Cu(II), Pb(II) and Cr(VI) Adsorption on the Modified Activated Carbon

Nasanjargal Shirendev¹, Munkhpurev Bat-Amgalan², Ariunaa Aleksandr³, Burmaa Gunchin³, Ganchimeg Yunden¹,*

¹Department of Chemical Engineering, School of Applied Sciences, Mongolian University of Science and Technology, Ulaanbaatar 14191, Mongolia
²Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan
³Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 13330, Mongolia
*Corresponding author. Email: ganchimeg.yu@must.edu.mn

ABSTRACT

In this study, the sorptions of Cu(II), Pb(II), and Cr(VI) on amine-functionalized activated carbon were investigated. Coal from the Tavantolgoi deposit of Mongolia was used as a precursor for the modification. After the coal carbonization, the char was activated with heated steam at different times (120, 180, and 240 min) and several temperatures (800 ºC and 850 ºC). The activated carbon at 850 ºC for 240 min was used for the treatment with 3-aminopropyltriethoxysilane (APTES). The interactions between metal ions and functional groups on the sorbent surface were confirmed by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) coupled with X-ray energy dispersive spectroscopy (EDS). The influence of various parameters such as pH (2-7), contact time (0.5-6 h), temperature (25 ºC, 35 ºC, 45 ºC, and 55 ºC), initial concentration of heavy metals ions (10, 25, and 50 mg/L), and common cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) was investigated. The optimum pH for Cu(II), Pb(II), and Cr(VI) sorption on the modified activated carbon was chosen as 4, 3, and 3, respectively. The sorption capacity was increased from 6.15 to 9.88 mg/g and 17.1 mg/g to 19.0 mg/g when increased the temperature from 25 ºC to 55 ºC for Cu(II) and Cr(VI) adsorption, respectively (initial concentration of metal ions were 50 mg/L). But the sorption capacity was decreased from 3.13 mg/g to 2.69 mg/g when increased the temperature from 25 ºC to 55 ºC for Pb(II) adsorption. The thermodynamic parameters such as enthalpy (ΔHº), entropy (ΔSº), and Gibb’s free energy (ΔGº) were estimated, and the results confirmed that all sorption processes are spontaneous and thermodynamically favorable. The sorption capacity was decreased when the amount of Na⁺, K⁺, Ca²⁺, or Mg²⁺ increased from 0 to 200 mg/L, and a remarkable decrease in sorption capacity was observed for Pb(II) adsorption. The order of adsorption capacity of modified activated carbon for metal ions was Cr(VI)>Cu(II)>Pb(II). The sorption mechanism was discussed for the processes.

Keywords: Modified activated carbon, Heavy metals, Sorption thermodynamics

1. INTRODUCTION

Nowadays, contamination of heavy metals in an aquatic environment is one of the significant problems of many countries, and it has attracted the attention of researchers. Heavy metals include chromium, cadmium, copper, lead, zinc, manganese, mercury, and nickel are affect the environment and living organisms. The main sources of water containing these heavy metals are metallurgy, leather, wool processing, cashmere processing, dyeing, and mining. There are many methods to remove heavy metals from the aqueous solution, such as chemical
precipitation, ion exchange, reduction, adsorption, electrochemical precipitation, extraction, membrane, cementation, evaporation, and reverse osmosis. Researchers have found that the most cost-effective and selective of these methods is the adsorption method.

Activated carbon has shown great potential for the removal of various inorganic and organic pollutants due to its properties such as large surface area, microporous structure, and adsorption capacity [1-4]. Recently surface modification of activated carbon has been recognized as an attractive approach to enhance the removal of heavy metals from wastewater [5]. Nowadays, the overall geological resources of coal of Mongolia are 175.5 billion tonnes, and the proven coal reserve is 37.4 billion tonnes. The coal reserves of Mongolia are ranked 12th in the world and, there are more than 300 coal deposits. Coal of Mongolia is containing mostly lignite, sub-bituminous and bituminous coals [6]. One of the largest coal deposits of Mongolia is Tavantolgoi, the total reserves cover 6 billion tons and 80 thousand hectares, and it is a strategically important deposit with 1.5 billion tons of coking and 4.9 billion tons of energy resources coal.

