Introducing a recycling method for iron oxide nanoadsorbent from mine waste and its application in wastewater treatment

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Abstract—In this study, a feasible and environmentally friendly method was used for the recycling of iron oxide nanopowder from steel industry waste, and its application in the removal of pollutants from wastewater was investigated. The iron content in the residue transformed to Fe3O4 powder through leaching and reacting with sodium sulfite and ammonium hydroxide. The obtained powder was consisted of spherical nano-crystals with high purity and was reacted with wastewater containing cobalt in different concentrations and pH levels giving rise to a removal of 91 percentage cobalt at alkaline ambiance.

Keywords—Iron Oxide, Nano Powder, Recycling, Waste

1. Introduction

The recycling and reuse of industrial wastes has been increasingly considered in the modern world. In addition to overcome environmental problems, this approach can lead to economic benefits [17].

Recovery of value added materials from wastes is one of the most important stages of waste management. When it is not possible to reduce the volume or toxicity of a hazardous waste, it is recommended to recover it due other process. The best place for the recovery and recycling of hazardous wastes is in situ, because transportation of hazardous waste out of the factory is dangerous, in addition to raising cost [16].

Wastes generated from mineral processing plants contained toxic heavy metals, could be transferred to soil and water resources and cause harmful environmental impacts [18].

With the increasing demand on iron and steel industry the proportion of iron ore tailings is also growing fast. The iron ore tailing is considered as a waste and its disposal poses a major environmental concern. The management of this kind of wastes is costive, too. On the other hand, mineral processing plant are unable to extract complete iron content or ore, and the residue contains considerable amount of iron compounds [4]. Therefore, it is viable try to re-handled these wastes and obtained secondary by-product from them.

Nanotechnology has been developed for the last decade, and production of nano materials is one of the most attractive and practical aspects of science in the world. An emerging technology in water treatment is the use of nanoadsorbents for heavy metals, organic pollutants and removal of radionuclides [14]. Among different nanoadsorbents that used in water and wastewater treatment, magnetite (Fe3O4) nanoparticles are more popular [2], [3], [6], [9], [11], [15].

For the synthesis of Fe3O4 nanoparticles it is necessary to have a good source of Fe compounds such as FeCl2, FeCl3, FeSO4 as precursors [1], [5], [8], [9]. This leads to high consumption of reagents for the production of these nanoparticles.

Taking both economic and environmental problems into account, as well as the high consumption of chemicals in the production of magnetite nanoparticles an alternative may propose that is to recover nanoscale magnetite powder from residuals and applying them in wastewater treatment is proposed as a new approach to waste management.

In first stage of this study a simple, feasible and environmentally friendly method is introduced for production of magnetite nano powder from steel industry waste. In the
second stage the derived magnetite powder is used in mine Wastewater purification.

2. Theory and research background

Konishi et al. have described a synthesis route to magnetic ferrite (NiFe$_2$O$_4$) nanoparticles from spent pickling solution of steel industry. Three stages were identified:

1. Microbial oxidation of ferrous iron(II) in pickling solution
2. Solvent extraction of ferric iron(III) in oxidized solution with the monocarboxylic acid extractant
3. Solvothermal synthesis of nickel ferrite from the organic carboxylate solution of iron(III) and (Ni(II)) [7].

Another group of researchers reported a method for the synthesis of magnetite nanoparticles from acid mine drainage. This method includes the selective precipitation of iron as a ferric hydroxide, the dissolution of iron with acid, the photoreduction of Fe$^{3+}$ to Fe$^{2+}$, and the conversion of ferric/ferrous hydroxides to magnetite [13].

In other method Giri et al. recovered magnetite powder and kaolinite from waste iron ore tailings for environmental applications. In this method the ferric iron recovered from waste iron ore tailings via acid leaching. Ferric (hydr)oxide was precipitated to produce magnetite powder through pyrometallurgical reduction route using CO in the temperature range 900–1300 °C for 4 h. The magnetite powder obtained from this method was utilized as an adsorbent for removal of organic dye pollution such as methylene blue from wastewater [4].

The need for special accessories such as bacteria, bioreactor, photoreduction equipment, high-temperature calcinations etc. in the above reported methods has limited to their wide industrial application. Common point in these methods is using the technology of leaching for almost complete recovery of iron. If the iron content of leaching dissolution can be converted to magnetite in simple process, it will be a positive step.

On the other hand, given that nana magnetite is able to absorbed a wide range of contaminants such as chloroform, organic pigments, nickel, cobalt, cadmium, and etc [2,8, 11,15] the idea of its using in Iron - based industries wastewater treatment is considerable as smarter management of these wastes.

3. Materials and methods

3.1. Chemicals and reagents

Cobalt nitrate (Co(NO$_3$)$_2$, 99%), sodium sulfite (Na$_2$SO$_3$, 99%), hydrochloric acid (HCl, 37%), ammonium hydroxide (NH$_4$OH, 25–30% of ammonia), de-ionized water, and ethanol (CH$_3$CH$_2$OH, 99.93%) were used in the experiments.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
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<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>28.63</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.73</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>28.6</td>
</tr>
<tr>
<td>CaO</td>
<td>9.32</td>
</tr>
<tr>
<td>MgO</td>
<td>14.1</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.85</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.42</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.02</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.29</td>
</tr>
<tr>
<td>LOI</td>
<td>10.04</td>
</tr>
</tbody>
</table>

3.2. Recycling method of nanoadsorbent from waste

Waste used in this study was obtained from Gol-e-Gohar Iron Plant. Waste sample after grinding in ball mill was concentrated by magnetic separation for the most purity of iron content. The chemical composition of magnetic seperation concentrate was shown in Table 1.

