REMOVAL OF THIOCYANATE BY INDUSTRIAL SOLID WASTE Fe(III)/Cr(III) HYDROXIDE: KINETIC AND EQUILIBRIUM STUDIES

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ABSTRACT

Removal of thiocyanate by adsorption onto industrial solid waste Fe(III)/Cr(III) hydroxide has been investigated. Pretreated adsorbent was found to be more efficient in the uptake of thiocyanate compared to untreated adsorbent. Effect of pH on the adsorption was studied in the pH range 4.0 to 10.0. Optimum pH for maximum removal was found to be 4.0. Langmuir and Freundlich isotherm models were used to study the adsorption equilibrium data. Adsorption follows the second order kinetics. Effects of background electrolytes show that inner sphere complex mechanism is predominant. pH effect and desorption studies showed that both ion exchange and chemisorption mechanisms are operative.

INTRODUCTION

Thiocyanate is used in various industrial processes such as photofinishing, herbicide and insecticide production, dyeing, acrylic fiber production, manufacturing of thiourea, metal separation and electroplating. Thiocyanate is also used in soil sterilization and corrosion inhibition [1]. Thiocyanate is commonly found in mining wastewater where the interaction of free cyanide (CN-) with sulfur forms SCN- [2]. Thiocyanate is introduced into the wastewater during the manufacture of coke from coal: concentrations range from 100 to 1500 mg L$^{-1}$ [2]. The toxic effects of SCN$^-$ include inhibition of halide transport to the thyroid gland, stomach, cornea, and gill as well as the inhibition of a variety of enzymes.

The degradation of thiocyanate has been studied using both biological and chemical methods [3-11]. Adsorption of thiocyanate onto uncalcined and calcined Mg-Al-CO$_3$ hydrotalcite has been reported [12]. Chemical industries use hexavalent chromium compounds as corrosion inhibitors in the cooling water systems [13]. Periodically fresh Cr(VI) solution is injected and the spent cooling water is let out. Chromium(VI) in the water is toxic and is reduced to less toxic Cr(III) using ferrous ion produced through an electrolytic process or ferrous sulfate under acidic conditions. The trivalent chromium and iron are precipitated as chromium hydroxide and ferric hydroxide under alkaline conditions. The resultant Fe(III)/Cr(III) hydroxide settles as sludge in lagoons and is removed periodically. The Fe(III)/Cr(III) hydroxide sludge is discarded as waste in the industries. The industrial solid waste Fe(III)/Cr(III) hydroxide has been investigated for the adsorptive removal of heavy metals [13,14], pesticide [15], dyes [16,17] and phenol [18]. The purpose of the present study was to explore the use of industrial solid waste Fe(III)/Cr(III) hydroxide for the removal and recovery of thiocyanate from aqueous solution and also study the mechanism of adsorption of thiocyanate on to Fe(III)/Cr(III) hydroxide.

MATERIALS AND METHODS

‘Waste’ Fe(III)/Cr(III) hydroxide was obtained from the Southern Petrochemical Industries Corporation Limited, Tuticorin, Tamil Nadu, India. It was ground and washed five times. Then it was dried at 65 °C for 12 h. The dried material was sieved to 75-150 μm size and used as adsorbent. The characteristics of waste Fe(III)/Cr(III) hydroxide are presented in Table 1 [19]. This material has a fractal dimension usually known from mineral surfaces. The specific surface area is due to very small non – micro pores particles. The total pore volume for pores filled up to a pore width of 40 nm, is mostly due to interparticle pores. The pore size distribution supports the above statement, a broad distribution with pores larger than the
**Table 1. Characteristics of Fe(III)Cr(III) hydroxide**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m² g⁻¹)</td>
<td>147.4</td>
</tr>
<tr>
<td>Total pore volume (cm³ g⁻¹)</td>
<td>0.2918</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>7.9</td>
</tr>
<tr>
<td>Apparent density (g mL⁻¹)</td>
<td>0.895</td>
</tr>
<tr>
<td>Acid (HNO₃) insoluble matter (%)</td>
<td>9.66</td>
</tr>
<tr>
<td>Water soluble matter</td>
<td></td>
</tr>
<tr>
<td>pH range</td>
<td>3.5 – 10.0</td>
</tr>
<tr>
<td>Fe(III) (mg L⁻¹)</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Cr(III) (mg L⁻¹)</td>
<td>&lt; 0.008</td>
</tr>
<tr>
<td>Mechanical moisture content (%)</td>
<td>16.78</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>32.8</td>
</tr>
<tr>
<td>Total Fe (%)</td>
<td>29.3</td>
</tr>
<tr>
<td>Total Cr (%)</td>
<td>5.3</td>
</tr>
<tr>
<td>Total Ca (%)</td>
<td>5.0</td>
</tr>
<tr>
<td>pH of 0.2% solution</td>
<td>8.11</td>
</tr>
<tr>
<td>Conductivity of 0.2% solution (μS cm⁻¹)</td>
<td>68.2</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>75-150</td>
</tr>
<tr>
<td>pHₚₑ</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Estimated particle diameter, and a maximum around 3 nm, which most likely corresponds to the small pores created by spheres with a diameter of 10 nm adjacent to each other. But, the particles alone are not porous. Table 1 shows that neither Fe³⁺ nor Cr³⁺ goes into solution in the pH range 3.5-10.0. Potassium thiocyanate was obtained from s.d. Fine Chemicals, Mumbai, India.

