Solid phase extraction of Fe(III) utilizing alumina modified with phenolic compounds produced via microwave approach

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This study describes the use of microwave approach to improve the adsorptive efficiency of alumina surface toward Fe(III). Due to the strong tendency of Fe(III) for reacting with phenolic compounds, the improvement process had been achieved via modification of alumina surface with 2-amino phenol and 1-naphthol by the microwave technique. The two new adsorbents are characterized by Fourier transform-infrared spectroscopy, scanning electron microscope and X-ray diffraction. The adsorption properties of the adsorbents for Fe(III) are studied, optimized and evaluated under various experimental conditions. The results show higher ferric ions extraction (≥98.2%) by the two new adsorbents as compared to native alumina. The experimental results are well fitted by Langmuir and Freundlich isotherms and pseudo-second order kinetics. High recovery values of Fe(III) spiked natural water samples are obtained (≥95.0%) by column and batch techniques.

Keywords: Solid phase extraction, Extraction, Iron, Alumina, Modified alumina, Phenols, Microwave technique, Chelates, Adsorption

An essential requirement of protected green environments and safe human life is the availability of uncontaminated water. However, in the past century, a large number of contaminants have found their way into water resources via the massive industrial activities and technological applications including mining, electroplating, steel production, etc. Heavy metal species derived from iron, lead, copper, etc. are of major concern as contaminants. Of these, iron ions have attracted wide attention of researchers as one of the heavy metal ions which is found in many manufacturing industries such as the metal finishing and galvanized pipe. Iron in drinking water and water supplies can cause problems even at relatively low concentrations. Iron can make the water unusable for food and beverage and give water a metallic taste, reddish color, turbidity and odour. High levels of iron cause environmental and human health problems, including anorexia, oligue, diarrhoea, hypothermia, metabolic acidosis and even death. Thus, the determination of heavy metal ions in natural water samples is a very important part of environmental and public health studies.

Strong emphasis on finding and developing analytical methods has been directed towards separation and determination of trace metal concentrations in natural waters. Among the various methods, solid phase extraction (SPE) is attractive due to its simplicity and rapidity. A large number of SP-extractors have been produced via modification of silica gel and alumina substrates with organic chelating reagents to increase their affinity for binding to heavy metal ions. Alumina is known as one of the most commonly used inorganic solid supports. Moreover, the surface of alumina is characterized by the presence of functional groups like hydroxyls in different arrangement and distribution. These hydroxyl groups are responsible for binding, adsorption and extraction processes. However, weak ion-exchange properties of these hydroxyl groups lead to low interaction with various species. Hence, improvement in the adsorption efficiency and extraction power of SP-extractor as well as incorporation of certain selectivity characters have been attempted via surface modification with certain functional groups.

The surface modification process is usually achieved under conventional reflux condition or impregnation for a long time and in presence of organic solvents. Recently, there has been growing interest in the use of microwave heating technique in the synthesis to eliminate the use of solvents and
catalysts and also to reduce the use of volatile organic compounds. Moreover, this technique is proved to be excellent in terms of very short reaction time in comparison with conventional procedures using traditional heating techniques. However, literature survey shows that microwave heating has not previously been used for modification of alumina surface with organic compounds in SPE technique for removal of metal ions purposes. The present work deals with the modification of alumina surface with 2-aminophenol and 1-naphthol (which show high capability for reaction with Fe(III)) using microwave technique. It also aims to optimize the different parameters for Fe(III) extraction by the newly obtained adsorbents and their application for purification of contaminated real water samples.

Materials and Methods

Alumina of standard grade (150 mesh, 58 Å and surface area 155 m²/g), 2-aminophenol, 1-naphthol, ferric chloride hexahydrate and other chemicals used were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Drinking tap water (DTW), mineral water (MW) and ground water (GW) were collected from El-Minia governorate, Egypt. Waste water (WW) was collected from Abou-Korkas Sugar Factory, El-Minia, Egypt.

