HEAVY METAL REMOVAL FROM WATER AND WASTEWATER USING RAW AND MODIFIED DIATOMITE

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Abstract heavy metal removal from water and wastewater was investigated by using raw and modified diatomite from Iranian mines. Modification of diatomite was done by impregnating the diatomite surface with 0.35 g of manganese oxide in one gram of diatomite. This modified diatomite was named Mn-Diatomite. The surface area measurements for Mn-diatomite showed a 2.2 fold increase, hence higher removal capacity for the heavy metals. The results of the removal showed an increase in adsorption capacity which was for Pb²⁺ about 40 mg/g, for Ni²⁺ about 34mg/g and for Cu²⁺ about 33mg/g. The filtration quality of diatomite was significantly enhanced with surface modification by manganese oxide.

Keywords Diatomite, Mn-Diatomite, Heavy Metals, Adsorption and Wastewater

1. INTRODUCTION

Treatment of water and wastewater needs serious attention all over the world especially in countries with dry climate. The most important pollutants in water and wastewater are heavy metals. Heavy metals and their compounds are widely used in many industrial applications resulting in their increase in aquatic systems. The methods of elimination are chemical precipitation, ion exchange, membrane systems, alum coagulation and adsorption [1-3]. Among the methods, adsorption systems are more effective in reducing heavy metal concentration. These systems have many advantages. They are simple, quick and suitable for water and wastewater containing moderate and low concentrations of metals. Also a wide range of adsorbents are available and the produced wastewater containing high concentration of metals is easy to recover. The only disadvantage of these processes can be the high cost of some adsorbents [4-5]. In principle any solid material with a micro porous structure can be used as an adsorbent e.g. bone and char coal, clays, iron oxides, synthetic and natural zeolites, molecular sieve and activated carbon. Adsorbents must have a structure with a large surface area. Furthermore, the chemical nature and
polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate. One of the most important adsorbents in water and wastewater treatment is activated carbon. However the use of activated carbon is not suitable for developing countries due to its high manufacturing costs [6]. Use of other alternatives with lower costs has been investigated and many materials like activated peat and clay have been tested. There is a comprehensive review on low-cost adsorbents [7].

Diatomite (SiO$_2$. nH$_2$O) or diatomaceous earth is a pale-colored, soft, light-weight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of a wide variety of shapes and sizes, typically 10-200 $\mu$m, in a structure containing up to 80-90% voids. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, large surface area, and low thermal conductivity, which makes diatomite suitable for a wide range of industrial applications such as a filter aid or a filter. In aqueous solutions, diatomite particles have negative charges so they possess a strong attractive force for particles with a positive charge. There are many diatomaceous mines around the world and it seems that diatomite will be employed for many industrial applications in the future [8].

Al-Degs and his coworkers [9] studied the capacity of Jordan’s diatomaceous earth as a potential adsorbent for Pb (II) ions. It was found that when diatomite was modified by manganese oxide, it showed to be efficiently adsorption of Pb ions from the solution, and this was due to an increase in surface area and also increasing the negative charge after modification. Decastro Dantas et al. investigated the removal of Cu in aqueous solutions by using modified diatomite; the diatomite was modified by micro-emulsion [10]. Al-Ghouti and his coworkers studied the thermodynamic behavior and the effect of temperature on the removal of dyes from aqueous solutions using modified diatomite [11]. Also they conducted research on physical characteristics and adsorption mechanisms of diatomite [12]. Khraisheh et al. studied on the remediation of wastewater containing heavy metals using raw and modified diatomite [13]. Al-Ghouti et al. also worked on the flow injection potentiometric stripping analysis method to study the adsorption of heavy metal ions through modified diatomite [14]. Al-Degs and his coworkers studied on the feasibility of using diatomite and Mn-diatomite for remediation of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ from water [15]. Straugynska et al. used diatomite as a conditioning agent for sludge. Their work confirmed that, in mechanical dewatering of sludge the absorbance by diatomite was very helpful. The sludge particles became larger in size and this simplified the separation [16].

There are several diatomite mines in Iran, mostly in the Azerbaijan Province, such as Tabriz diatomite mine in east Azerbaijan and Mamaghan mine in Miyaneh. Azarshahr industrial company produces 5000 tons/year diatomite powder from the Mamaghan mine. The diatomite can be used as a suitable alternative for activated carbon [17]. In this study the Iranian diatomite soil and the form modified by Mn oxide were investigated as an adsorbent and a filtration agent for the purpose of Pb, Ni and Cu removals from water and wastewater.