**Pretreated adsorbent**

The final pH of the thiocyanate solutions with untreated Fe(III)/Cr(III) hydroxide was found to be above 8.0 which is not favorable for the adsorption of thiocyanate since the pHₚₑ of the adsorbent is 8.1 (Table 1). Hence the pretreated adsorbent was used in the adsorption studies to control the final pH which increased the adsorption capacity of the adsorbent. Pretreated adsorbent was prepared by shaking required amount of Fe(III)/Cr(III) hydroxide with 50 mL double distilled water in 250 mL polythene bottles till the final pH maintained at a desired pH. pH was controlled by adding dilute solutions of HCl and NaOH. Then the supernatant solution was decanted and the wet adsorbent was used for the adsorption of thiocyanate.

**BATCH MODE ADSORPTION EXPERIMENTS**

500 mg of pretreated adsorbent and 50 ml thiocyanate solution of desired concentration were transferred into 250 ml polythene bottles and agitated at 160 rpm, 32 °C on a thermostated rotary shaker. At the end of the predetermined time intervals, the samples were taken and the supernatant solution was separated from the adsorbent by centrifugation at 20,000 rpm for 20 min. Then the concentration of the residual thiocyanate was determined by colorimetric method [20] using UV-Visible spectrophotometer (Analytik Jena AG, Model Specord 200, Germany). Effect of pH was studied in the range 4.0-10.0 using 1 M HCl and 1 M NaOH solutions by means of a pH meter (Elico, Mode LI-107, Hyderabad, India).

Langmuir and Freundlich isotherms were used to study the equilibrium adsorption data and adsorption capacity of the adsorbent. Effect of adsorbent dose was studied with different adsorbent doses of pretreated adsorbent (100-1000 mg) for the SCN⁻ concentrations of 10-50 mg L⁻¹.

1. **Temperature Study**

Effect of temperature was studied using 10 mg L⁻¹ of SCN⁻ and 500 mg of pretreated adsorbent at 32, 40, 50 and 60 °C in the thermostated rotary shaker.

2. **Desorption Studies**

The pretreated adsorbent that was used for the adsorption of SCN⁻ (10 or 20 mg L⁻¹) solution was separated from the solution by filtration using Whatmann filter paper and washed gently with water to remove unadsorbed SCN⁻. Then the spent adsorbent was agitated for equilibrium time with 50 mL of distilled water aliquots at different pH values adjusted using HCl/NaOH solutions. Then the desorbed SCN⁻ was estimated as before.

3. **Effects of Background Electrolytes and Foreign Ions**

Solutions of electrolyte NO₃⁻, Cl⁻, SO₄²⁻ and foreign anions PO₄³⁻, SeO₃²⁻, VO₃⁻ were prepared from their Na or K salts. Adsorption of SCN⁻ alone and adsorption of SCN⁻ in the presence of electrolytes/foreign ions and the adsorption of electrolytes/foreign ions in the absence and presence of thiocyanate were studied. Equimolar quantities (0.78 mM) of SCN⁻ and electrolyte/foreign ion were used to study the electrolyte/foreign ion effect. Phosphate [20], selenite [21], vanadate [22] and molybdate [23] were analyzed by standard spectrophotometric methods. NO₃⁻, SO₄²⁻ and Cl⁻ were analyzed using ion chromatograph.