Considering the above discussions, adsorption experiments removing Cr(VI), Cu(II), and Pb(II) from aqueous solution were carried out using activated carbon modified with 3-aminopropyltriethoxysilane (APTES) in this study. 3-aminopropyltriethoxysilane has been used for improving the properties of adsorbents by several researchers [7-9] due to its containing active functional groups, low toxicity, and simple structure. Based on that, this chemical was selected for this modification study. Coal from the Tavantolgoi deposit of Mongolia was used as a precursor for the modification. The activated carbon has been modified with amino-functional groups to remove heavy metal ions due to its limited functional groups (hydroxyl, epoxy, carbonyl, and carboxyl groups) with not enough efficiency on the removal of heavy metal ions. The objectives of this work are to obtain chemical functionalized activated carbon and investigate its properties. In this study, the influence of various parameters (pH, contact time, temperature, initial concentration of heavy metals ions, and common cations) on the adsorption was studied. The thermodynamic parameters and activation energy were determined to discuss the adsorption mechanism.

2. EXPERIMENTAL

2.1. Material and Reagents

All chemicals and reagents including, 3-aminopropyltriethoxysilane (APTES), toluene (98%), NaOH (>98%, pellets), HNO₃, and HCl (>36%) were analytical grades. The standard solutions of Pb(II), Cu(II) and, Cr(VI) were prepared by dissolving Cu(NO₃)₂, Pb(NO₃)₂, K₂Cr₂O₇ into redistilled water.

The coal from the Tavan Tolgoi deposit of Mongolia was used for activation. The results of proximate and elemental analysis of the coal are summarized in Table 1. The activation was carried out in two stages: (1) carbonization, and (2) activation. The coal samples, with the size of 3-5 mm were carbonized in a retort at a temperature of 700°C and with a heating rating of 20°C min⁻¹ for 270 min. This experiment found that carbonized char 77.9%, tar, and water 9.56%, and gas loss 12.54%, respectively.

After the carbonization, the char was activated with heated steam in the vertical quartz’ reactor at different times (120, 180, and 240 min) and temperatures (800°C and 850°C).

Table 1. Result of proximate and elemental analysis

<table>
<thead>
<tr>
<th>Proximate analysis, %</th>
<th>Elemental analysis, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture W</td>
<td>0.97</td>
</tr>
<tr>
<td>Ash A</td>
<td>8.7</td>
</tr>
<tr>
<td>Ash A</td>
<td>8.8</td>
</tr>
<tr>
<td>Volatile V</td>
<td>25.1</td>
</tr>
<tr>
<td>Sulfur S</td>
<td>0.72</td>
</tr>
<tr>
<td>S</td>
<td>0.73</td>
</tr>
</tbody>
</table>

2.2. Modification of Activated Carbon

Activated carbon was washed with distilled water (temperature of 80°C) to remove fine powders contaminants, after that the sample was dried at 110°C for 2 h before use. 10 g of pretreated coal was added into 100 mL of 3-aminopropylenoxyxycyclane solution (30% (vol) in toluene) and stirred for 3 h at a temperature of 50°C. Then, the mixture was filtered, the solid residue was washed several times with distilled water and dried in the oven for 4 h at 110°C. The modified activated carbon was cooled on a vacuum desiccator for further use.
2.3. Characterization of Activated Carbon and Modified Activated Carbon

Various characterization methods have been used to determine physicochemical properties of activated carbon and modified activated carbon. The surface morphologies and elemental mapping of these samples were surveyed by using the scanning electron microscope (SEM) equipped with an X-ray energy dispersive detector (EDS), JCM-6000, JED-2300, JEOL. Surface functional groups were identified by the KBr disc method, with wavenumbers from 400 to 4,000 cm⁻¹ on an FT-IR (FTIR-4200, Jasco). X-ray Powder Diffraction (XRD) of the samples was carried out on a RINT2500HR-PC (RIGAKU Corporation) using Cu Kα radiation in the scanning range of 2-80°. The Brunauer Emmet Teller (BET) method with nitrogen gas adsorption/desorption test was applied to measure the surface area of the samples using TriStar II 3020, Micromeritics.

