Kinetic and Adsorption Isotherms Study of Cyanide Removal from Gold Processing Wastewater Using Natural and Impregnated Zeolites

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ABSTRACT: The extraction of gold involves using cyanide which has the potential to impact the environment. Many studies have been done to reduce the environmental effects of cyanide. In this research, the cyanide adsorption on zeolite from gold processing plant tailing dam wastewater was investigated. Results indicated that the pH of the solution, contact time duration, temperature, zeolite amount and size of zeolite particles were the most important parameters in the adsorption process. Zeolite was used in two fraction sizes; (100-300)µ and (300-1000)µ in two types of natural and impregnated with copper sulfates. The optimum amounts of both natural and impregnated zeolite in the solutions and the maximum cyanide adsorption percentage were determined as 30, 24g/L and 50.2, 86.1% for small fraction size, and 36, 24g/L and 39.5, 64% for large fraction size, respectively. The optimum values of pH were 10.5 and 10 for natural and impregnated types in both fraction sizes. Contact time duration in equilibrium conditions for fraction sizes of (100-300)µ and (300-1000)µ were 40 and 50 min, respectively. The optimum temperature in all situations was 22 ºC. The adsorption process in a size of (100-300)µ for natural zeolite was fit into the Freundlich model and for impregnated zeolite type there was no significant difference between two models, although, the Langmuir model was more accurate. In a fraction size of (100-300)µ for two types of zeolites, the kinetic adsorption was fit into the Lagergren second-order kinetic model. In a fraction size of (300-1000)µ, the adsorption kinetics for the natural type has no sensible difference between the first and second Lagergren kinetic model, but for the impregnated zeolite type it follows the second-order kinetic model. The results showed that the cyanide adsorption on impregnated zeolite was more than the natural type.

KEYWORDS: Cyanide; Zeolite; Kinetic and Adsorption; Freundlich; Langmuir and Lagergren isotherm model.

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INTRODUCTION

Cyanide is a dangerous and very toxic substance and 0.05 ppm of it could cause death and its entrance to water resources and soils leads to serious environment pollution [1]. Typically, the gold extraction process by the cyanidation method involves ore grinding followed by the tank leaching with sodium cyanide. In this stage, the ore is solved in cyanide solution and converted to soluble gold complexes. These complexes are adsorbed on the activated carbon surface in adsorption columns and the final effluent enters the dewatering stage. Residue of the dewatering stage contains cyanide and its components that pollute tailing dam wastewater[2, 3].

The chemistry of cyanide is complex and many forms of it exist in mining effluents. Four major categories of cyanide compounds are important from a toxicity viewpoint [4]:
- Free cyanide
- Iron cyanides
- Weak Acid Dissociable cyanides (WAD’S)
- Cyanide related compounds

HCN and CM⁺ are free cyanide and will be the dominant species when pH is below 9.2 and redox potential is more than 600 mV. As the pH approaches 8, most of the free cyanide (99.5%) exists as hydrogen cyanide, HCN, which has a relatively high vapor pressure [5].

Therefore, the removal and degradation of cyanide is an important issue for environmental protection in industries that use it. Many different methods, such as biological treatment, activated carbon and mine minerals adsorption, solvent extraction, chemical oxidation with ozone, calcium and sodium hypochlorite, chlorination, use of polysulfurs, ion exchange and ultraviolet radiation are widely used for removing cyanide and complex ions including iron-cyanide complexes which are anionic, and very stable complexes from wastewaters [6-8].

Natural zeolites, due to their large surface areas, high cation exchange capacities, favorable hydraulic characteristics, and low cost, are a major class of materials being considered for the adsorption of different species. Recent studies have shown that modification of zeolites with certain surfactants or other cations yield sorbents with a strong affinity for many anions. In order to adsorb anions, the modified surface must either possess positively charged exchange sites, or there should be replacement of weakly held counter ions of the surfactant by more strongly held counter ions [9].

Free cyanide compound, weak-acid dissociable and powerful cyanide complexes have affinity for being adsorbed on the zeolite surface.

Consequently, cyanide and its compounds reduce appreciably in this method. HCN capacity was enhanced significantly when zeolites were loaded with Cu[10, 11]. Impregnated zeolite with weak salts of Fe, Ni, Cu, Ag and Co caused an increase in the adsorption ability of cyanide compounds [12, 13]. It has been the equations and terms with the concentrate of adsorbed material and remaining concentrate in constant temperature of the studying of components adsorption and transfer on adsorbents [14].