Effect of background electrolytes at different concentrations (0.5 to 50 mM) on the removal of SCN⁻ was also studied.

Preliminary experiments showed that there was no adsorption of SCN⁻ due to container walls. Experiments were carried out in duplicates and mean values were employed for calculations. Maximum deviation was found to be 3.5%.

**RESULTS AND DISCUSSION**

1. **Optimization of pH**
Effect of initial pH on the adsorption of SCN was studied to find out the optimum pH at which maximum removal occurred. A pH range of 4.0 to 10.0 and the SCN concentrations of 10, 20, 30 to 40 mg⁻¹ SCN were used (Fig. 1a). The final pH was found to be above 6.3 for all the initial pH values studied (Fig. 1b). Figure 1a further shows that maximum removal is obtained at pH 4.0.

The adsorption of thiocyanate progressively decreases with the increase in pH in accordance with the equation:

\[
\text{MOH} + \text{H}^+ + \text{SCN}^- \rightarrow \text{MSCN} + \text{H}_2\text{O} \tag{1}
\]

where MOH is a surface hydroxyl group and MSCN is the adsorbed thiocyanate species. This is a characteristic of anion adsorption. Similar observation was reported for the adsorption of other anions by chitosan [24], bauxite [25] and ion exchange fiber [26]. Figure 1a shows that at lower pH the % removal is high due to electrostatic attraction between the protonated group of the adsorbent and the anionic thiocyanate species. The removal of SCN is decreased with the increasing initial pH from 4.0 to 10.0, because at higher pH adsorbent surface is modified with hydroxyl ions. On increasing the initial pH, the final pH was also found to be increased (Fig. 1b). At the initial pH 10, final pH was above 7.8 for all concentrations studied, which is not favorable for the adsorption of anionic SCN on to Fe(III)/Cr(III) hydroxide, since the pHzpc of the adsorbent is 8.1 (Table 1). The adsorption of SCN is hindered due to electrostatic repulsion between adsorbed OH⁻ ions and anionic SCN⁻ species. For the subsequent adsorption studies the initial solution pH was maintained at 4.0.

### 2. Adsorption Isotherms

Langmuir and Freundlich isotherm models are used to study the equilibrium data. The Langmuir model assumes that the surface of the adsorbent is homogeneous, adsorption energy is uniform for each adsorption site and solute uptake occurs by monolayer adsorption. It also predicts that solute immobilization occurs without natural interaction between the adsorbate molecules on the surface. The Freundlich model is based on an exponential distribution of sorption sites and energies. But it allows molecules adsorbed on the surface to interact. The Langmuir isotherm is represented as:

\[
\frac{C_e}{q_e} = \frac{1}{Q_\infty b} + \frac{C_e}{Q_\infty} \tag{2}
\]

where \(C_e\) is the equilibrium concentration of SCN⁻ solution (mg L⁻¹). The constant \(Q_\infty\) gives the maximum sorption capacity at monolayer coverage (mg g⁻¹) and \(b\) is the affinity coefficient of the sorbent for the adsorbate (L mg⁻¹). Figure 2 shows the fit of experimental data with Langmuir isotherm. The monolayer adsorption capacity, \(Q_\infty\), and \(b\) were evaluated form linear Langmuir plot of \(C_e/Q_e\) vs \(C_e\) (figure not shown) and found to be 3.28 mg g⁻¹ and 0.027 L mg⁻¹, respectively.
The Freundlich model is expressed as:

\[
\log\left(\frac{x}{m}\right) = \log k_f + \frac{1}{n} \log C_e
\]

where \(x\) is the mass of the adsorbate (mg) and \(m\) is the mass of the adsorbent (g). \(k_f\) is related to adsorption capacity and \(n\) is related to intensity of adsorption. Figure 3 shows the fit of experimental data with the Freundlich isotherm for 10 mg L\(^{-1}\) SCN\(^{-1}\) as an example. The Freundlich constants, \(k_f\) and \(n\), were evaluated from the linear Freundlich plot of \(\log (x/m)\) vs \(\log C_e\) (figures not shown) and are presented in Table 2. Langmuir isotherm is a better fit with the experimental data compared to Freundlich isotherm.