2.4. Adsorption Experiment

Modified activated carbon was thoroughly mixed with 50 mL solution of a known amount of Pb(II), Cu(II) and, Cr(VI) in a 200 mL conical flask, and the suspension was shaken in a temperature-controlled shaker. After equilibrium, the mixture was filtered and the filtrate was analyzed to determine the remaining metal ion concentrations. Cr(VI) was analyzed by spectrophotometer (U2910, Hitachi) at a fixed wavelength of 540 nm using 1,5-diphenilcarbazide as the complexing reagent. Pb(II) and, Cu(II) were analyzed by ICP (ICP-OES 7300DV).

2.5. Mathematical Procedures

The adsorption capacity was calculated by the following Equation (1):

\[ q = \left( C_0 - C_e \right) \frac{V}{m} \]  

where, \( q \) is the adsorption capacity, mg/g; \( C_0 \) and \( C_e \) are initial and equilibrium concentrations of Cr(VI), mg/L; \( m \) is the mass of modified activated carbon, g; \( V \) is the volume of solution, mL.

The thermodynamic parameters of the adsorption, i.e. the standard Gibb’s free energy \( \Delta G^0 \) (kJ/mol), standard enthalpy \( \Delta H^0 \) (kJ/mol), and entropy \( \Delta S^0 \) (J/mol·K) were calculated from the Van’t Hoff Equations (2) and (3).

\[ \Delta G^0 = -RT \ln K_c \]  
\[ K_c = \frac{C_{Ad}}{C_e} \]  
\[ \ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]

where, \( R \) is the gas constants, (8.314 J/mol·K); \( T \) is the absolute temperature, K; \( K_c \) is equilibrium constant, \( C_{Ad} \) is the amount of adsorbed metal ion at equilibrium, mg/L; \( C_e \) is the equilibrium concentration of metal ion, mg/L.

The slope and intercept of the plot of \( \ln K_c \) versus \( 1/T \) were used to determine the values of \( \Delta H^0 \) and \( \Delta S^0 \).

The activation energy of the process \( E_a \) (kJ/mol) was calculated by the following Equation (4) [10].

\[ \Delta H = E_a - RT \]

3. RESULTS AND DISCUSSION

3.1. Activation of Carbon

The result of the activation experiment is shown in Table 2. As can be seen from Table 2, the yield of activated carbon was 88.0%, 83.5%, and 79.4%, the iodine number was 4.8%, 9.8%, and 11.1% for 120, 180, and 240 min, respectively, at the constant temperature of 800°C of activation. When the activation temperature was increased to 850°C, the yield decreased and, the iodine number increased for all cases. Compared with the volatile matter of activated carbon and the solid residue after the activation, the volatile matter was reduced and, the ash was increased. This is due to the decomposition of the organic mass of coal, increased content of inorganic components, and the free radicals from the decomposition were oxidized by oxygen of water steam. According to [11], the iodine number and surface area increase when the activation temperature increased. Based on the results, the coal activated at 850°C for 240 min was chosen for chemical modification.

