Into a plastic container, 4 g of commercial tannin powder and 10 mL of 37% formaldehyde solution were added and stirred for five minutes. To the resulting solution, 20 mL of 25% ammonia solution was added, and continued the stirring for five min. A brown precipitate obtained was kept for fifteen days, yellow precipitate was observed at the bottom. The reaction mixture was then neutralized with 10.8 N hydrochloric acid solution and filtered through 0.45 µm Millipore filter paper. The precipitate obtained was washed with deionized water followed by drying under reduced pressure at 80°C for 10 h. The monomer composition of tannin-formaldehyde resins using ammonia as catalyst is presented in Table 1.

Table 1. Monomer compositions of tannin-formaldehyde (TFA) resins using ammonia as catalyst.

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>TA (g)</th>
<th>FO (mL)</th>
<th>AM (mL)</th>
<th>Basic medium</th>
<th>Acidic medium</th>
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<tr>
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</tr>
<tr>
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<td>Tm</td>
<td>S</td>
</tr>
<tr>
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<td>S</td>
<td>L</td>
</tr>
<tr>
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<td>20</td>
<td>S</td>
<td>L</td>
</tr>
<tr>
<td>TFA 08</td>
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<td>20</td>
<td>Tm</td>
<td>S</td>
</tr>
<tr>
<td>TFA 09</td>
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<td>20</td>
<td>Tm</td>
<td>S</td>
</tr>
<tr>
<td>TFA 10</td>
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<td>20</td>
<td>Tm</td>
<td>L</td>
</tr>
</tbody>
</table>

TA – Tannin; FO – Formaldehyde; AM – Ammonia; S - Solid powder; Tm - Thick mass; L - Liquid.

2.3 Preparation of Tannin-Aniline-Formaldehyde Resin (TAFA resins)

Into a plastic container 3 g of commercial tannin powder, 1 mL of aniline, and 10 mL of 37% formaldehyde solution were placed and stirred for five min. To the resulting solution, 20 mL of 25% ammonia solution was added and stirring was continued for additional five min, and a brown precipitate obtained was kept for fifteen days. The resulting mixture was neutralized by 10.8 N hydrochloric acid solution, and yellow precipitate obtained was separated by filtration and washed with deionised water followed by drying under reduced pressure at 80°C for 10 h. The monomer composition of tannin-aniline-formaldehyde resins using ammonia as catalyst is given in Table 2.
Table 2. Monomer compositions of tannin-aniline-formaldehyde (TFA) resins using ammonia as catalyst.

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>TA (g)</th>
<th>AN (mL)</th>
<th>FO (mL)</th>
<th>AM (mL)</th>
<th>Basic medium</th>
<th>Acidic medium</th>
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<tr>
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<td>S</td>
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<tr>
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<td>40</td>
<td>L</td>
<td>S</td>
</tr>
<tr>
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<td>40</td>
<td>L</td>
<td>S</td>
</tr>
<tr>
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<td>1.0</td>
<td>20</td>
<td>40</td>
<td>L</td>
<td>S</td>
</tr>
<tr>
<td>TFA 05</td>
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<td>1.0</td>
<td>10</td>
<td>40</td>
<td>L</td>
<td>S</td>
</tr>
<tr>
<td>TFA 06</td>
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<td>1.0</td>
<td>50</td>
<td>20</td>
<td>Tm</td>
<td>S</td>
</tr>
<tr>
<td>TFA 07</td>
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<td>1.0</td>
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<td>20</td>
<td>Tm</td>
<td>S</td>
</tr>
<tr>
<td>TFA 08</td>
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<td>1.0</td>
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<tr>
<td>TFA 09</td>
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<tr>
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<td>10</td>
<td>20</td>
<td>Tm</td>
<td>S</td>
</tr>
</tbody>
</table>

TA - Tannin; AN - Aniline; FO - Formaldehyde; AM - Ammonia; S - Solid powder; Tm - Thick mass; L - Liquid.

2.4 Adsorption Studies

The arsenic solutions were prepared by dissolving 0.173 g of sodium arsenite (NaAsO₃) in 1000 mL deionised water for As(III) and 0.450 g of sodium arsenate (NaH₂AsO₄·7H₂O) in 1000 mL deionised water for As(V) respectively.