A Fisher Scientific Accumet pH-meter (model 825) calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH-measurements. Microwave oven (KOR-131G, Korea) emitting 2.450 GHz microwave frequency was used for heating. FT-IR spectra were recorded from KBr pellets using a FT-IR (model 410) JASCO (Japan) spectrometer. Scanning electron microscope analysis was obtained using JSM-5400 LV JEOL (Japan) instrument. X-ray diffraction analysis was made on a Philips X-ray diffractometer (PW 1370) with Ni filtered Cu-Kα radiation (1.5406 Å). Wrist Action mechanical shaker (model 75, USA) was used for shaking process. Flame atomic absorption determinations (FAAS) of metal ions were performed using Perkin Elmer 2380 spectrometer.

Modification of alumina with 2-aminophenol and 1-naphthol using microwave technique

Alumina was first dried by heating in an oven at 150 °C for 5 h. Then, 1:1 weight ratios of alumina-to-2-aminophenol were irradiated at different powers and times in a watch glass using a microwave oven. 1:1 and 1:2 weight ratios of alumina-to-1-naphthol were also irradiated at the same previous conditions. The products, alumina modified 2-aminophenol (AM-2AP) and alumina modified 1-naphthol (AM-N), were then washed with water, separated by filtration and left to dry in an oven at 60 °C.

Solid phase extraction of Fe(III) using AM-2AP and AM-N

The percentage extraction of Fe(III) using AM-2AP and AM-N were determined in triplicate under static conditions by batch technique. Thus, 50.0 mg of the adsorbent was added to 0.5 mL of 0.1 M Fe(III) at pH range 1.0-4.5 (pH adjustment was achieved using solutions of 0.1 M HCl and 0.1 M NaOH). The total volume was made up to 50 mL with doubly distilled water. The mixture was mechanically shaken for 30 min at room temperature to attain equilibrium. Then the solid phase was separated by filtration and the unretained Fe(III) in the filtrate was determined by complexometric EDTA titration. The percentage extraction was obtained using the following equation: 

\[
\% \text{ Extraction} = \left( \frac{C_f - C_i}{C_i} \right) \times 100
\]

where \(C_i\) is the initial concentration of Fe(III) and \(C_f\) is its final concentration.

The effect of adsorbent dosage (5.0–100.0 mg), equilibration time (5–60 min) and initial Fe(III) concentration (4.0×10⁻⁴–2.0×10⁻³ M) was also studied by the batch technique.

Stability studies

The effect of medium on the stability of the two alumina adsorbents was investigated in acetate buffer at pH 1.0–6.0 and ammonia buffer at pH 8.0 and 10.0 under static conditions. In this study, 100.0 mg of the adsorbent was soaked with 25 mL of the selected buffer in 50.0 mL measuring flask for 1 h, and then mechanically shaken for another 1 h. The treated adsorbent was separated by filtration, thoroughly washed with doubly distilled water, till the pH of filtrate equaled 7.0, and then dried. To explore the extent of hydrolysis of the organic modifier loaded on alumina surface, 50.0 mg of treated adsorbents and untreated taken as standard, were used to evaluate Fe(III) ion adsorption capacity under the same conditions as in the batch experiments. The obtained Fe(III) uptake values of treated adsorbents were compared with that of the standard untreated one.

Surface coverage of adsorbents

For determination of the concentration of organic modifier (2AP and N) on the alumina surface, 100.0 mg of the modified alumina phase in a dry porcelain crucible was gradually heated in an oven to
700 °C. The sample was maintained at this temperature for 1 h to ensure complete decomposition of the organic modifier, then left to cool to room temperature. The weight loss due to desorption was evaluated by difference in weights. Blank sample of dry, unmodified alumina was subjected to the same treatment for comparison.

Results and Discussion

Synthesis of AM-2AP and AM-N

The details of the effect of the modification conditions of alumina surface (weight ratio, power and time) using microwave oven on the percentage extraction of Fe(III) ions are provided in Table 1. It was observed that the reaction time became shorter with increase of the microwave power. Also, the percentage extraction of Fe(III) using AM-2AP and AM-N reached the highest values (100.0% and 98.2%, respectively) under power of 20 W microwave radiation and time 5 min with weight ratio 1:1 and 1:2, respectively. This behaviour is because the expected binding sites with ferric ions in AM-2AP adsorbent (-OH and -NH\(_2\)) are twice as that in AM-N adsorbent (-OH), see Fig. 1. Thus, it may be concluded that, the optimum power and time required for the microwave synthesis of alumina adsorbents is 20 W and 5 min, respectively for weight ratio 1:1 and 1:2 for AM-2AP and AM-N, respectively.