3.2. Characterization of the Activated Carbon and Modified Activated Carbon

The FT-IR spectra of the activated carbon and modified activated carbon are shown in Figure 1. It was observed that the pattern of the activated carbon and modified activated carbon with APTES are almost the same. Two major peaks corresponding to the O-H group and C=C bond of carbon structure were assigned at 3439 cm⁻¹ and around 1630 cm⁻¹.
Table 2. Properties of steam activated carbon

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>Yield, %</th>
<th>Iodine number, %</th>
<th>Moisture, W%,</th>
<th>Ash, A%,</th>
<th>Volatile, Vdaf, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>120</td>
<td>88.0</td>
<td>4.8</td>
<td>0.94</td>
<td>26.8</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>83.5</td>
<td>9.8</td>
<td>0.91</td>
<td>20.7</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>79.4</td>
<td>11.1</td>
<td>1.11</td>
<td>27.4</td>
<td>3.02</td>
</tr>
<tr>
<td>850</td>
<td>120</td>
<td>80.9</td>
<td>12.7</td>
<td>1.13</td>
<td>23.7</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>80.7</td>
<td>13.0</td>
<td>0.65</td>
<td>25.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>71.1</td>
<td>17.8</td>
<td>0.81</td>
<td>35.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

However, there are new peaks with low intensity detected at 2922 and 2852 cm\(^{-1}\) (\(\nu\) C-H) CH\(_3\) and (\(\nu\) C-H) CH\(_2\)) on the spectrum of modified activated carbon. Also, after the modification intensity of the peak at 3439 cm\(^{-1}\) was decreased due to the stretching vibration of O-H and N-H functional groups, and the peak corresponding to C-O was shifted from 1090 to 1050 cm\(^{-1}\). The FTIR spectral differences indicate that APTES was grafted onto the activated carbon surface.

The morphology of activated carbon and modified activated carbon with APTES was characterized by SEM (Figure 2). Comparing Figures 2a and c, the surface porosity of activated carbon was reduced after the modification. It is confirmed by 3-aminopropyltriethoxysilane attached to inside the pores of the activated carbon and, the pores were filled with amino-functional groups. It can affect the increase in adsorption capacity. Moreover, from Figures 2b and d, the modified activated carbon seemed to exhibit a more compact stacking morphology than the activated carbon due to cohesive forces, which may be generated from amine-containing functional groups.

![Figure 1. FT-IR spectra activated carbon and modified activated carbon](image1)

![Figure 2. SEM micrographs of activated (a and b) and modified activated carbon (c and d) at 500 and 3000 x magnification, scale = 50 µm, respectively](image2)

![Figure 3. XRD pattern of the activated carbon and modified activated carbon](image3)

The XRD pattern of activated carbon and modified activated carbon are compared in Figure 3.

On the XRD pattern of activated carbon, peaks of carbon C (002) and C (100) appeared at 2\(\theta\) values of 24 and 42°. Also, the sharp peaks of aluminum oxide
were detected at 26, 35, 56, and 68° [12]. After the modification, new peaks at 2θ values of 39 and 60º correspond to SiO$_2$ detected [13], indicating the activated carbon surface may be functionalized by APTES.

The result of the elemental analysis is shown in Table 3. The carbon, oxygen, magnesium, and aluminum contents in activated carbon and modified activated carbon were performed. These results show that after the modification, the content of carbon increased from 74.94% to 86.4% in presence of silicon-organic monomer (3-aminopropyltrimethoxysilane) and oxygen, magnesium, and aluminum were decreased.

**Table 3. Result of elemental analysis of activated and modified carbon**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements, wt%</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td></td>
<td>74.94</td>
<td>10.64</td>
<td>0.95</td>
<td>13.47</td>
</tr>
<tr>
<td>Modified activated carbon</td>
<td></td>
<td>86.4</td>
<td>7.87</td>
<td>0.41</td>
<td>5.32</td>
</tr>
</tbody>
</table>

The BET surface areas of activated carbon and modified activated carbon analyzed by N$_2$ adsorption were 136.76 and 102.11 m$^2$/g, respectively and the corresponding pore volumes were 0.0568 and 0.0415 cm$^3$/g. The decrease in BET surface area and pore volume after the modification indicates that 3-aminopropyltriethoxysilane molecules loaded into the activated carbon.