2. MATERIALS AND METHODS

2.1. Modification of Diatomite 300g of Iran’s diatomaceous earth was washed with distilled water and filtered. The filter cake was dissolved in 1500ml distilled water and 100ml 1N sodium hydroxide. The solution was kept boiling at 90-100°C for 45 minutes. The 100ml of manganese chloride 30 % was added, the PH of manganese chloride was adjusted to 1 (by 3 N hydrochloric acid) after 9 hours the solution was filtered, 300ml sodium hydroxide 25 % was added and the solution was filtered after 3 hours. It was then acidified and allowed to dry for 2 days. The cake was kept in an oven at 100°C for 3 days, until its moisture was removed completely then desiccated and stored in tightly stoppered glass bottles. The modified diatomite is referred to as Mn-Diatomite. The manganese contents of the samples were determined by atomic absorption spectroscopy (Varian A A 220). Prior to analysis, the samples were immersed in a 4 N hydrochloric acid solution at 40°C to dissolve the deposited oxides.
2.2. Determination of Surface Area of Particles  The surface area of the particles was estimated from the BET equation by (Quantachrome Nova 2000e), then the samples were degassed at 70 °C for 6 hours [18].

2.3. Adsorption Isotherms  The standard solutions of Pb\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) were prepared by dissolving Pb (NO\(_3\))\(_2\), Ni (NO\(_3\))\(_2\) and hydrated CuCl\(_2\) into distilled water. (all the chemicals used in this research were of standard grade, MERK Germany). The adsorption capacity for diatomite and Mn diatomite was determined by adding 0.05g of adsorbent to 50ml of solution. The concentration range for Ni\(^{2+}\) and Pb\(^{2+}\) was 0-300 mg/l and for Cu\(^{2+}\) was 0-200 mg/l. Due to high capacity of diatomite and Mn-diatomite for the ion, PH of the adsorbate solution was adjusted to 4, by using sodium hydroxide. The suspensions of adsorbent and solutions were sealed and equilibrated in a shaker at 22±1 °C and 190 rpm for 3 days then centrifuged and metal concentrations were analyzed by an atomic absorption spectroscopy.

2.4. Filtration Rate  The filtration rate of diatomite and Mn diatomite was determined using the filtration method as below. A 3 g sample was mixed with 50 ml of distilled water and filtered. After this filtration, another 100ml distilled water was added and the filtration time was recorded. The filtration rate was estimated according to the Bazhal method and the related equation is given below [19].

\[
V_F = \frac{W_F}{F \times t}
\]

Where \(V_F\) is the filtration rate (ml m\(^{-2}\) s\(^{-1}\)), \(W_F\) the volume of the filtrate (ml) F the effective filter paper surface (m\(^2\)) and t is the filtration time (s).

3. RESULTS AND DISCUSSION

The analysis has shown that SiO\(_2\) is the main component of diatomite (72 %). The diatomite has a large void volume, and a highly porous structure. The high porosity of this material was one of the main reasons for choosing it as a potential sorbent for heavy metals. It has previously been reported that structural Mn\(^{2+}\) can be desorbed from the surface during adsorption of heavy metals [13]. The low desorption of Mn\(^{2+}\) from the surface reflects the strong interaction between diatomite and the manganese oxides, hence adding more stability and value to the modified adsorbent. It seems that, the amount of manganese oxide loaded on the diatomite surface depends on the nature of the surface, the solution’s acidity and the duration of the treatment. In this study loading on the surface of the diatomite (determined by the mentioned method) was estimated to be approximately 0.35 g g\(^{-1}\). Hence the surface area of Mn-diatomite was increased to 81.2 m\(^2\) g\(^{-1}\), while the surface area for raw diatomite was 36.9 m\(^2\) g\(^{-1}\). This shows a 2.2 fold increase after the modification. The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The adsorption experiments for Pb\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) were performed at pH = 4 for 3 days.

The adsorption isotherms are shown in Figures 1 to 3, as \(q_e\) versus \(C_e\) where \(q_e = \frac{C_o - C_e}{X_o}\) in which \(C_o\) and \(C_e\) are concentrations of initial and final metals respectively and \(X_o\) is the mass of the adsorbent. The pH was adjusted to slightly acidic

![Figure 1: Adsorption isotherm Ni\(^{2+}\) on diatomite and Mn-diatomite](image-url)
conditions for two reasons, first, heavy metals normally started to precipitate (by forming metal oxides and hydroxides) under alkaline conditions. Second, diatomite powder is slightly unstable in higher values of pH, and contains perceptible material under alkaline condition. As it is shown in Figures 1 to 3, heavy metal removal becomes more efficient when diatomite is modified by manganese chloride. The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm; the graph of the amount adsorbed against the equilibrium concentration, at a specific temperature. The nature of the interaction between the adsorbate and adsorbent, i.e., to be favorable or unfavorable, can be determined from the isotherm shape. Adsorption of heavy metals on Mn-diatomite decreases in the order of Ni^{2+} > Pb^{2+} > Cu^{2+}. Metals of higher electronegativity are expected to have higher affinities. The maximum adsorption capacities (Q) for heavy metals are reported in Table 1. The values of adsorption capacity of diatomite are 131.5, 120 and 105 mgg^{-1} for Ni^{2+}, Pb^{2+} and Cu^{2+} respectively, while the values of 165.5, 160, and 138 mgg^{-1} were obtained for Mn-diatomite. This shows higher adsorption capacity of Mn-diatomite for all the metals compared to diatomite.