### 3. Adsorption Kinetics

First order and second order kinetics were used to study the adsorption data. The first order kinetic model is based on the following Lagergran first order rate equation [27]:

\[
\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303}
\]

where \(q_e\) and \(q\) are the amounts of SCN\(^{-}\) adsorbed (mg g\(^{-1}\)) at equilibrium and at time \(t\), respectively, and \(k_1\) is the rate constant of first order adsorption (min\(^{-1}\)).

Values of \(q_e\) and \(k_1\) were calculated from the slope and intercept of the plots of \(\log(q_e-q)\) vs \(t\) (figures not shown). It was found that the calculated \(q_e\) values do not agree with the experimental \(q_e\) values (Table 3). This suggests that the adsorption of SCN\(^{-}\) does not follow first order kinetic model. The adsorption kinetic data were then described by the second order equation [28]:

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

where \(k_2\) is the rate constant of second order adsorption (g mg\(^{-1}\) min\(^{-1}\)).

Values of \(k_2\) and \(q_e\) were calculated from the slope and intercept of the plots \(t/q\) vs \(t\) (Fig. 4). It was found that the calculated \(q_e\) values agree with experimental \(q_e\) values (Table 3). It indicates that the adsorption system studied belongs to the second order kinetic model. Similar phenomenon has been observed in the adsorption of phosphorus on alunite [29] and ZnCl\(_2\) activated coir pith carbon [30].

### 4. Effect of Temperature

Figure 5 shows that the effect of temperature on the adsorption of SCN\(^{-}\) onto pretreated Fe(III)/Cr(III) hydroxide is not significant. Using Lagergran rate equation, first order rate constants (\(k_1\)) and correlation coefficients were calculated for different temperatures. The calculated \(q_e\) values obtained from the first order kinetics do not agree with the experimental \(q_e\) values (Table 3). This indicates that this system does not follow first order kinetic model at different temperatures. Second order kinetic model shows that the calculated \(q_e\) values agree with the experimental \(q_e\) values (Table 3). This indicates that the adsorption follows second order kinetic model at different temperatures used in this study.
Table 3. Comparison of first order and second order adsorption rate constants and calculated and experimental qe values for different initial SCN concentrations and temperatures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>First order kinetic model</th>
<th>Second order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qe(exp) (mg g(^{-1}))</td>
<td>k(_1) (min(^{-1}))</td>
</tr>
<tr>
<td>Initial SCN(^{-}) conc. (mg g(^{-1}))*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.453</td>
<td>0.12</td>
</tr>
<tr>
<td>20</td>
<td>0.806</td>
<td>0.18</td>
</tr>
<tr>
<td>30</td>
<td>1.076</td>
<td>0.18</td>
</tr>
<tr>
<td>40</td>
<td>1.350</td>
<td>0.16</td>
</tr>
<tr>
<td>50</td>
<td>1.640</td>
<td>0.09</td>
</tr>
<tr>
<td>Temp. (°C)**</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>0.453</td>
<td>0.12</td>
</tr>
<tr>
<td>40</td>
<td>0.454</td>
<td>0.16</td>
</tr>
<tr>
<td>50</td>
<td>0.450</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>0.456</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Conditions: *Adsorbent dose, 500 mg 50 mL\(^{-1}\); initial pH, 4.0; temp, 32 °C.
** Adsorbent dose, 500 mg 50 mL\(^{-1}\); initial pH, 4.0; initial conc., 10 mg L\(^{-1}\).

5. Desorption

Figure 6 shows that the % SCN desorbed is minimum at pH 4.0 (~10%) and maximum at pH 10.0 (40-50%). The results confirm the ion exchange mechanism for SCN adsorption onto Fe(III)/Cr(III) hydroxide. On increasing the pH the adsorbed SCN ions are replaced by OH ions. This shows that ion exchange mechanism is operative. Incomplete desorption shows that chemisorption might also play in the removal process.

6. Effect of Background Electrolytes

Adsorption of 0.5 mM SCN\(^{-}\) onto pretreated Fe(III)/Cr(III) hydroxide in the presence of back-ground electrolytes such as chloride, nitrate and sulfate at varying concentrations (0.5, 1.0, 10, 25 and 50mM) was examined. There was no significant effect of background electrolyte on the adsorption of SCN\(^{-}\). This may be due to the fact that these ions are not adsorbed when present as sole adsorbates. Ionic strength affects the outer sphere complex greatly than inner sphere complex since the background electrolyte ions are placed in the same plane as the outer sphere complex. Since the SCN\(^{-}\) adsorption does not depend on the ionic strength contributed by background electrolytes, inner sphere coordination mechanism is predominant for the adsorption of SCN\(^{-}\) onto Fe(III)/Cr(III) hydroxide. Similar observations have been reported on the adsorption of molybdenum by soil and clay minerals [31,32] and phosphate by ‘waste’...
Fe(III)/Cr(III) hydroxide [33].