In a study of transmission and adsorption of particles on specific material in constant temperatures, we should have terms and equations between primary solution concentration and residual solution concentration. These equations are called surface adsorption isotherms. Langmuir and Freundich isotherm models show this term [15, 16].

Many studies have been done on the cyanides adsorption process but we find that there are few researches on eliminating cyanides from dam tail or the gold processing plant waste waters based on isotherms and kinetic model investigation. Thus, in this research we investigated the effective parameters on cyanide adsorption and models were used to determine the best fit of equilibrium isotherm for cyanide adsorption on natural and impregnated zeolites.

EXPERIMENTAL SECTION

Materials and preparing

Cyanide solution and zeolite samples are obtained from the Aghdareh gold processing plant tailing dam water and Firozkoh mine, respectively. The solution pH and cyanide concentration were determined as 9 and 140 mg/L, respectively. Chemical analysis of gold processing wastewater is shown in Tables 1 and 2. The zeolite properties are shown in Table 3.

Zeolite was used in two fraction sizes of (100-300)µ and (300-1000)µ and two types of natural (NZ) and impregnated (IZ) with copper sulfates as the adsorbent material. Sodium hydroxide 0.04M (blank solution) was employed for dilution of cyanide solution. Rhodanine and silver nitrate with the MERC Deutsche mark were provided to determine the cyanide concentration.
Table 1: The results of physicochemical parameters and the major cations and anions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unite</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Eh</td>
<td>(mV)</td>
<td>-43/6</td>
</tr>
<tr>
<td>EC</td>
<td>(μS/cm)</td>
<td>343</td>
</tr>
<tr>
<td>Turbidity</td>
<td>(0/00)</td>
<td>0.2</td>
</tr>
<tr>
<td>temperature</td>
<td>(°C)</td>
<td>12.2</td>
</tr>
<tr>
<td>TDS</td>
<td></td>
<td>211</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>K⁺</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Na⁺</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>(mg/L)</td>
<td>221</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>Cl⁻</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>CN⁻</td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>Total hardness</td>
<td></td>
<td>286</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td></td>
<td>245</td>
</tr>
</tbody>
</table>

Table 2: Chemical analysis of major and trace elements.

<table>
<thead>
<tr>
<th>Zn</th>
<th>V</th>
<th>U</th>
<th>Ti</th>
<th>Se</th>
<th>Sb</th>
<th>S</th>
<th>Pb</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Co</th>
<th>Cd</th>
<th>Ba</th>
<th>As</th>
<th>Amount (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.2</td>
<td>0.58</td>
<td>0.01</td>
<td>0.5</td>
<td>0.73</td>
<td>5.0</td>
<td>0.3</td>
<td>0.05</td>
<td>10</td>
<td>0.4</td>
<td>0.02</td>
<td>0.05</td>
<td>78.2</td>
<td>29.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Chemical analysis of zeolite.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>67.24</td>
<td>11.71</td>
<td>0.58</td>
<td>0.42</td>
<td>3.04</td>
<td>1.16</td>
<td>1.19</td>
<td>1.48</td>
<td>13.47</td>
</tr>
</tbody>
</table>

as a titration solution. The titration method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in waters and wastewaters. This method uses silver nitrate with Rhodanine indicator and is used for measuring concentrations of cyanide exceeding specified amount (0.025mg/250 mL). Rhodanine- Initial cyanide solution must be colorless. Color change is canary yellow to salmon pink. Since the zeolite has a limited capability to remove cyanide (because of negative surface charge), copper sulfate was used as a catalyst agent in the adsorption tests. To increase the adsorption capacity of zeolite, it stirred up in a solution of copper sulfate at 0/15 M with mechanical stirrer (25 g zeolite aggregation mentioned in 300 mL of copper sulfate 15/0 M) for 24 hours. After 24 hours, zeolite was filtered and washed with distilled water. Then it was oven dried for 12 hours at 110 °C in an oven and absorption experiments were performed on raw and modified zeolite.

**Test method**

Batch adsorption studies were carried out at room temperature. For preventing cyanide evaporation, the pH was initially kept constant at a level of 11. Various amounts of zeolites (0.2, 0.4 and 0.6 gr) are added to the
solution and the mixtures were agitated in a shaker for 30 min using a magnetic shaker. Thereafter, the solutions were allowed to stand for 15 minutes and filtered through Whatman filter paper.