### 3.3. Influence of Parameters on the Adsorption

#### 3.3.1. pH

After the modification, the adsorption capacities of activated carbon for Pb(II), Cu(II), and Cr(VI) increased by 18, 32, and 50%. Figure 4 compares the values of the adsorption capacity of the modified activated carbon for Pb(II), Cu(II), and Cr(VI). The range values of adsorption capacity of modified activated carbon at the pH=2-6 were 0.544-0.752, 1.5-1.937, and 1.234-3.589 mg/g for Pb(II), Cu (II), and Cr (VI), respectively. Figure 4 shows that the order of heavy metal adsorption capacity is Cr(VI) Cu(II) Pb(II). Moreover, the maximum value of the adsorption capacity is 0.752 mg/g at pH=3 for Pb (II), 1.937 mg/g at pH=4 for Cu (II), and 3.589 mg/g at pH=3 for Cr (VI) adsorption. Therefore, the optimum pH for Cu(II), Pb(II) and, Cr(VI) adsorption on the modified activated carbon was chosen as 4, 3, and 3, respectively.

#### 3.3.2. Contact Time and Initial Concentration

The investigation for the effect of time on Pb(II), Cu (II), and Cr (VI) adsorption was carried out at pH=4 and 3, respectively using metal ions solutions with initial concentrations of 10, 25, and 50 mg/L. Results are shown in Figure 5.
The adsorption capacities of modified carbon increased rapidly within the first hour and then gradually decreased to reach equilibrium point (approximately 3 h for (Pb(II) and Cu(II)), and 4 h for (Cr(VI) adsorption). The fact of adsorption at the first stages may be due to the available active sites of the adsorbents. The adsorption of heavy metal ions was found to be dependent upon the initial concentration. At the equilibrium, the capacity of modified activated carbon increased from 0.75 to 3.13 mg/g, 1.92 to 6.18 and, 3.90 to 8.55 mg/g when an increase in initial concentration from 10 to 50 mg/L; this indicates that at lower initial metal ions concentrations the adsorbent was not yet saturated with metal ions.

3.3.3. Temperature

The effect of temperature on the adsorption capacity of modified activated carbon was investigated at 25°C, 35°C, 45°C and, 55°C at optimum pH with different initial metal ions concentrations (Figure 6).

![Figure 6](image-url)

**Figure 6.** Effect of contact temperature on the adsorption of Pb(II), Cu (II) and, Cr (VI). [Adsorbent dose 0.1 g, contact time 2 h, stirring 100 rpm]

The adsorption capacity was increased for Cu(II) and Cr(VI) adsorption with a rise of temperature from 25 to 55°C. It is further evidence of an endothermic reaction, where heat input enhances the adsorption performance. But adsorption capacity was decreased for Pb(II) adsorption suggesting that Pb(II) adsorption may be caused by the exothermic reaction.

3.4. Competitive Cations

This study was conducted to investigate the effect of common cations in wastewater composition on the selectivity of modified coal. The initial concentration of the metal ions was taken as 50 mg/L to study the effect of competitive ions on the adsorption. Each activated modified carbon sample was contacted with a solution of heavy metals under the different concentrations (i.e., 0, 10, 20, 50, 100, and 200 mg/L) of sodium (Na), potassium (K), calcium (Ca), or magnesium (Mg) ion separately and in combinations of all 4 ions (where the concentrations of each ion were 0, 10, 20, 50, 100 and, 200 mg/L) (Figure 7).

![Figure 7](image-url)

**Figure 7.** Effect of competitive cations on the adsorption of Pb(II) (a), Cu(II) (b) and Cr(VI) (c)
As shown in Figure 7, the adsorption capacity decreased consequently in the presence of Na\(^+\), K\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\) with concentrations from 0 to 200 mg/L in all cases. A remarkable decrease in adsorption capacity was observed for Pb(II) adsorption. The order of heavy metal selectivity of the modified carbon was Cr(VI) Cu(II) Pb(II).