The Langmuir isotherm has been applied to many adsorption systems including organic and inorganic adsorbates. [13]

The Langmuir equation can be presented as:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_a}C_e
\]

Where \( K_L \) and \( a \) are the isotherm constants for a particular solute-solvent combinations. The essential characteristics of the Langmuir equation can also be expressed in terms of a dimensionless factor \( R_1 \)

\[
R_1 = \frac{1}{1 + K_L C_0}
\]

The magnitude of the factor indicates the nature of the interaction and the isotherm type; unfavorable \( (R_1 > 1) \), linear \( (R_1 = 1) \) favorable \( (0 < R_1 < 1) \), or irreversible \( (R_1 = 0) \). The amount of \( K_L \) and \( a \) and \( R_1 \) for Ni^{2+}, Pb^{2+} and Cu^{2+} were calculated and are shown in Table 1. This table also shows the values of Q which is the maximum amount of adsorption. Table 1 shows that the metal uptake data agrees strongly with the Langmuir model. The model shows correlation coefficients of greater than 0.99 for all systems studied. This supports the theory that the number of sites on the diatomite surface is limited and the heavy metals form a
monomolecular layer on the surface at maximum capacity. According to $R_1$ Values detailed in Table 1, the adsorption behavior of the three metals is extremely favorable ($R_1<<1$) tending to be a weakly irreversible adsorption ($R_1=0$). Adsorption on the Mn-diatomite is more favorable as compared with the diatomite, as indicated by $R_1$ Values for the former being lower.

Numerous types of adsorbents have been tested for their ability to remove heavy metals, such as peat and chitosan, and inorganic types such as zeolite and clay [1]. As diatomite is inorganic in nature it must be compared with inorganic materials such as zeolite and clay. Table 2 shows the comparison of the adsorption capacities of some adsorbents. As Table 2 indicates, the adsorption capacity of Mn-diatomite is more than raw diatomite, and these two adsorbents reveal higher adsorption capacities than all the other adsorbents in the table.

Filtration quality is an important factor related to adsorbents used in water treatments. The measurements of the filtration rate of diatomite and Mn-diatomite of Iran revealed that this factor was difficult to determine for raw-diatomite because it went under a gel situation formation and was not filterable, but after modification of diatomite it was measured and was 72.2 m$^3$ m$^{-2}$ sec$^{-1}$ according to

<table>
<thead>
<tr>
<th>Metal</th>
<th>Q(mg g$^{-1}$)</th>
<th>a(l mg$^{-1}$)</th>
<th>$K_L$(l g$^{-1}$)</th>
<th>$R_1(\times 10^{-3})$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite Ni$^{2+}$</td>
<td>131.5</td>
<td>0.011</td>
<td>2.33</td>
<td>1.42</td>
<td>0.998</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>120</td>
<td>0.02</td>
<td>28.4</td>
<td>0.117</td>
<td>0.998</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>105</td>
<td>0.159</td>
<td>17.92</td>
<td>0.279</td>
<td>0.994</td>
</tr>
<tr>
<td>Mn-Diatomite Ni$^{2+}$</td>
<td>165.5</td>
<td>0.1142</td>
<td>20.4</td>
<td>0.163</td>
<td>0.994</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>160</td>
<td>0.247</td>
<td>42.0</td>
<td>0.079</td>
<td>0.991</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>138</td>
<td>9</td>
<td>1250</td>
<td>0</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Cu Mg/g</th>
<th>Pb Mg/g</th>
<th>Ni Mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>102.48</td>
<td>66.28</td>
<td>105.5</td>
</tr>
<tr>
<td>Mn-Diatomite</td>
<td>120</td>
<td>103</td>
<td>143.6</td>
</tr>
<tr>
<td>Zeolite</td>
<td>84.3</td>
<td>155.4</td>
<td>-----</td>
</tr>
<tr>
<td>Clay</td>
<td>16.5</td>
<td>58</td>
<td>-----</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>13</td>
<td>22</td>
<td>-----</td>
</tr>
<tr>
<td>Iran Diatomite</td>
<td>105</td>
<td>120</td>
<td>131.5</td>
</tr>
<tr>
<td>Mn-Diatomite in This Research</td>
<td>138</td>
<td>160</td>
<td>165.6</td>
</tr>
</tbody>
</table>
4. CONCLUSION

Diatomite and its modified form created through the use of manganese oxides are effective adsorbents for the removal of Ni^{2+}, Pb^{2+} and Cu^{2+} ions from water and wastewater, at PH = 4. When diatomite is modified by manganese oxide its absorption capacity goes up. This is due to an increase in surface area after coating, as well as the resultant surface change due to the formation of manganese oxide on the diatomite surface. Filtration quality of diatomite is also significantly increased after modification with Mn-oxide. Improvements in filtration quality widen the application of diatomite in filtration systems.

5. REFERENCE