Removal of Fe (III) from Aqueous Solution Using Thiosalcylic Acid as an Efficient and Novel Adsorbent

A.I. Abd-Elhamid1* and H. F. Aly2
1Composite and Nanomaterials Department, Advanced Technology and New Materials Research Institute, City for Scientific Research and Technology Applications, P. O. Box 21934, SRTA, Egypt.
2Hot Laboratories Center, Atomic Energy Authority, Nasr 13759, Egypt.

THE REMOVAL of Fe (III) from aqueous solution using thiosalcylic acid (TSA) as adsorbent have been demonstrated in this work. TSA was characterized by SEM, EDX, FTIR and XRD. Various factors affecting the removal include the contact time, initial concentration of ions, adsorbent dose, initial pH and temperature have been studied. The experimental data showed that, the removal percent of Fe (III) ion is increased by increasing contact time, adsorbent dose and pH values. The sorption reaction was found to obey a pseudo second-order rate model with $q_e = 275.78$ mg g$^{-1}$. The sorption isotherms data fit Langmuir and Freundlich models. The waste solid from the adsorption process (thiosalcylic acid adsorbed Fe (TSA-Fe)) successful in removal of methylene blue (MB) and crystal violet (CV) dyes from binary system.

Keywords: Thiosalcylic acid, Fe (III), TSA-Fe, Dye.

Introduction

Iron is the fourth most common element in the Earth’s crust. It is a very important in human nutrition, where iron forms complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability (range from about 10 to 50 mg/day). The natural fresh waters contain iron at levels ranging from 0.5 to 50 mg/liter and the drinking-water contaminated by iron as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution. World Health Organization (WHO) has set a guideline value of the iron in drinking-water about 2 mg/liter, which does not present a hazard to health. [1].

Recently, pollution and nutritional studies highly interest in studying the toxicity and the effect of trace elements on human health and the environment. The removal of iron from drinking water was carried out via several methods such as, ion exchange and water softening [2], activated carbon and other filtration materials [3], supercritical fluid extraction [4], bioremediation [5] and limestone treatment [6], oxidation by aeration, chlorination, ozonation followed by filtration [7], by ash [8], by aerated granular filter [9] and by adsorption [10].

Nowadays, adsorption has been shown to be a cost effective technique for the removal of trace metals from wastewater and water supplies, such as UO$_2$$^{2+}$ ion [11] and Cd(II) and Pb(II) under estuarine and seawater conditions [12], Cu$^{2+}$ [13], Pb$^{2+}$[14], Fe(II) and Mn(II) [15], Cr(III) [16] and Ni(II) [17].

Different materials such as Clays, oxides and other colloidal materials were supplied to control the concentration of trace soluble metal in the heterogeneous systems. It is greatly significance to use a new promising solid sorbents for adsorption of toxic metal ions from aqueous solutions, e.g., Thiosalcylic acid as an efficient adsorbing material with suitable active groups (-COOH and –SH) that interact with metal ions, stable under highly acidic conditions, (slightly soluble in water, ethanol and diethyl ether, and alkanes, but more soluble in DMSO) [18]. Moreover, TSA has fast, quantitative sorption, elution, high mass exchange and capacity.
Several literatures reported that TSA and its derivative have ability to form a complex with metal ions, e.g. copper(II) with thiosalicylic acid and pyridine [19], copper(II) complexes with S-alkyl derivatives of thiosalicylic acid [20], gold(III)-thiosalicylate and salicylate complexes [21], palladium(II)-thiosalicylate complexes [22], Cobalt and Thiosalicylic Acid [23] and triphenylphosphine-mercury(II) thiosalicylate complexes [24]. This report studies the removal of Fe (III) from aqueous solution using TSA as a novel and efficient adsorbent. TSA-Fe produced as a waste solid form the adsorption process subjected to remove of MB and CV dyes in binary system from aqueous solution.