Adsorption experiments were carried out by agitating 1 L of metal ion solution with 1 g of tannin resins at room temperature. When the initial pH of the adsorption medium was adjusted to a higher value of pH 4, some of the metal ions were precipitated due to existence of OH⁻ ions in the adsorption medium. The mixture was stirred continuously at 150 rpm for 3 h, the solutions were filtered through 0.45 µm Millipore filter paper. The amounts of metal adsorbed were calculated from the concentration in solutions before and after adsorption process.

Batch sorption experiments were conducted to examine the adsorption of As(III) and As(V) ions on TFA and TFAA resins. Adsorption isotherms were obtained for individual metal ions under similar conditions. The sorption was also measured as a function of time and pH under similar conditions.

2.5 Measurements

Infrared spectra of resins were obtained with a FTIR spectrophotometer. The resin was dried at 80°C under reduced pressure for 8 h where as potassium bromide (spectrometry grade) was dried at 300°C for 4 h. Potassium bromide pellet was prepared by mixing 1 mg of resin with 100 mg of KBr at 10000 kg/cm² pressure for 30 min under vacuum. The spectra were recorded using spectral width of 4000-450 cm⁻¹ (8 scans). The particle size of the tannin resins was determined by AccuSizer 780 Optical Particle Sizer, Santa Barbara, USA and particle size distribution of the resin is reported in Table 3. The results indicated that the particle size was in the range of 0.8 - 2.0 µm and narrower particle size distribution of the particles compared to suspension polymerization.
Table 3. Data of particle size and exchangeable protons of tannin-formaldehyde (TFA) resins.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Particle size (μm)</th>
<th>H⁺ mmol/g</th>
<th>Sample code</th>
<th>Particle size (μm)</th>
<th>H⁺ mmol/g</th>
</tr>
</thead>
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<tr>
<td>TAFA 01</td>
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<td>TFA 01</td>
<td>1.48</td>
<td>4.9</td>
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<td>0.78</td>
<td>8.2</td>
<td>TFA 02</td>
<td>0.93</td>
<td>5.8</td>
</tr>
<tr>
<td>TAFA 04</td>
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<td>TFA 03</td>
<td>1.71</td>
<td>7.6</td>
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<tr>
<td>TAFA 05</td>
<td>0.99</td>
<td>8.0</td>
<td>TFA 04</td>
<td>1.46</td>
<td>7.9</td>
</tr>
<tr>
<td>TAFA 06</td>
<td>0.87</td>
<td>8.1</td>
<td>TFA 05</td>
<td>0.98</td>
<td>8.1</td>
</tr>
<tr>
<td>TAFA 07</td>
<td>0.81</td>
<td>9.6</td>
<td>TFA 08</td>
<td>1.23</td>
<td>7.6</td>
</tr>
<tr>
<td>TAFA 08</td>
<td>0.80</td>
<td>9.4</td>
<td>TFA 09</td>
<td>1.27</td>
<td>7.9</td>
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<tr>
<td>TAFA 09</td>
<td>0.83</td>
<td>8.9</td>
<td>TFA 10</td>
<td>0.88</td>
<td>8.1</td>
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<tr>
<td>TAFA 10</td>
<td>0.85</td>
<td>7.4</td>
<td></td>
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</tbody>
</table>

2.6 Analytical Methods

The residual arsenic in water sample was determined using molybdenum blue method [35]. The method was used to estimate As(III) and As(V) concentrations in treated water samples to assess the efficiency of the oxidation step and subsequent removal of arsenic. Spectrophotometric measurements were made at a wavelength of 865 nm using absorbance cell of 1 cm path length for arsenic determination.

Procedure: Two sets of concentrations starting from 1-15 ppm/L of As(III) to As(V) were prepared from the standard solutions. One set is used for treated (oxidized) aliquot and other for untreated one. One mL of 1 N hydrochloric acid and 1 mL of 0.017 M potassium iodate were added successively to each of the treated aliquots with thorough mixing after each addition. Ten minutes were allowed for oxidation of As(III) to As(V), and 4 mL of mixed reagent* was added to each of the treated (oxidized) and untreated aliquots with thorough mixing. After 2 h the complex was formed and developed a blue color. The amount of complex formation is directly proportional to the arsenic concentration, which was determined as a function of absorbance measured at 865 nm wave lengths with an UV spectrophotometer. Suitable blank samples were run using above procedure along with the samples for two times.