It can be related to the ionic radius \(r_{\text{Cr}}^{6+}=58\text{ pm}, r_{\text{Ca}}^{2+}=87\text{ pm}, r_{\text{Pb}}^{2+}=133\text{ pm}\) of these metals.

### 3.5. Adsorption Thermodynamics

The thermodynamic parameters of the adsorption process play the main role in explaining the mechanism of the adsorption process. The mechanism of metal ion adsorption can be described as either physical adsorption, ion exchange, or chemical adsorption, or in combination [14]. Previous studies have shown that for physical adsorption the value of the activation energy may be less than 7.18 kJ/mol, for chemical adsorption more than 20 kJ/mol. If the value of activation energy belongs in the range of 8-16 kJ/mol, then the adsorption mechanism is controlled by ion exchange mechanisms. The value of the enthalpy of chemical adsorption is 20.9 to 418.4 kJ/mol, and the value of the change in Gibbs free energy of physical adsorption is in the range from -20 to 0 kJ/mol [15].

Table 4 represents thermodynamic parameters such as the standard Gibbs free energy change \(\Delta G^0\), standard enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\), and activation energy \(E_a\) were calculated by the procedure as shown in the experimental section.

The negative value of \(\Delta G^0\) at all temperatures indicated the spontaneous nature of the adsorption of the heavy metals on the modified activated carbon. Positive (Cu(II) and Cr(VI) adsorption) and negative values (Pb(II) adsorption) of the enthalpy change suggested the endothermic and exothermic nature of the adsorption process. In addition, the positive value of entropy change has indicated the increased randomness at the solid/solution interface during the adsorption process.

Based on the values of thermodynamic parameters, Pb(II) adsorption \((-20<\Delta G^0<0, \Delta H^0<0, E_a<7.18\text{ kJ/mol})\) may be controlled by physical adsorption. A negative value of activation energy is an indication that an exothermic process has taken place. When temperature increases, the solubility of the adsorbate would also be consequently increased, and so that the interaction between the adsorbate and the solvent may become more interactive than the interaction between adsorbate and adsorbent. The electrostatic attraction between positively charged Pb(II) and the negatively charged surface of modified activated carbon provides a driving force for the adsorption process and the interaction can be expressed as [16]:

\[
\text{R-NH}_2\text{OH}^- + \text{Pb}^{2+} \rightarrow \text{R-NH}_2\text{OH}^-\text{Pb}^{2+} \quad (5)
\]

\[
\text{R-COO}^- + \text{Pb}^{2+} \rightarrow \text{R-COO}\text{Pb}^{2+} \quad (6)
\]

<table>
<thead>
<tr>
<th>T, K</th>
<th>(C_n), mg/L</th>
<th>(\Delta G^0), kJ/mol</th>
<th>(\Delta H^0), kJ/mol</th>
<th>(\Delta S^0), J/mol K</th>
<th>(E_a), kJ/mol</th>
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</thead>
<tbody>
<tr>
<td>298</td>
<td>10</td>
<td>-12.79 -17.33 -16.01</td>
<td>-9.83 57.49 13.49</td>
<td>9.61 249.05 99.34</td>
<td>-7.36 59.96 15.97</td>
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<tr>
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<td></td>
<td></td>
<td>-7.28 60.04 16.05</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>-7.11 60.21 16.21</td>
</tr>
<tr>
<td>298</td>
<td>25</td>
<td>-13.38 -16.04 -15.65</td>
<td>-6.56 39.95 7.85</td>
<td>22.74 187.36 78.77</td>
<td>-4.09 42.42 10.33</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>24.81 122.30 67.91</td>
<td>-2.46 22.05 7.24</td>
</tr>
<tr>
<td>308</td>
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</tr>
<tr>
<td>328</td>
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<td></td>
<td></td>
<td></td>
<td>-2.21 22.30 7.49</td>
</tr>
</tbody>
</table>
As shown in Table 5, the mechanism of the Cu(II) adsorption ($\Delta G^\circ$<0, $\Delta H^\circ$>0, $E_a$$>$20 kJ/mol) process can be both physical and chemical process. Chemical adsorption can be described as [7]:

$$\text{R-NH}_2 + \text{Cu}^{2+} \rightarrow \text{R-NH}_3\text{Cu}^{2+}$$  \hspace{1cm} (7)