The zeolite, retained on the filter paper, was thoroughly washed with distilled water to collect the soluble cyanide species in the filtrate. The volume of the filtrate was made up to 100 ml. After appropriate dilution the cyanide concentration was analyzed by the titration method with AgNO₃.

To determine the adsorption isotherm, the 140 mg/L cyanide solution is diluted to 25, 50, 75, 100, 125, 150 mg/L concentration by distilled water. After providing the cyanide solution, zeolite (their optimum weight) was added to 50 ml of these solutions and the adsorption experiments were carried out in a constant temperature (22ºC). Ultimately, residual cyanide concentration is assayed for any fractions.

RESULTS AND DISCUSSION
Effect of zeolite amount
Although the primary pH of wastewater solution was 9, the pH value is stabilized at 11 with sodium hydroxide to prevent cyanide evaporation. Temperature and agitation time are adjusted at 22º C and 30 minutes, respectively. Experiments were carried out in two fraction sizes of (100-300)μ and (300-1000)μ for two types of natural and impregnated zeolite with copper sulfates. Adsorbed cyanide versus zeolite amount is shown in Fig. 1.

As shown in this Figure, the cyanide adsorption improved with an increase of zeolite amount in the solution. 30, 24 g/L zeolite amount in (100-300)μ for natural type, and 36 and 24 g/L for (300-1000)μ of impregnated type are optimum for cyanide removal in the solution. After this stage, a greater zeolite increase was not very effective for cyanide treatment and the adsorption concentration remained almost unchanged.

Cyanide adsorption increases with an increase of zeolite because the adsorbent surface area of the zeolites are increased.

The maximum adsorption value of cyanide in optimum conditions for (100-300)μ and (300-1000)μ for natural type are 50.2 and 86.1%, and for impregnated type they are 39.5 and 64%, respectively. Results showed that cyanide adsorption in (100-300)μ for impregnated conditions are higher than others.

Effects of increasing pH
PH of the cyanide solution has a high effect on the adsorption of cyanide on zeolite, while the other parameters such as temperature and contact time were kept constant. To define the optimum value, indifferent pH values (8.5 to 12.5) were implemented. Temperature and time was constant as the last step and the density of the adsorbent in all of the 4 types were considered in optimum conditions. The effect of different pH values on cyanide adsorption with zeolite are shown in Fig. 2.

Results for natural and impregnated types of zeolites showed that by increasing the pH value to 10.5 and 10, the cyanide adsorption was increased and it was declined sharply with a further increase in pH. Cyanide adsorptions were 66.02 and 17 mg/L for (100-300)μ and 879 and 31 mg/L for (100-300)μ in natural and impregnation types, respectively. The results indicated that the value of adsorbed cyanide for impregnated zeolite in all sizes is greater than the same size of the natural type. Fig. 2 shows that in smaller particle sizes, the amount of adsorbed cyanide is more than the greater size of zeolites. The reason of reduction in cyanide adsorption after higher optimum pH values is that, the solution and zeolite cyanide concentration have arrived at equilibrium state or it will be due to the decrease of attraction force between the cyanide molecules and zeolite’s surface.
Effect of contact time

The effect of contact time on the cyanide adsorption has been studied by taking an optimum amount of adsorbent and pH with 50 mL of a cyanide solution for both sizes. The flasks were shaken for different time intervals in a constant temperature. Fig. 3 showed the contact time effect on cyanide adsorption.

While contact time achieved 40 and 50 minutes for (100-300)μ and (300-1000)μ in natural and impregnation types, cyanide adsorption increased directly and with a further increase in contact time, cyanide adsorption had no change. It can be stated that in these points (40 and 50 min.) residual cyanide has reached a minimum state and increasing the contact time will not have any effect. This study does not claim any kinetic evaluation of the adsorption process, but it has shown that the equilibrium was attained at about 40 and 50 minutes.

Effect of temperature

Temperature is an effective and important parameter in the cyanide removal process. Therefore, a series of experiments were undertaken to study the effect of temperature by performing at 15, 20, 25, to 65°C. In all experiments, the initial cyanide concentration, agitation time, and zeolite amount were in optimum conditions which had been determined from the earlier tests. The results of these experiments and the influence of temperature on the remnant cyanide have been shown in Fig. 4.