**Experimental**

**Materials**

Thiosalicylic acid (Acros, 98%), Iron (III) chloride anhydrous (Fisher Scientific, UK., Laboratory reagent grade), Sodium thiocyanate (LOBA chemie Pvt.LTD., Extra pure). All chemicals were used without further purification.

**Preparation of Adsorbent**

Thiosalicylic acid used without any further purification, milled using ceramic mortar to obtain powder with desired fineness.

**Batch adsorption**

Adsorption experiments were conducted by varying contact time, initial Fe\(^{3+}\) concentration, TSA dose, initial pH and temperature under the aspects of adsorption isotherms and adsorption kinetics. The experiments were carried out in 100 mL glass beaker and the total volume of the reaction mixture was kept at 25 ml. The contact time was varied from 0 to 15 min. Fe\(^{3+}\) solutions of different concentrations, i.e. from 1000 to 3000 ppm. The adsorbent dose in range 0.01 to 0.1 g/25ml. The pH of the solution was maintained at a desired value by adding 0.1 M NaOH or HCl.

At predetermined time, 0.5 ml of the solution was withdrawn from the beaker and centrifuged at 5000rpm. The concentration of iron before and after sorption was then determined by the thiocyanate method using UV/Visible spectrophotometer (Double beam) (T80+, PG Instruments Ltd., UK.). The % removal of iron was calculated using the following expression;

\[
\% R = \left(1 - \frac{C_0}{C_t}\right) \times 100
\]

Where, \(C_0\) and \(C_t\) are the initial concentration and the concentration of Fe\(^{3+}\) ion at time \(t\), respectively.

**The decolorization activity of TSA-Fe**

Briefly, 50 mg of the waste solid of the previous adsorption process (TSA-Fe) was added to 10 mL of MB = 25mg/L and CV = 25mg/L in a binary system in the presence of 300 µL of hydrogen peroxide (\(\text{H}_2\text{O}_2\)) at room temperature. The degradation or decolorization of methylene blue and crystal violet was monitored by a UV–visible spectrophotometer (\(\lambda = 662\) nm for MB and \(\lambda = 590\) nm for CV) at different reaction periods.

**Characterization**

The characterization of the mortared TSA was carried out by Scanning Electron Microscope (SEM, JSM-636 OLA, Jeol, Japan.), Fourier Transmission Infrared Spectroscopy (FT-IR, 8400s, Shimadzu, Japan) covered the range from 400-4000 cm\(^{-1}\). IR spectra of solid samples were detected using the KBr disc. X-Ray Diffraction (XRD, XRD-7000 Shimadzu, Japan) was utilized to estimate crystalline structure of the prepared nanoparticles. EDX used to determine the elemental analysis.

**Results and Discussion**

**Morphology and chemical properties of TSA**

Figure 1a-c, shows the SEM images at different magnification (300x, 1000x and 15000x) of the as-obtained TSA with high resolution SEM. The particles TSA appear well dispersed, with spherical shape and uniform size with an average size of 3.8 µm. The elemental analysis (EDX) of thiosalicylic acid (TSA) and thiosalicylic acid adsorbed Fe\(^{3+}\) (TSA-Fe) were investigated in Fig. 1d and e, respectively. The resulted data showed that, the TSA composed of (7C: 2O: 1S; 69%: 21%: 9%) and TSA-Fe possess similar composition of TSA with the presence of Fe. The Chemical structure of TSA was investigated by FTIR spectra (Fig. 1f). In which the peak at 3,452 cm\(^{-1}\) attributed to OH (SH) stretching vibration and the peak at 1,653 cm\(^{-1}\) to OH bending vibration indicate the existence of adsorbed water molecules and structural OH groups [25].

At predetermined time, 0.5 ml of the solution was withdrawn from the beaker and centrifuged at 5000rpm. The concentration of iron before and after sorption was then determined by the thiocyanate method using UV/Visible spectrophotometer (Double beam) (T80+, PG Instruments Ltd., UK.). The % removal of iron was calculated using the following expression;
REMOV AL OF FE (III) FROM AQUEOUS SOLUTION USING THIOSALCYLIC ...