7. Effect of Foreign Ions

Since the real industry effluents contain other oxyanions apart from thiocyanate, it is essential to study the effect of these ions on the adsorption of thiocyanate. Since the oxyanions have greater binding affinity to metal oxide, it will be of great importance to study the competition for surface binding sites among various anions. Studies showed that in the aqueous systems anion partitioning onto oxide surface is also greatly affected by competitive adsorption of coexisting anions [34]. Reyden et al. [35] studied the competitive adsorption of inorganic anions by ferric oxide gel. It was found that the sorption decreased in the order: H2PO4\(^{-}\) (orthophosphate) > H2AsO4\(^{-}\) (arsenate) > HSeO4\(^{-}\) (selenite) > H2SiO4 (silicate) > MoO4\(^{2-}\) (molybdate) > SO4\(^{2-}\) (sulfate) > SeO4\(^{2-}\) (selenate) > Cl\(^{-}\) (chloride) = NO3\(^{-}\) (nitrate) when each ion was added in equimolar quantity. In the present investigation effects of foreign ions such as VO3\(^{-}\), PO4\(^{3-}\), SeO3\(^{2-}\) and MoO4\(^{2-}\) on the adsorption of SCN\(^{-}\) onto pretreated and untreated Fe(III)/Cr(III) hydroxide have been studied. It was found that the extent of adsorption of seven inorganic anions by pretreated Fe(III)/Cr(III) hydroxide decreased in the order, VO3\(^{-}\) > PO4\(^{3-}\) > SeO3\(^{2-}\) > MoO4\(^{2-}\) > SCN\(^{-}\) when these ions were present as sole adsorbates (Table 4). Parfitt [36] reported that anion adsorption by soil decreased in the order: H2PO4\(^{-}\) > HAsO4\(^{-}\) > HSeO4\(^{-}\) = MoO4\(^{2-}\) > SO4\(^{2-}\) > Cl\(^{-}\) > NO3\(^{-}\). The removal of VO3\(^{-}\), PO4\(^{3-}\), SeO3\(^{2-}\), MoO4\(^{2-}\) and SCN\(^{-}\) was above 8.0 and 6.5 for pH untreated and pretreated adsorbent, respectively. Because, the final pH cyanate uptake was 32 and 2% for pretreated and untreated adsorbent, which might be due to chemisorption of these ions on to Fe(III)/Cr(III) hydroxide. Thiocyanate adsorption was affected by foreign ions in the order: VO3\(^{-}\) > PO4\(^{3-}\) > SeO3\(^{2-}\) > MoO4\(^{2-}\). The result shows that there is no exclusive binding site for SCN\(^{-}\) on the adsorbent surface. There is no significant effect of SCN\(^{-}\) on the removal of VO3\(^{-}\), PO4\(^{3-}\), SeO3\(^{2-}\) and MoO4\(^{2-}\) (Table 4).

CONCLUSIONS

The pretreated Fe(III)/Cr(III) hydroxide adsorbent is more efficient for the removal of thiocyanate than untreated Fe(III)/Cr(III) hydroxide. Optimum pH for maximum removal was 4.0 in the pH range 4.0 to 10.0 studied. It shows that electrostatic attraction between the protonated hydroxyl group of the adsorbent surface and the anionic thiocyanate was responsible for adsorption. Equilibrium adsorption data fit better with Langmuir isotherm model than Freundlich. Experimental data follow second order kinetics. Effect of ionic strength on the adsorption shows that thiocyanate is adsorbed onto pretreated Fe(III)/Cr(III) hydroxide by inner sphere complex mechanism. Adsorption of thiocyanate is lowered by foreign anions such as vanadate, phosphate, selenite and molybdate. pH effect and desorption studies show that both ion exchange mechanism and chemisorption are operative in the removal process.

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REFERENCES

Namasivayam and Prathap: SCN Removal by Fe(III)/Cr(III) Hydroxide


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