Mixed reagent preparation: The solutions of 15 mL of 0.1 M ascorbic acid (freshly prepared), 7.5 mL of 0.032 M ammonium molybdate, and 2.5 mL of 0.0082 M potassium antimony tartarate were mixed. To this solution, a solution of 25 mL of 5N sulfuric acid was added immediately after the addition of potassium antimony tartarate to avoid the generation of turbidity in the color reagent.

2.7 Determination of Exchange Capacity of the Resins

The exchange capacity of the tannin resin was measured by the proton exchange method [36]. The proton titration experiments were carried out to determine the number of valid sites for adsorption present on adsorbent particles. Into a flask, 10 mL of 0.1 N sodium hydroxide solution and 0.1 g of resin particles were placed and the flask was kept in a thermostatic water shaker bath and shaking was continued for 24 h at 25°C at 100 rpm. The stirred solution was titrated against 0.1 N hydrochloric acid solution using phenolphthalein as an indicator.
3. RESULTS AND DISCUSSION

3.1 Tannin-Aniline-Formaldehyde Resins

Tannins are composed of polyphenolic compounds having higher molecular weights ranging from 500-20000 g/mol. Due to the enormous structural diversity, tannins are divided into two major groups: (a) condensed and (b) hydrolysable tannins. Generally, low molecular weight tannins are soluble in water. Condensed tannins are oligomeric and polymeric proanthocyanidins formed by linkage of C-4 on one catechin with C-8 or C-6 of the next monomeric catechin [37]. A-ring of the condensed tannin serves as very reactive nucleophiles, where as B-ring provides antioxidant properties and excellent sites for complexation with metal ions due to the presence of ortho-hydroxyl groups [38, 39]. The nucleophile centers on the A-ring of flavanoid unit tend to be more reactive than those on the B-ring. This is due to the presence of vicinal hydroxyl substituent and also steric hindrance. Therefore formaldehyde reacts with tannin to produce resin through methylene bridges at reactive positions on the flavanoid molecules of the A-ring. The free C-6 and C-8 sites on the A-ring react with formaldehyde due to the strong nucleophilicity to form insoluble tannin resin. The high reactivity of tannin towards formaldehyde is the result of the reactivity of A-ring which has 10 to 50 times higher the reaction rate than those of phenol with formaldehyde.

Two steps are involved during formation of tannin-formaldehyde resins, methylation and condensation reaction. The first step involves methylation, which is an electrophilic aromatic substitution reaction. The second step is condensation reaction, where the methanol group of one molecule reacts with a second tannin molecule, thus forming a methylene linkage. Due to high molecular weight and complex structure of tannin, the process of cross linking is complicated, where resole resins produce linear and regular crosslinking.

3.2 FTIR Spectroscopy

Figure 1 represents FTIR spectra of tannin (TA), tannin-formaldehyde resins (TFA), tannin-aniline-formaldehyde resins (TFAA), tannin-formaldehyde resins adsorbed with arsenic (TFA-As), and tannin-aniline-formaldehyde resins adsorbed with arsenic (TFAA-As). IR spectrum of tannin showed that the absorption of broad band observed in the range of 3550 - 3100 cm\(^{-1}\), is attributed to phenolic and methylool –OH groups of tannin resins. The presence of absorption bands in the region of 1612 - 1447 cm\(^{-1}\) are characteristic of the elongation of aromatic -C=C- bonds. The absorption bands appeared in the range of 1533 - 1447 cm\(^{-1}\) due to the deformation vibration of -C-C- bonds in the phenolic groups. The absorption band observed at 1210 cm\(^{-1}\) is associated with the >C=O stretching of the benzene ring. The presence of absorption bands in the region of 1085 - 1031 cm\(^{-1}\) is due to >C=O stretching and C-H deformation.