Adsorption process

Contact Time

The relationship between contact time and removal percent of Fe$^{3+}$ from aqueous solution onto TSA particles at ([Fe (III)]: 1000 ppm, Dose: 0.10g /25m, pH: 2.5 and Temperature: 20°C) is explained in Fig. 2a. The adsorption was initially fast (i.e., first 10 min), with progressive time (10-15 min) it reaches equilibrium. The initial fast adsorption might be referred to the large number of binding sites are available at the adsorption startup; as the adsorption sites were gradually filled up, the adsorption became stable.

Adsorption reaction models

The relationship between the adsorption rate of the adsorbate and the adsorption time, explained by using adsorption kinetics. Two well-known kinetic models, pseudo-first-order presented by Lagergren equation [27]. Eq. 2.

$$\log(q_e - q_t) = \log(q_e) + \frac{K_{ads}t}{2.303}$$  \hspace{1cm} (2)

Where, $q_e$ (mg/g) is the amount of sorption at equilibrium time, $q_t$ (mg/g) is amount of sorption at time and $K_{ads}$ (min$^{-1}$) is the rate constant of pseudo first order sorption.

$$q_e = \frac{(C_0 - C_e)V}{1000w}$$  \hspace{1cm} (3)

Where $C_0$ is the initial concentration (mg/L), $C_e$ is the dye concentration at equilibrium time intervals (mg/L), $V$ is the volume of dye solution (mL) and $W$ is the mass of adsorbent (g.)

$$q_t = \frac{(C_0 - C_t)V}{1000w}$$  \hspace{1cm} (4)

Where \( C_i \) is the dye concentration at different time intervals (mg/L)

And pseudo-second-order expressed by Ho equation [28] the equation developed in a linear form as Eq. 5.

\[
\frac{t}{q_i} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(5)

Where, \( K_2 \) (g mg\(^{-1}\)min\(^{-1}\)) is the rate constant of pseudo second order reaction.

The adsorption kinetics of Fe\(^{3+}\) ions by TSA were investigated by three kinetic models which are pseudo 1st order, pseudo 2nd order, and intraparticle diffusion. The pseudo 1st and 2nd order plots obtained by plotting \( \log(q_e - q_i) \) versus \( t \) (min) (Fig. 2b) and \( t/q_i \) against \( t \) (Fig. 2c), respectively. The experimental data were calculated and listed in Table 1. As compared correlation coefficients (R\(^2\)) the adsorption of Fe\(^{3+}\) was fitted well by 2nd order pseudo kinetics.

The mechanism and rate controlling step affecting the kinetics of adsorption is determined by fitting the kinetic experimental results by Weber’s intraparticle diffusion. The intraparticle model is expressed as:

\[
q_t = k_p t^{0.5} + C
\]

where \( C \) is the intercept and \( k_p \) is the intraparticle diffusion rate constant, (mgg\(^{-1}\)min\(^{0.5}\)), which can be evaluated from the slope of the linear plot of \( q_t \) versus \( t^{0.5} \) as shown in Fig. 2d. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. However, the regression of \( q_t \) versus \( t^{0.5} \) the linear plot did not pass through the origin. This indicates that the intraparticle diffusion was not only a rate controlling step.

**Effect of [Fe]**

Increasing the initial Fe\(^{3+}\) concentration from 1000 ppm to 3000 ppm in solutions with an initial pH 2.5 leads to decrease the percent removal of Fe\(^{3+}\) from about 99 to 22 %, as explained in Fig. 3a. This can be illustrated by increasing ratios between the initial number of moles of Fe\(^{3+}\) and the limited number of available sorption sites on the TSA.