The concentration of phenolic compounds loaded on alumina surface as determined by the thermal desorption method indicates a fairly high surface coverage equal 4.226 and 3.089 mmol g\(^{-1}\) for AM-2AP and AM-N, respectively. The higher value of surface coverage of AM-2AP than AM-N can be attributed to the effect of lower molecular size of the phenolic ring in AM-2AP as compared to the naphthalene ring in AM-N.

Characterization of AM-2AP and AM-N adsorbents

The FT-IR spectra of alumina phases before and after adsorption of Fe(III) were recorded to determine the vibration frequency changes in their functional groups in the range of 4000–400 cm\(^{-1}\) (Supplementary data, Fig. S1). The FT-IR spectra of the native γ-alumina displayed a broad band at 3450 cm\(^{-1}\) which may be attributed to hydrogen bonded surface hydroxo groups. There is an intense broad band located in the vicinity of 560 cm\(^{-1}\) as signed to Al-O stretching vibration\(^\text{27,28}\). The loading of 2-aminophenol and 1-naphthol moieties to alumina surface was confirmed by IR spectral analysis of the

Table 1—Extraction of Fe(III) at varying microwave conditions, alumina-to-phenol ratio, radiation power and time on modified alumina. [pH: 3.5; adsorbent: 50.0 mg]

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Ratio (alumina:phenol)</th>
<th>Power (watt)</th>
<th>Time (min)</th>
<th>Fe(III) extracted (%)</th>
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<tr>
<td>AM-2AP</td>
<td>1:1</td>
<td>40</td>
<td>10</td>
<td>78.5</td>
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<td></td>
<td></td>
<td>20</td>
<td>5</td>
<td>98.20</td>
</tr>
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</table>

Fig. 1—Suggested binding modes of the organic modifiers to alumina surface along with their binding sites to Fe(III) ions. [(a) AM-2AP; (b) AM-N].
newly synthesized adsorbents. New bands appeared that were not present in the native alumina. For AM-2AP, strong bands appeared at 3375.78, 3303.46, 1602.56, 1270.86, 1081.87 and 743.42 cm\(^{-1}\) due to aromatic primary amines \(\nu(-\text{NH})\) in addition to bands at 1602.56 and 1409.71, 1081.87 cm\(^{-1}\) due to \(\nu(C=C)\) in the aromatic ring and \(\nu(\text{Aryl-OH})\), respectively. For AM-N also, new peaks appeared at 1586.16, 1511.92, 1455.03, 1377.89, 766.57 and 565.04 cm\(^{-1}\), characterized to the naphthalene rings which confirm the modification process. The band related to \(\nu(-\text{OH})\) groups in alumina were merged with that of phenolic \(\nu(-\text{OH})\) of 2AP and N to form broad band in range 3500–3000 cm\(^{-1}\). Comparison of the IR spectra of the modified alumina phases after ferric ions adsorption with that of the metal-free phase clearly shows the presence of several functional groups (-NH\(_2\), -OH of 2-aminophenol, -OH of 1-naphthol and -OH of alumina surfaces as well) which are able to bind with heavy metal ions, in particular Fe(III), in the new alumina adsorbents\(^{29}\). The proposed mechanism of alumina modification mode and adsorption of the two adsorbents with Fe(III) is illustrated in Fig. 1. Figure 1 shows a physical loading of 2AP and N to alumina surface via hydrogen bonding. In addition, the binding mechanism of Fe(III) is suggested to occur through chelate ring formation in the case of 2-aminophenol and coordination binding with phenolic oxygen in the case of 1-naphthol. Moreover, the obvious color change occurring after ferric ions adsorption by the two adsorbents also supports metal binding via complex formation. For example the color of AM-2AP and AM-N changed from buff and pink to dark brown and dark violet respectively after adsorption of Fe(III) at optimum pH.