IR spectrum of TFA resins showed small absorption bands observed in the range of 2800-2650 cm\(^{-1}\) are associated with methylene (-CH\(_2\)-) bridges formed by reaction with formaldehyde [40-42]. It has been demonstrated that large number of methylene ether bridges (-CH\(_2\)-O-CH\(_2\)-) occur, which rearrange themselves to form methylene (-CH\(_2\)-) bridges with release of formaldehyde [43]. The comparative study of IR spectra of tannin and TFA resins shows that the peaks intensity of >C=O peak at 1117 cm\(^{-1}\) is increased and also broadened. It indicates the formation of dimethylene ether (-CH\(_2\)-O-CH\(_2\)-) linkages by the condensation of formaldehyde with tannin [44]. The intensity of absorption bands decreased in the region of 827 - 760 cm\(^{-1}\) is due to the substitution at 6 and 8 positions of tannin. The presence of the band in the region 1510- 1750 cm\(^{-1}\) which could be assigned to -C=C- stretching.
observed. This could be due to the effect of metal ion chelating on the double bonds present in the aromatic rings. Comparison of tannin, TFA, and TAFA with arsenic adsorbed spectra of TFA and TAFA resins showed that the relative intensities of peaks at 1031-1713 cm\(^{-1}\) were changed because of metal-tannate complex formation between arsenic species and phenolic groups of tannin [45].

3.3 Particle Size Distribution and SEM

The particle size distribution data of tannin-formaldehyde resins is presented in Table 3. It illustrates that the particle size distribution is in the range of 0.8 - 1.71 μm. Representative particle size distribution data was obtained by particle size analyzer (AccuSizer 780 Optical Particle Sizer, Santa...
Barbara, USA). Figure 2 depicts the SEM micrographs of the resin surface. Many small pores and particles with diameter >3 μm diameter are observed on the surface of tannin resins.

**Figure 2.** SEM micrographs of tannin-aniline-formaldehyde (TAFA) resins.

### 3.4. Exchange Capacity of the Resins

The exchange capacity of tannin resins was determined by the proton exchange method [46]. Proton titration experiments were carried out to determine the number of valid sites for adsorption present on adsorbent particles. The surface exchange capacity of tannin resins is reported in Table 3, which was found to be in the range of 4.9 – 9.6 H⁺ mmol/g. The titration results showed that H⁺ ion exchangeable groups are largely –OH groups dominating the resin surface. The comparative study of TFA and TAFA resins (Table 3) shows that TAFA resins have higher proton exchange values than TFA resins. It clearly indicates that amino group of aniline with phenolic –OH groups of tannin improves proton exchange capacity than that of phenolic –OH groups of tannin alone and it may be attributable to the synergistic effect of additional amine functional group and phenolic –OH group of tannin within resins.

### 3.5 Adsorption Behavior of Metal Ion on Resins

The percentage adsorption of As(III) and As(V) at different pH is presented in Tables 4-7. In the literature, different adsorption mechanism for the adsorption of metal ions on tannin based adsorbents has been proposed. These include ion exchange, surface adsorption, chemisorptions, complexation and adsorption-complexation [47-51]. It is commonly believed that ion exchange is mostly a pentavalent mechanism. Metal ion forms bonding with –OH groups of tannin resins to release protons with their anion sites to displace on existing metal.

Other studies have found evidence that tannin resins adsorb metal by complexation, surface adsorption and chemisorptions [52] and concluded that the catechol or pyrogallol B ring offers special opportunities for formation of metal complexes [45]. The results presented in Tables 5 and 6 show that the binding of As(III) metal ions is almost 8-12 times higher than that of As(V). It is due to the proton exchange capacity of As(III) which is higher than that of As(V). The results presented in Tables 6 and 7 show that TAFA resins adsorb higher amount of metal ions of As(III) than that of TFA resins.
### Table 4. As(V) binding on TAFA at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>TAFA 01 (mg/g)</th>
<th>TAFA 03 (mg/g)</th>
<th>TAFA 04 (mg/g)</th>
<th>TAFA 05 (mg/g)</th>
<th>TAFA 06 (mg/g)</th>
<th>TAFA 07 (mg/g)</th>
<th>TAFA 08 (mg/g)</th>
<th>TAFA 09 (mg/g)</th>
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### Table 5. As(V) binding on TFA resins at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>TFA 01 (mg/g)</th>
<th>TFA 02 (mg/g)</th>
<th>TFA 03 (mg/g)</th>
<th>TFA 04 (mg/g)</th>
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### Table 6. As(III) binding on TAFA resins at different pH.