Physical adsorption (the electrostatic attraction between positively charged Cu(II) and the negatively charged surface of modified activated carbon) can be described as follows:

$$\text{R-NH}_2\text{OH}^- + \text{Cu}^{2+} \rightarrow \text{R-NH}_3\text{OH}^-\text{Cu}^{2+}$$  \hspace{1cm} (8)
$$\text{R-COO}^- + \text{Cu}^{2+} \rightarrow \text{R-COO}\text{Cu}^{2+}$$  \hspace{1cm} (9)

In other words, copper ions interacted with COOH, OH, and NH$_2$ functional groups of the adsorbent material.

Based on the values of the thermodynamic parameters and activation energy of the Cr(VI) adsorption on the modified carbon ($\Delta G^\circ$<0, $\Delta H^\circ$>0, $E_a$ = 7.236-16.215), the adsorption mechanism is a combination and, Cr(VI) is adsorbed by physical, chemical, and ion exchange mechanisms.

Chemical adsorption (formation of a complex compound of Cr(III)) can be described as:

$$\text{HCrO}_4^- + 7\text{H}^+ + 3e^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$$  \hspace{1cm} (10)
$$\text{R-NH}_2 + \text{Cr}^{3+} \rightarrow \text{R-NH}_2\text{Cr}^{3+}$$  \hspace{1cm} (11)
$$3\text{R-OH} + \text{Cr}^{3+} \rightarrow 3\text{R-OCr}^{3+} + 3\text{H}^+$$  \hspace{1cm} (12)
$$(\text{R-COOH}) + \text{Cr}^{3+} \rightarrow 3\text{R-COO}\text{Cr}^{3+} + 3\text{H}^+$$  \hspace{1cm} (13)

Physical adsorption (the electrostatic attraction between the negatively charged Cr(VI) and the positively charged surface of modified activated carbon) can be described as:

$$\text{R-NH}_2\text{OH}^- + \text{Cu}^{2+} \rightarrow \text{R-NH}_3\text{OH}^-\text{Cu}^{2+}$$  \hspace{1cm} (14)
$$\text{R-COO}^- + \text{Cu}^{2+} \rightarrow \text{R-COO}\text{Cu}^{2+}$$  \hspace{1cm} (15)

Ion exchange process can be described as:

$$\text{HCrO}_4^- + 7\text{H}^+ + 3e^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$$  \hspace{1cm} (16)
$$3\text{(-NH}_2\text{)} + \text{Cr}^{3+} \rightarrow 3\text{(-NH}_3\text{)-Cr}^{3+} + 3\text{H}^+$$  \hspace{1cm} (17)

4. CONCLUSION

The optimum pH for Cu(II), Pb(II), and Cr(VI) sorption on the modified activated carbon was determined as 4, 3, and 3, respectively. The sorption capacity was increased from 6.15 to 9.88 mg/g and 17.1 mg/g to 19.0 mg/g when increased the temperature from 25°C to 55°C for Cu(II) and Cr(VI) sorption was, respectively (initial concentration of metal ions were 50 mg/L). But the sorption capacity was decreased from 3.13 mg/g to 2.69 mg/g when increased the temperature from 25°C to 55°C for Pb(II) adsorption. Based on values of the thermodynamic parameters and the activation energy, the Pb (II), Cu (II), and Cr (VI) adsorption can be followed by physical, physical-chemical, and physical-chemical adsorption and ion exchange mechanisms, respectively. To confirm the adsorption mechanism, further investigations on the adsorption kinetics and isotherm study are needed.

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