The rate of cyanide adsorption decreases quickly with increasing temperature, for in the 45°C amount of remnant cyanide in the solution 15 and 10 mg/L is achieved for both sizes of adsorbent, respectively. It seems that adsorption increased with increasing temperature, but the increasing adsorption values in temperature higher than 26°C are not relevant the increase of zeolite adsorption ability; and is only due to the conversion of cyanide to HCN gas; however, the cyanide odour (garlic allium and bitter almond odour) is sensible by increasing temperature. Thus, in the following experiments, the temperature was maintained below 26°C.

Effect of zeolite particle size

The different particle size causes different specific surface area, and thus has a significant effect on the zeolites adsorption ability. Effective factors that have been
Table 4: Cyanide adsorption in optimum condition.

<table>
<thead>
<tr>
<th>Type and Grain Size</th>
<th>Amount of Zeolite (gr/l)</th>
<th>pH</th>
<th>Time Duration (minute)</th>
<th>Temperature (°C)</th>
<th>Cyanide Adsorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ (100-300) μ</td>
<td>30</td>
<td>10.5</td>
<td>40</td>
<td>25</td>
<td>57</td>
</tr>
<tr>
<td>IZ (100-300) μ</td>
<td>24</td>
<td>10</td>
<td>40</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>NZ (300-1000) μ</td>
<td>36</td>
<td>10.5</td>
<td>50</td>
<td>25</td>
<td>46</td>
</tr>
<tr>
<td>IZ (300-1000) μ</td>
<td>24</td>
<td>10</td>
<td>50</td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

optimized before the mentioned experiments have been used for natural and impregnated types of zeolites in both sizes. In small sizes with respect to higher specific surface, the adsorbent efficiency is increased, but for large particles the efficiency is decreased. Results showed that the adsorbed cyanide in a size of (100-300)μ is more than a size of (300-1000)μ in both natural and impregnated types.

Effect of modifier factor
In this research, the copper’s sulfate was used as the zeolites modifier agent. After analyzing the effective factors on the cyanide adsorption process and defining the optimum values of each parameter in both sizes ((100-300) and (300-1000)μ) and both types of zeolite (natural and impregnated), the cyanide adsorption test has been performed in optimum values.

The amount of adsorbed cyanide in optimum values for all of the 4 types of zeolites was shown in Table 4.

Results show that the amount of adsorbed cyanide for both sizes in the impregnated zeolite type are more than the natural zeolite type.

RESULTS AND DISCUSSION
Cyanide adsorption isotherms on the zeolite
The adsorption isotherms were analyzed for defining capacity and zeolite adsorption process properties. Sodium cyanide solution with 50, 75, 100, 125, 150, 200, 250 and 300 mL/L concentrations was prepared and 1.5 g of natural and 1.2 g impregnated zeolite with a size of (100-300)μ and 1.8g natural and 1.2 g impregnated zeolite with a size of (300-1000)μ were added to 50 mL of each solution. All adsorption tests were done in 40 min. at 20ºC and optimum pH. After specifying the amounts of adsorbed and residual cyanide in the solutions (in stable conditions), the adsorption isotherm parameters were defined and the Langmuir and Freundlich isotherm diagrams were drawn and their compatibility with the models was analyzed.

Fitting adsorption process data into the Langmuir model
The equation form of the Langmuir model is:

\[
\frac{1}{q_e} = \frac{1}{b} \times \frac{1}{c_e} + \frac{1}{a b c_e}
\]

(1)

Where,

\(q_e\) (mg/gr) is the adsorbed portion in the adsorption mass unit
\(C_e\) (mg/L) is the concentration of the residual part in the solution and \(a\) and \(b\) are Langmuir constants[17].

\((1/c_e)\) is plotted as a function of \((1/q_e)\) and the resulted shape was linear so the adsorption process follows the Langmuir isotherm. In obtained results with pure sodium cyanide solution, the capacity and adsorption process is more accurate with Langmuir and Freundlich models because in these solutions the impurity is much lower than the tailing dam water.

The charts in Figs. 5, 6, 7 and 8 show the fitness of resulted arcs of adsorbed cyanide and the amount of residual cyanide with the Langmuir model.

By using Excel software and processing the obtained arc with the Langmuir model, it is clear that the maximum R² coefficient belongs to the (100-300)μ size of the impregnated zeolite. This is because the processing and correlation coefficient of the resulted arc of the plotted dots collation with the Langmuir model is greater than other samples and its adsorption capacity in this state is also greater than the others. The results of analyzing the waste dam water shows that the amount of adsorbed cyanide in this size is more than other sizes and this is probably because of the fine size of adsorption grains or saturating them with Copper Sulfate. The charts show that the correlation of impregnated samples is more than the natural type. Also, the adsorption process on impregnated samples is chemical, but in the natural type the adsorption process is physical because in the impregnated type the cyanide
could react with cooper ions that adsorbed on zeolite but in natural samples the cyanide usually enters the pores of zeolite.