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<tr>
<th>pH</th>
<th>TAFA 01 (mg/g)</th>
<th>TAFA 03 (mg/g)</th>
<th>TAFA 04 (mg/g)</th>
<th>TAFA 05 (mg/g)</th>
<th>TAFA 06 (mg/g)</th>
<th>TAFA 07 (mg/g)</th>
<th>TAFA 08 (mg/g)</th>
<th>TAFA 09 (mg/g)</th>
<th>TAFA 10 (mg/g)</th>
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Table 7: As(III) binding on TFA resins at different pH

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<th>TFA 02 (mg/g)</th>
<th>TFA 03 (mg/g)</th>
<th>TFA 04 (mg/g)</th>
<th>TFA 05 (mg/g)</th>
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It is due to presence of aniline in TAFA resins, in which primary amino group of aniline increases complex formation due to lone pair of electrons present on nitrogen. It is also due to the synergistic effect of additional amine group present in aniline and phenolic –OH groups within tannin resins. Adsorption of As(III) binding on TAFA and TFA resins shows that adsorption increases with increase in formaldehyde concentration (Tables 6 and 7). To make a tannin resin insoluble in both acidic and basic media, tannin is crosslinked with formaldehyde so as to more and more tannin molecule attached together. Due to crosslinking of tannin with formaldehyde more surface hydroxyl groups are available for metal chelation.

In order to explain the adsorption mechanism, FTIR spectroscopy (Fig. 1) and Energy-dispersive X-ray spectroscopy (EDX) (Fig. 3) studies were carried out. IR spectrum of TFA-As adsorbed resins revealed that the absorption of methylol groups (-C-O) in the region of 1170 - 1050 cm$^{-1}$ decreased in intensity and broadened the peak than those of tannin and TFA resins spectra. EDX spectrum also confirmed arsenic adsorption on tannin resins.

![Figure 3](image.png)

**Figure 3.** EDX spectrum of metal adsorbed on tannin (TAFA) resins.

### 3.6 Effect of pH

The effect of pH on adsorption of As(III) and As(V) were studied in the range of 2-10. The percentage adsorption of As(III) and As(V) on tannin resins at different pH is presented in Tables 4-7. It shows that the adsorption of arsenic (III) or (V) is independent on pH. This is attributable to the arsenic
solutions formed in the aqueous which are subsequently adsorbed on the resins surface.

At lower pH, the functional groups of tannin resins are protonated to a higher extent and such a condition is not favorable for As(III) removal resulting almost no change in the extend of adsorption within the pH range 2-5 [53]. Arsenic present in natural waters in two common forms: arsenite (AsO\(_3^{3-}\)) and arsenate (AsO\(_4^{3-}\)) are referred to arsenic (III) and arsenic (V) respectively. Smedley and Kinniburgh [1] demonstrated that arsenate is the dominant form of arsenic in oxidized environment, whereas arsenite dominates in reduced system. Pentavalent arsenates exist in different species namely H\(_3\)AsO\(_4\), H\(_2\)AsO\(_4^−\), HAsO\(_3^{2-}\), AsO\(_4^{3-}\) in the pH range of <2, 3-6, 8-10, and >12 respectively. Trivalent arsenites include As(OH)\(_3\), As(OH)\(_2^−\), AsO\(_2\)OH\(^2\), and AsO\(_3^{3−}\). As(V) species predominates and stable in oxygen rich aerobic environments while trivalent arsenates predominates in moderately reducing anaerobic environments such as ground water [54]. It is thus considered that the metal anions are adsorbed by releasing protons from phenolic –OH groups of tannin in the pH range of 3-5 according to anion exchange mechanism.

3.7 Effect of Contact Time

Figures 4 and 5 show the effect of contact time for the adsorption of As(V) and As(III) on tannin-formaldehyde resins respectively. It is evident that time has a significant influence on the adsorption of As(V). It was observed that the percentage removal of As(V) from aqueous solution increases rapidly and reaches up to 83% within 10 min. After that, the percentage removal of As(V) increases slowly and reaches up to 86% in a total period of 30 min. A further increase in contact time has negligible effect on the percentage removal of As(V). In the case of percent removal of As(III) the rate of adsorption is lower, and it takes almost 30 min. to reach 90% adsorption. Later on adsorption becomes almost steady. It may be due to the saturation of adsorption capacity of tannin resins.