The surface morphology of alumina, and AM-AP and AM-N before and after Fe(III) adsorption, was analyzed using a scanning electron microscope (SEM) (Fig. 2). The modification of alumina showed some changes in its surface (Fig. 2a). The modified alumina adsorbents (AM-2AP and AM-N) present an adequate morphological profile to retain target metal ions. The microphotographs before the Fe(III) adsorption show a rough surface with large particles which is an important factor facilitating the mass transfer rate of metal ions toward the adsorbent surface and consequently improving its adsorption capacity\(^{15}\) (Fig. 2(b, d)). After adsorption, the micrographs show the presence of a smooth surface with fine and small particles (Fig. 2(c, e)). These differences in surface morphology support the adsorption process on alumina adsorbents.

Figure 3 shows the XRD pattern of alumina and its adsorbents (AM-2AP and AM-N). \(\gamma\)-Alumina (GCPDS-29–1486) showed characteristic peaks at 29 (deg.) = 67.225, 46.841, 40.690, 37.175, 34.810, 20.210, 18.793 for a crystal shape of the phase in its XRD pattern (Fig. 3(curve 1))\(^{30}\). After modification of alumina surface with 2AP and N, there were obvious changes in the X-ray patterns (Fig. 3(curves 2, 3)). The crystalline structural characteristics of AM-2AP and AM-N adsorbents were identified based on sharp diffraction peaks at 29(deg.) = 67.424, 42.658, 37.108, 33.057, 28.391, 27.763, 27.189, 25.877, 24.461, 15.775, 15.207, 7.495 and 67.201, 46.711, 33.127, 30.304, 27.766, 27.179, 25.895, 24.027, 20.688, 15.761, 15.107, 7.475 for AM-2AP and AM-N, respectively. Moreover, there are strong differences in intensity and shape of the peaks\(^{31}\). These results show the successful alumina modification process. The uptake of Fe(III) by the new modified alumina adsorbents is strongly reflected through their XRD patterns (Fig. 3(curves 4, 5)). Firstly, strong shifts of 29 (deg.) = 50.019, 40.17, 32.395, 17.949, 8.95 and to 58.530, 40.239, 36.955, 31.784, 21.482, 18.906, 8.863 for AM-2AP and AM-N after ferric ions adsorption, respectively. Secondly, disappearance of the sharp peaks at 29 (deg.) = 33.057, 27.763, 27.189, 25.877, 24.461 of AM-2AP and 27.766, 27.179, 25.895, 24.027, 20.68 of AM-N after Fe(III) binding.

**Effect of pH and adsorbent dose on Fe(III) extraction**

2-Aminophenol and 1-naphthol are immobilized on the skeleton of alumina surface. Therefore, the formation of a complex between Fe(III) and both 2AP and N and hence the adsorption of Fe(III) from aqueous solution is expected to be influenced by the pH of solution. The Fe(III) ions binding and adsorption interaction processes were studied and investigated at different pH values. The two adsorbents have the high affinity over the studied pH range (1.0-4.5) towards Fe(III) and give high percentage extractions (100.0% and 98.2% for AM-2AP and AM-N, respectively) at pH 3.5 (Fig. 4). As shown in this figure maximum uptake starts from pH 3.5 and continues to pH 4.0 and 4.5, however the pH value of 3.5 is preferred as optimum to avoid iron hydroxide precipitation. Figure 4 shows interesting results depending on using native alumina for the uptake of Fe(III); the percentage extraction did not exceed 30.0%, which strongly supports the
participation of phenolic and amino groups of the two organic modifiers to alumina surface for interactions with Fe(III) ions.

According to the above results, the interaction of Fe(III) with the loaded 2-aminophenol and 1-naphthol is mainly based on direct complex formation due to the presence of nitrogen and/or oxygen donor atoms as well as the weak cation exchange characteristics of the phenolic groups. The contribution of the alumina surface hydroxyl groups as cation exchangers is expected to be minimum, especially at the lower pH range. The results show the vital role of phenolic compounds in improving the percentage extraction and adsorption capacity of alumina surface toward removal of ferric ions.