**Fitting adsorption process data into the Freundlich model**

The non-linear expression of the Freundlich isotherm model is:

\[ q_e = k C_e^\frac{1}{n} \]  \hspace{1cm} (2)

and its linear form expression is:

\[ \log(q_e) = \log(k) + \frac{1}{n} \times \log(C_e) \]  \hspace{1cm} (3)

Where \( q_e \) and \( C_e \) are Langmuir parameters but \( n \) and \( k \) are Freundlich constants. If the resulted arc of plotted dots with a basis of \( \log(q_e) \) and \( \log(C_e) \) was linear, then the adsorption process is based on the Freundlich model. The resulted charts of adsorbed and residual cyanide logarithmic values in the solution are shown in Figs. 9-12.

The constant values and coefficients of Langmuir and Freundlich models are shown in Table 5. With respect to Table 3 and Figs. 9 to 12, the coefficient is defined and it is found that the adsorption process in (100-300)\( \mu \) is fit into the Freundlich model. Although, there is no significant difference between two models in sizes of (100-300)\( \mu \) for impregnated zeolites, it fits well into the Langmuir model. Finally, a comparison of the charts...
showed that the $R^2$ for impregnated zeolites in a size of (300-1000)$\mu$ is greater than (100-300)$\mu$ and the adsorption process is like the Freundlich model. In samples that, cyanide concentration is high, the adsorption of cyanide is more than the other samples.

**Kinetic models of cyanide adsorption by zeolites**

**Lagergren first order kinetic model**

For controlling the mechanism and kinetic adsorption processing such as transferring the adsorbed unit on the adsorbent, chemical reaction and data adjustment of kinetic adsorption were used in the two different kinetic models. The first one is Lagergren first order kinetic model that is shown in equation (4):

$$
\log(q_e - q) = \log(q_e) - \log \frac{k_{ads} \cdot t}{2.303}
$$

The data of cyanide adsorption by zeolite in the Lagergren first order kinetic model is shown in Table 6. In the equilibrium time, the amount of $q$ and $q_e$ is equal. The obtained Lagergren first order kinetic model, regression line equation and correlation coefficient for each size of grain and zeolite are calculated and shown in Figs. 13 and 14.

**Lagergren second order kinetic model**

Table 7 shows the kinetic information of Lagergren second order kinetic model for cyanide adsorption by zeolites. The Lagergren second order kinetic model equation is[1, 14]:

$$
\log(q_e - q) = \log(q_e) - \log \frac{k_{ads} \cdot t}{2.303}
$$
Table 5: Isotherm models data for cyanide adsorption in 20 °C.

<table>
<thead>
<tr>
<th>Type and Grain Size</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>NZ (100-300) µ</td>
<td>0.0001</td>
<td>47.4</td>
</tr>
<tr>
<td>IZ (100-300) µ</td>
<td>-0.0194</td>
<td>-13.59</td>
</tr>
<tr>
<td>NZ (300-1000) µ</td>
<td>0.0011</td>
<td>25.641</td>
</tr>
<tr>
<td>IZ (300-1000) µ</td>
<td>-0.0068</td>
<td>-16.695</td>
</tr>
</tbody>
</table>

Table 6: Lagergren first order kinetic model data for cyanide adsorption by zeolite.

<table>
<thead>
<tr>
<th>Time Duration (minute)</th>
<th>(100-300)µ</th>
<th>(300-1000)µ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural zeolite</td>
<td>Impregnated zeolite</td>
</tr>
<tr>
<td>10</td>
<td>13.16</td>
<td>3.05</td>
</tr>
<tr>
<td>20</td>
<td>14.08</td>
<td>4.78</td>
</tr>
<tr>
<td>30</td>
<td>15.65</td>
<td>6.39</td>
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<tr>
<td>40</td>
<td>15.76</td>
<td>7.75</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 13: Lagergren first order kinetic model, regression line equation and correlation coefficient for natural and impregnated zeolite (100-300)µ.

\[
\frac{t}{q} = \frac{1}{k_{ads}q_e} + \frac{1}{q_e} 
\]

Fig. 14: Lagergren first order kinetic model, regression line equation and correlation coefficient for natural and impregnated zeolite (300-1000)µ.