Initially, 50 gr of the waste sample was leached with 30% HCl at 120 °C for 1 h. The brown solution derived from the leaching process after cooling, was filtered to separate the acid insoluble residue. According to atomic adsorption result the solution derived from leaching was FeCl$_3$ with concentration of 0.65 M, that was diluted to 0.4M measured to be 50 CC in volume. By adding sodium sulfite 0.5 M and then ammonium hydroxide under vigorously stirring of 500 rpm a black suspension was formed. The derived precipitate was drained for three times with distilled water, and dried at 70 °C for 4 h. The resultant powder was characterized by XRD, SEM and EDS analysis.

3.3. Application of recycled nanoadsorbent in wastewater treatment

It has been postulated that magnetite nanoparticles can remove heavy metals such as cobalt from industrial and mining wastewater [6], [11], [12]. Cobalt is a toxic heavy metal that cannot be biodegraded, instead it can be accumulated in living organisms, thus causing various disease and disorders even in relatively lower concentrations [10]. In recent years, various nanoadsorbsents specially magnetite has been widely applied to remove chemical pollutants from waste water [12].
In the second stage of tests in this study, the efficiency of magnetite nanoparticles derived from mine waste was evaluated specifically for the removal of Co ions from wastewater. For preparation of synthetic wastewater, desired amount of $\text{Co(NO}_3\text{)}_2$ dissolved in distilled water and 4 Solution samples with concentration of 25, 50, 75 and 100 ppm were provided. The pH of the solutions was adjusted in three ranges: 3, 7 and 10 using 0.1 M NaOH and HNO$_3$ stock solutions. Then, 50 mg of synthesized nano-magnetite was added to 30 ml of each simulated wastewater solution and reacted for 1 h at 60 °C and 200 rpm in a flask shaker. When the adsorption equilibrium was reached, the adsorbent was separated via an external magnet and then remained solutions were analyzed by ICP-OES for determining Co Concentration.

4. Results and discussion

Fig. 1 shows the XRD pattern of the nano-powder recovered from the mine waste. XRD results confirm the formation of magnetite. In addition, the average particle size
was calculated to be 30 nm using the Sherrer's equation (1):

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(1)

where \( D \) is equivalent of particles average core diameter; \( K \) is the grain shape factor (for spherical particles \( K=0.94 \)); \( \lambda \) is the incident X-ray wavelength; \( \beta \) denotes the full width at half-maximum of the highest intensity and \( \theta \) is the corresponding diffraction angle.

SEM micrograph of magnetite recycled from waste was shown in Fig. 2. This image showed that particles are homogeneously dispersed and are almost spherical with 30-45 nm average diameter.

In order to investigate the purity of these nanoparticles their EDS spectra was taken and as shown in Fig. 3. The presence of Fe and O as the main constituents of magnetite \((Fe_3O_4)\) powder demonstrated the purity of the obtained powder.

<table>
<thead>
<tr>
<th>No</th>
<th>Co(^{2+}) concentration</th>
<th>pH</th>
<th>R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
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<td>7</td>
<td>58.1</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>10</td>
<td>68.3</td>
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</tr>
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<td>5</td>
<td>50</td>
<td>7</td>
<td>50.3</td>
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<td>6</td>
<td>50</td>
<td>10</td>
<td>90.8</td>
</tr>
<tr>
<td>7</td>
<td>75</td>
<td>4</td>
<td>11.6</td>
</tr>
<tr>
<td>8</td>
<td>75</td>
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<td>31.8</td>
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<td>9</td>
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<td>10</td>
<td>69.7</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>4</td>
<td>7.5</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>7</td>
<td>29.3</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>10</td>
<td>43.8</td>
</tr>
</tbody>
</table>
The ICP-OES results was used to evaluate the recovery of cobalt metal contaminant by magnetite nanosorbent. The removal of cobalt ions was calculated proportionally using equation (2):

$$
R\% = 100 \left( \frac{C_0 - C_t}{C_0} \right)
$$

(2)

where $C_0$ and $C_t$ are the initial and the equilibrium concentration of Co$^{2+}$ ions, respectively.

The calculated results for recovery of cobalt ions is shown in Table 2. The highest recovery was obtained for 50 ppm solution to be in the order of (90.8 ~ 91) %. Furthermore it can be seen that the highest Co ions removal take places at alkaline ambiance, that is pH=10.

5. Conclusions

A feasible and environmentally friendly method was used for the recycling of iron oxide nano-powder from steel industry waste, and its application in the removal of pollutants from wastewater was investigated.

Leaching with hydrochloric acid was found to be an acceptable method for recovery of iron from the waste.

FeCl$_3$ solution obtained from leaching was recycled to form magnetite powder upon reaction with sodium sulfite and ammonium hydroxide.

The application of magnetite nanoparticles in wastewater treatment was found to be feasible demonstrating an adsorption capacity of 91% for cobalt ions from synthesized wastewater in an alkaline environment.

ACKNOWLEDGMENT

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References