**Equilibrium isotherms studies**

The analysis of the equilibrium adsorption isotherm model is a prerequisite for predicting the adsorption uptake of the adsorbent, which is one of the main parameters required for designing an optimized adsorption system. Two available isotherm models, that are, the Langmuir [29] and Freundlich [30], are used for this purpose. Applying Langmuir isotherm (by plotting \( 1/C_i \) against \( 1/q_i \) as shown in Fig. 3b) and Freundlich isotherm (by plotting \( 1/C_i \) against \( 1/q_i \) as shown in Fig. 3c); the extracted isotherm information is summarized in Table 2. From the Fig. 3b and 3c as well as the Table 2, it was obvious that both Langmuir and Freundlich models better fitted the experimental equilibrium adsorption data. The Langmuir model postulates a complete monolayer of adsorption, in which there is no transmigration of the adsorbate on the surface plane [29]. This model involves a homogeneous surface with equal energy and equally available sites for adsorption [31]. The Langmuir \( q_m \) value was 217.39 mg g\(^{-1}\). The Freundlich model [30] assumes a heterogeneous adsorption of Fe\(^{3+}\) on the adsorption sites of TSA. The Freundlich intensity constant \((1/n)\) is less than unity, indicating a concentration dependent sorption for Fe\(^{3+}\) adsorbed into TSA.

**Effect of Dose**

The variations in the adsorption of Fe\(^{3+}\) with the change in the TSA dose using a constant volume of aqueous solution (25 ml) and varying mass of TSA (0.01–0.10 g) is shown in Fig. 4. The removal percent, %R, was found to increase sharply with increasing the dose weight from 0.01 to 0.10 g, this is due to as the dose weight increase the active sites available for Fe\(^{3+}\) adsorption increases and hence the %R increases [32, 33].

**Effect of initial pH**

It has been recognized that the adsorption process is highly affected by the pH of adsorbate solution, this is referring to the pH not only influencing on the adsorbent surface charge but also on adsorbed species [34-36]. The effect of pH in the range from 1 to 2.5 on the adsorption of Fe\(^{3+}\) onto TSA is illustrated in Fig. 5a. It was observed that the amount adsorbed, \( q_e \), increased with the increase in pH values. This is can be clarified as seen in Scheme in Fig. 5b. Whereby adding HCl to the reaction mixture it retarded the dissociation reaction of both TSA and FeCl\(_2\) by the effect of common ion phenomena. Moreover, the difference between initial pH and final pH of the reaction media (\( \Delta pH \); i.e. H\(^+\) ion concentration or liberated H\(^+\) ion) increase with increase pH values as illustrated in Fig. 5c.
TABLE 1. Calculated parameters of the pseudo First-order and pseudo Second-order kinetic models.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{t,\text{exp}} ) (mg /g)</th>
<th>First-order kinetic parameter</th>
<th>( q_{t,\text{cal}} ) (mg /g)</th>
<th>Second-order kinetic parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{3+} )</td>
<td>248.4</td>
<td>( K_1 ) (min(^{-1}))</td>
<td>-0.190</td>
<td>162.180</td>
</tr>
</tbody>
</table>

Fig. 2. Effect of a) contact time, b) Pseudo first-order plot, c) Pseudo second-order plot, d) Intraparticle diffusion plot on the removal of \( \text{Fe} \) (III) from aqueous solution.
[\( \text{Fe} \) (III)]: 1000 ppm
\( \text{Dos}: 0.10 \) g /25ml
pH: 2.5
Temperature: 20°C
Fig. 3. Effect of a) TSA dose, b) Langmuir adsorption isotherm and c) Freundlich adsorption isotherm on the removal of Fe (III) from aqueous solution.

- Time: 10 min.
- Dose: 0.10 g /25ml
- pH: 2.5
- Temperature: 20°C

**TABLE 2. Langmuir and Freundlich constants for adsorption of Fe$$^{3+}$$ by TSA.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$$q_o$$ (mg/g)</td>
<td>$$K_L$$ (l/mg)</td>
</tr>
<tr>
<td>Fe$$^{3+}$$</td>
<td>217.39</td>
<td>- 0.011</td>
</tr>
</tbody>
</table>
REMOVAL OF FE (III) FROM AQUEOUS SOLUTION USING THIOSALCYLIC Acid