The SP-extractor dosage as an influential parameter in the SPE process was also investigated to illustrate the relationship between ferric ions adsorption and mass of the alumina adsorbents using seven dosages, viz., 5, 10, 15, 20, 25, 50, and 100 mg. The percentage extraction of Fe(III) by the two adsorbents increase to reach 100.0% and 98.2% for AM-2AP and AM-N, respectively with the increase in the selected adsorbent dose till 50.0 mg. This trend is mainly due
to an increase in the number of available adsorption sites and functional groups of the alumina adsorbents, which results in enhanced removal of Fe(III). Rate of adsorption of iron(III) by alumina adsorbents is appreciable at dosage of 20.0 mg and 25.0 mg (98.5%, 97.0% and 99.0%, 97.8% for AM-2AP and AM-N, respectively), but at 50.0 and 100.0 mg it records a remarkable increase in extraction (100.0% and 98.2% for AM-2AP and AM-N, respectively).

Effect of initial Fe(III) concentrations (Isotherm studies)

The effect of initial concentration of Fe(III) on percentage extraction was studied at concentrations of (4.0×10⁻⁴–2.0×10⁻³ M) at fixed adsorbent weight of 50.0 mg, pH 3.5 and contact time 15 and 30 min for AM-2AP and AM-N, respectively. The results showed that as the concentration was increased from 4.0×10⁻⁴–2.0×10⁻³ M, the percentage extraction decreased, indicating that the metal extraction is highly dependent on the initial concentration of Fe(III) in solution.

Adsorption isotherm studies are important to determine the efficiency of adsorption. Various models have been commonly used to describe the adsorption isotherm, and these are mainly based on Langmuir and Freundlich isotherm models. The Langmuir model assumes that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules. The Freundlich model is based on adsorption on a heterogeneous surface. The Langmuir and Freundlich isotherm constants for binding of Fe(III) using AM-2AP and AM-N at room temperature have been summarized in Table 2. From this table, it is clearly obtained that the adsorption data are fitting well to the Langmuir and Freundlich models.

Effect of time (Kinetic studies)

The effect of time was studied over varying contact time intervals (5, 10, 15, 20, 30 and 60 min) on Fe(III) adsorption by 50.0 mg each of AM-2AP and AM-N, at optimum pH value (pH 3.5). A 100.0% and 98.2% extraction of Fe(III) by AM-2AP and AM-N, respectively were obtained after only 15 and 30 min of shaking time, respectively. Thus, one can conclude that the presence of surface loaded 2AP and N on
alumina at pH 3.5 favors fast equilibrium, interaction and adsorption of Fe(III).

To investigate the mechanism of SPE and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to analyze the experimental data. The adsorption kinetic data of Fe(III) measured on AM-2AP and AM-N were analyzed in terms of pseudo-second order sorption equation \( \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \) (Eq.1), where \( k_2q_e^2 \) the initial adsorption rate (mmol g\(^{-1}\) min\(^{-1}\)) and \( q_e \) can be obtained from the intercept and slope of plotting \( t/q_t \) versus \( t \), respectively. These were calculated to be \( k_2q_e^2 = 8.474 \) and 0.942, \( q_e = 1.104 \) and 1.127 mmol g\(^{-1}\) and \( k_2 = 6.953 \) and 0.742 min\(^{-1}\) for AM-2AP and AM-N, respectively. The calculated \( q_e \) values (1.104 and 1.127 mmol g\(^{-1}\)) for AM-2AP and AM-N, respectively agree very well with the experimental values (1.10 and 1.08 mmol g\(^{-1}\)) for AM-2AP and AM-N, respectively. The results above showed that the adsorption kinetics data were best fitted with the pseudo-second order model, which gives a correlation factor (\( r^2 \)) of 0.999 for AM-2AP and AM-N.

**Effect of medium (Stability studies)**

AM-2AP and AM-N were found to be stable after a long contact time in the pH range from 3.0 to 10.0 and from 5.0 to 10.0, respectively (percentage of hydrolysis was 0.0%). However, a small hydrolysis of AM-2AP and AM-N was obtained at high hydrogen ion concentration, judging from the decrease of percentage of extraction found in the first extraction with flow rate < 1.0 mL/min. Table 4 compiles the percentage extraction of Fe(III) in presence of these coexisting cations given in Table 3. It shows that the studied coexisting cations had no or very low interfering effect in the extraction of Fe(III) by the two adsorbents at all molar concentration ratios.