The mechanism of solute transfer to the solid includes diffusion through the film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. Initially the concentration gradient between the film and the solid surface is large, and hence the transfer of solute onto the solid surface is faster. Thus, it takes lesser time to attain 83 percentage removal of As(V). As the time increases, intraparticle diffusion becomes predominant. Thereby, solute takes more time to transfer from solid surface to internal adsorption sites through the pores [55].

![Figure 4: Effect of contact time for the adsorption of As(V) on tannin-formaldehyde resins](image-url)
3.8 Adsorption Kinetics

To evaluate sorption dynamics, it requires consideration of two important physico-chemical parameters such as kinetics and equilibrium of adsorption. Kinetics describing the solute adsorption rate which governs the contact time. The study of equilibrium is the determining distribution of the solute between solid-liquid phases and determining feasibility and capacity of the sorbent for adsorption. Several kinetic models currently in use to explain the mechanism of adsorption progress are of the most simple and widely used is pseudo-first order equation of Lagergren [56].

\[
\log(q_e - q_t) = \log q_e - k_{ad}t/2.303
\]

The \( q_e \) is the mass of metal adsorbed at equilibrium (mg/g), \( q_t \) is mass of metal adsorbed at time \( t \) (mg/g) and \( K_f \) is the first order reaction constant (L/min). The pseudo-first order kinetics considers the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. A graph of log \( (q_e-q_t) \) verses \( t \) indicates the application of the first order kinetic model (Figures 6 and 7).
On the other hand, equilibrium capacity may be expressed by pseudo-second order equation as follows:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}q_e^2} + \frac{t}{q_e}$$

Where, $K_{2,ad}$ is the second order reaction rate equilibrium constant (g/mg.min). A plot of $t/q_t$ versus $t$ gives a linear relationship for the applicability of the second order kinetic (Figures 8-9).
3.9 Desorption Study

Reuse of tannin-formaldehyde resins is an important step in order to make the adsorption process more economical. The desorption of arsenic from the tannin resins may be the reverse process of adsorption, in which the arsenic adsorbed onto the solid surface of tannin resins released to the aqueous phase. For desorption study, various eluents such as HCl, HNO₃, NaCl and NaNO₃ are used. The regeneration efficiency of tannin resins at 1M HNO₃ solution was studied. In order to study the reusability of tannin resins, the adsorption/desorption cycles of As(III) and As(V) were repeated three times by using same adsorbent. When HNO₃ was used as a desorbing agent, the tannin resins surface was completely covered by H⁺ ions. The coordination spheres of chelated As(III) and As(V) ions could not compete with H⁺ ions for desorption sites and subsequently heavy metal ions were released from solid surface into the solution. Nearly 95% of the adsorbed As(III) and As(V) ions were desorbed from tannin resins by using 1M HNO₃ solution in the first step, which then decreased to 85% at the third step.

4. CONCLUSION

The present study demonstrated the use of tannin-formaldehyde and tannin-aniline-formaldehyde based resins as adsorbents for As(III) and As(V) metal ions. Tannin-formaldehyde resins were prepared by condensation reaction between tannin and formaldehyde, whereas tannin-aniline-formaldehyde resins were prepared by condensation of tannin and aniline with formaldehyde. Synthesized tannin-formaldehyde resins are insoluble in water, whereas the natural tannin is soluble in water. Tannin-formaldehyde resins were characterized by FTIR and EDX before and after adsorption of the metal ions. The batch experiments were studied as a function of particle size, initial pH, proton exchange capacity and initial concentration of As(III) and As(V). Equilibrium and kinetic studies were conducted for the adsorption of As(III) and As(V) from aqueous solution on to tannin resins with the concentration of 25 mg/g for As(V) and 200 mg/g for As(III) at pH 5. The adsorption mechanism may be partly results of the ion exchange or complexation between arsenic ion and phenolic –OH groups on tannin resin surfaces. Chemically modified tannin resins have been proposed to be an efficient and economical alternative sorbent in arsenic ion removal from water.

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REFERENCES AND NOTES


The authors declare no conflict of interest

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