Fig. 4. Effect of TSA dose on the removal of Fe (III) from aqueous solution.
- Time: 10 min.  
  - [Fe (III)]: 1000 ppm  
  - pH: 2.5  
  - Temperature: 20°C

Fig. 5. a) Effect of pH on the adsorption amount of Fe (III) from aqueous solution, b) Scheme of common ion effect, c) Effect of initial pH on the pH difference, d) FTIR of TSA & TSA-Fe and e) Scheme of Fe³⁺ adsorption
- Time: 10 min.  
  - [Fe (III)]: 1000 ppm  
  - Temperature: 20°C

By comparing the FTIR- spectrum of TSA and Fe adsorbed on TSA (TSA-Fe), (Fig. 5d), it is found that the bands at 1653cm⁻¹, 2654cm⁻¹, 2874cm⁻¹, 2955and 3452cm⁻¹ were shifted to 1670cm⁻¹, 2658cm⁻¹, 2866cm⁻¹, 3007cm⁻¹ and 3441cm⁻¹, respectively. Furthermore, the band at 2534cm⁻¹ in TSA disappeared upon adsorption of Fe(III). This variation may be attributed to the adsorption of Fe (III) and liberation of H⁺-ions.

Based on the above analysis, the mechanism of Fe (III) adsorption on TSA can be supposed as explained in Scheme in Fig. 5e. As indicated in Fig.5e, the Fe³⁺ adsorbed on TSA and H⁺-ions become free to move to the bulk of solution causing a decrease in solution pH value.

Effect of temperature

Figure 6 illustrates that the amount of Fe³⁺ adsorbed onto TSA does not influence by further increase in the temperature.

Decolorization Activity of TSA-Fe

The decolorization activity of the MB and CV dyes from binary system using TSA-Fe in the presence of H₂O₂ was investigated. The UV-vis- spectrum (Fig7a) showed the decrease of the maximum peaks at 662 nm (for MB-dye) and 590 nm (for CV-dye) within the time range (0.0-60.0 min). The plot Ln A₀/A vs t (Fig. 7b) gives a linear relation, its slope expressed as the first order rate constant (k). It’s necessary to note that the decolorization rate constant for CV (k = 0.043 min⁻¹) is two times of (k = 0.026 min⁻¹) for MB. To conclude, in this study, we report the first trial to use the waste solid from the adsorption process in another application process without any further purification.

Conclusion

The results of ion sorption indicated that TSA is an efficient sorbent for the removal of Fe³⁺ ion from aqueous media. The removing of Fe³⁺ ion by the sorbent material carried out via pseudo 1st, 2nd, particle diffusion mechanism, Langmuir, Freundlich models are the best choice to describe the observed equilibrium data. The results show that TSA is effective in removal of Fe³⁺ ion in a wide range of concentration. Finally, TSA-Fe, from the adsorption process shows an active behavior towards the removal of (MB&CV- dyes) from binary system.

Fig. 6. Effect of temperature on the removal of Fe (III) from aqueous solution.

Time: 10 min.                                    [Fe (III)]: 1000 ppm
Does: 0.10 g /25ml                            pH: 2.5

Fig. 7. Effect of time on the reaction kinetic (TSA-Fe dose = 50 mg, [H₂O₂] = 300µl, [MB] = [CV] = 25 mg/L, dye solution volume = 10 ml, T = 25 °C.

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Removal of Fe (III) from Aqueous Solution Using Thiosalicylic Acid

Ahmed Ibrahim, Emad El-Sayed

Institute of Advanced Materials and Applications, Alexandria, Egypt.

This research paper investigates the removal of iron (III) from aqueous solutions using thiosalicylic acid as a high-efficiency adsorbent. The acid was characterized using electron scanning microscopy and X-ray diffraction. The factors affecting iron removal from water, such as contact time, initial ion concentration, adsorbent dosage, and solution pH, were studied. The experimental data showed that the percentage of iron removal increases with contact time, adsorbent dosage, and pH. The adsorption process was found to follow a pseudo-second-order model. Finally, the solid waste produced during the adsorption process was found to be effective in removing blue and orange dyes from the system.