**Regeneration of modified AM-2AP and AM-N adsorbent**

EDTA solution as strong complexing agent was selected to back-extract the Fe(III) ions from metal binding-alumina adsorbent in the regeneration process. Fe(III)-AM-2AP or Fe(III)-AM-N complexes (100.0 mg each) was mixed with excess (0.1 M EDTA) solution and shaken for 60 min, filtered off, washed with doubly distilled water and dried. The percentage extraction determined after the second extraction using AM-2AP was 100.0±0.5% and 90.0±0.5% with AM-N which are equal and close to percentage extraction found in the first extraction (100.0% and 98.2%) with AM-2AP and AM-N, respectively.

**Removal of ferric ions from real water samples using column and batch modes**

Removal of Fe(III) from real water samples, viz., drinking tap water (DTW), mineral water (MW), waste water (WW) and ground water (GW) was studied using AM-2AP and AM-N. Removal experiments were carried out using a glass column of 30 cm length and 2 cm internal diameter. The adsorbent (50.0 mg) was conditioned with 50.0 mL of water sample spiked with Fe(III) at concentration of 1.0 and 2.0 ppm (adjusted at pH 3.5 using conc. HCl) with flow rate < 1.0 mL/min. Table 4 compiles the percentage extraction of Fe(III) ions with AM-2AP and AM-N.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Mole ratio</th>
<th>CaCl(_2)</th>
<th>NiCl(_2)</th>
<th>CuCl(_2)</th>
<th>ZnCl(_2)</th>
<th>CdCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM-2AP</td>
<td>3.5</td>
<td>1:1</td>
<td>100.0±0.10</td>
<td>100.0±0.12</td>
<td>100.0±0.10</td>
<td>100.0±0.05</td>
<td>100.0±0.10</td>
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<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>100.0±0.02</td>
<td>100.0±0.20</td>
<td>99.75±0.25</td>
<td>100.0±0.05</td>
<td>100.0±0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5</td>
<td>98.60±0.01</td>
<td>99.50±0.40</td>
<td>98.50±0.30</td>
<td>100.0±0.03</td>
<td>99.50±0.20</td>
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<tr>
<td>AM-N</td>
<td>3.5</td>
<td>1:1</td>
<td>100.0±0.40</td>
<td>100.0±0.30</td>
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<td>100.0±0.10</td>
<td>99.75±0.15</td>
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</table>

\(^a\)N = 5; RSD = 0.01-0.4%.
results of Fe(III) removal via applications of a multistage mini-column technique, as well as batch mode at 15 and 30 min shaking time using AM-2AP and AM-N, respectively. Then, the residual concentration of metal ion was determined in 10.0 mL of the filtrate solution by FAAS. It is evident from Table 4 that the percentage extraction of ~100.0% was produced after four column and batch runs of the four water samples by both modes. This behavior may be attributed to the saturation phenomenon of the adsorbent surfaces with the targeted metal ions. In fact, Table 4 shows that satisfactory removal (60.0−78.2%) was obtained at the second run. For a quantitative recovery, a third (80.1−95.0%) or fourth (95.0−100.0%) run can be carried out. The quantitative recovery of Fe(III) indicates the validity of using AM-2AP and AM-N for its selective removal of Fe(III) from real water samples either by column or batch modes.

**Conclusions**

A novel method for modification of alumina surface with two simple phenols by microwave heating in absence of organic solvents was achieved. The two new adsorbents thus produced, AM-2AP and AM-N, exhibited high capability for extraction of Fe(III) from aqueous solution at pH 3.5 (100.0% and 98.2%, respectively). The adsorption performance fitted well with Langmuir and Freundlich models along with fast kinetics obeying pseudo-second order. High percentage recovery (≥95.0%) of Fe(III) was obtained either using column or batch mode from spiked water samples. In comparison to several adsorbents prepared by conventional methods reported in literature for the determination of Fe(III), the new adsorbents described in this study showed high affinity and selectivity for Fe(III). This is in addition to safety (solvent-less), simplicity and fast of adsorbent synthesis using microwave approach.

**Supplementary Data**

Supplementary data associated with this article, viz., Fig. S1, is available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_54A(03)324-332_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_54A(03)324-332_SupplData.pdf).

**References**