The obtained charts of the Lagergren second order kinetic model, the equation of regression line and correlation coefficient value of each sample are shown in Figs. 15 and 16.

Figs. 13, 14 and 16 for both natural and impregnated zeolite type in a size of (100-300)µ show that the adsorption kinetic is fit into the Lagergren second order kinetic model because the obtained value of correlation coefficient from the Lagergren second order kinetic model charts is higher than the first order kinetic model. Also, a comparison of Figs. 10 and 11 for natural and impregnated zeolite type in a size of (300-1000)µ shows that the adsorption kinetic for natural zeolite is not different in the first and second order kinetic models.
Table 7: Lagergren second order kinetic model data for cyanide adsorption by zeolite.

<table>
<thead>
<tr>
<th>Time Duration (minute)</th>
<th>(100-300)µ</th>
<th>(300-1000)µ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log (qe-q)</td>
<td></td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>Impregnated zeolite</td>
<td>Natural zeolite</td>
</tr>
<tr>
<td>10</td>
<td>0.26</td>
<td>0.10</td>
</tr>
<tr>
<td>20</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>-0.18</td>
<td>-0.24</td>
</tr>
<tr>
<td>40</td>
<td>-1.37</td>
<td>-0.49</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-1.43</td>
</tr>
</tbody>
</table>

Fig. 15: Lagergren second order kinetic model, regression line equation and correlation coefficient for natural and impregnated zeolite (100-300)µ.

Fig. 16: Lagergren second order kinetic model, regression line equation and correlation coefficient for natural and impregnated zeolite (300-1000)µ.

However, the impregnated zeolite type fits into the Lagergren second order kinetic model. With respect to the regression line that is obtained from the adsorption model for all of the 4 states and their comparison with previous models, we can calculate the value of the adsorption rate constant ($K_{ads}$). $K_{ads}$ for a size of (100-300)µ for natural and impregnated zeolite are 9.19 and 0.039, and in sizes of 300 to 1000 for natural and impregnated zeolite it is 2.5 and 0.083, respectively.

CONCLUSIONS

1) The results show that by increasing the amount of zeolite, the residual cyanide decreases. If the amounts of zeolite exceed a size of (100-300)µ for the natural and impregnated type more than 30 and 24(gr/l) and a size of (300-1000)µ for the natural and impregnated type, at more than 36 and 24(gr/l), no changes occur in the amounts of cyanide adsorption. The optimum value of cyanide adsorption in a size of (100-300)µ for natural and impregnated zeolite type are 50.2 and 86.1 percent and in a size of (300-1000)µ for natural and impregnated zeolite they are 39.5 and 64 percent.

2) Increasing pH to 10 and 10.5 in both sizes of zeolite grains for impregnated and natural type lead to increasing cyanide adsorption and by increasing pH above 10.5, the cyanide adsorption decreases. With an optimum pH in the size of (100-300)µ, the cyanide adsorption for natural and impregnated type are about 53 and 88 percent and for samples in a size of (300-1000)µ, the adsorbed cyanide is about 43 and 78 percent.

3) The amount of adsorbed cyanide for impregnated zeolite type in both sizes is more than the natural type and the main reason is probably the reaction of molecules and free cyanide ions with adsorbed or changed copper ions on zeolite.
4) Increasing the time of solution mixing with zeolite for natural and impregnated zeolite type in a size of (100-300)μ to 40 minutes and in a size of (300-1000)μ to 50 minutes lead to a linear increase in the amount of adsorbed cyanide, but with increasing the time beyond this, we have no perceptible changes in the amount of adsorbed cyanide.

5) In all tests, the amount of adsorbed cyanide for a size of (100-300)μ is more than a size of (300-1000)μ for both types of zeolites.

6) The adsorption process in a size of (100-300)μ for natural zeolite is fit into the Freundlich model and for the impregnated zeolite type, there is no significant difference between the two models; however its seems that the Langmuir model is more accurate.

7) In a size of (100-300)μ for two types of zeolites the kinetic adsorption is fit into the \textit{Lagergren second order kinetic model}.

8) In a size of (300-1000)μ, the adsorption kinetic for the natural type has no sensible difference with the first and second \textit{Lagergren kinetic model}, but for the impregnated zeolite type it follows the \textit{second order kinetic model}.

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