EXTENDED ABSTRACT

Clinoptilolite, which was modified with hexadecyltrimethylammonium-bromide solution (HDTMA-Br) in a proportion of 1/8 (modified zeolite I) and 1/4 w./v. (modified zeolite II), was used for the adsorption of chromate anions from aqueous solutions. Different initial concentrations of chromate anions from 0 to 145 ppm were added as K$_2$Cr$_2$O$_7$ to 1 g of each modified zeolite adsorbent. Clinoptilolite was also used for comparison reasons. Equilibrium isotherms of chromate anions were studied for clinoptilolite and modified zeolites at temperature equal to 25 °C. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were applied to the experimental data. According to the results, the chromate anions adsorption capacity of adsorbents follows the order: modified zeolite I>modified zeolite II>clinoptilolite. Isotherm studies showed that the adsorption data from zeolite and modified zeolite II are best described by Langmuir isotherm while the adsorption data from modified zeolite I are best described by Langmuir and Temkin isotherm. Clinoptilolite adsorbed a low amount of chromate anions equal to 35.05 mg Kg$^{-1}$. Modified zeolite I and II presented a maximum adsorption of chromate anions equal to 2000.01 and 379.86 mg Kg$^{-1}$, respectively. The modification of clinoptilolite with HDTMA-Br leads to the increase of the positive surface charge of zeolite increasing the adsorption of hexavalent chromium in the form of chromate anions. Such modified zeolite adsorbents can be applied as filters for the removal of anions and anionic dyes from wastewaters, where negative charged clinoptilolite presents low adsorption capacity.

Keywords: adsorption, clinoptilolite, chromium, HDTMA-Br

1. INTRODUCTION

The levels of various pollutants in water, air, and soil have increased continuously in recent years, together with global increases in industrialization and urbanization. In particular, heavy metals in aqueous streams represent an important pollutant class due to their undesirable characteristics such as toxicity, persistency and accumulation in living organisms, ground water and soils which cause various disorders and diseases (Deveci and Kar, 2013). Chromium compounds are widely used in industrial activities such as metal surface finishing, steel production, leather tanning, paint manufacturing, electric and electronic components, and pulp processing (Thanos et al., 2012). Cr(III) and Cr(VI) are important from the point of view of environmental pollution (Yadav et al., 2012). Cr(VI) species are in the form of chromate (CrO$_4^{2-}$, HCrO$_4^{-}$) and dichromate (Cr$_2$O$_7^{2-}$) with their high solubility, mobility and toxicity (Wang et al., 2012). In contrast, Cr(III) usually has a toxicity of 500-1000 times less than Cr(VI) (Costa, 2003). According to the guidelines recommended by the World Health Organization (WHO), the maximum level for Cr(VI) in drinking water is 0.05 mg L$^{-1}$ (Yadav et al., 2012). Zeolites are widely used in several applications such as ion exchange, adsorption, heterogeneous catalysis, biosorption supports, polymer catalytic degradation. Due to their unique physical and chemical properties zeolites have been used as heavy metal
adsorbents, chemical sieves and water softeners (Zeng et al., 2010). Natural zeolites normally possess a negatively charged surface and therefore only cation exchange properties. However, zeolite surfaces can be modified with substances possessing positively charged groups, which can provide these inexpensive and readily available materials with anion sorption properties (Noroozifar et al., 2008). One of the most widely employed organic modifiers is hexadecyltrimethylammonium (HDTMA), an aliphatic hydrocarbon with a hydrophobic alkyl long tail and a hydrophilic quaternary ammonium cation charged part. Br⁻ or Cl⁻ salts of HDTMA are used for mineral and clay surface modification.

In the present paper two zeolites, called as I and II modified with hexadecyltrimethylammonium-bromide solution (HDTMA-Br) in a proportion of 1/8 and 1/4 w./v., respectively, were used for the adsorption of chromate ions from aqueous solutions. Different initial concentrations of chromate ions from 0 to 145 ppm were added as K₂Cr₂O₇ to 1g of each adsorbent. Clinoptilolite was also used for comparison reasons. Equilibrium isotherms of chromate ions were studied for clinoptilolite and modified zeolites at temperature equal to 25 °C. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were applied to the experimental data.

2. MATERIALS AND METHODS

2.1. Materials
Clinoptilolite, a common zeolite in Greece, was obtained from S&B Company. The surface charge of zeolite was modified according to Bowman method (Bowman et al., 2000). Clinoptilolite was modified by using 0.05N hexadecyltrimethylammonium-bromide solution (HDTMA-Br) in a proportion of 1/8 w./v. (called as modified zeolite I) and 1/4 w./v. (called as modified zeolite II).

Adsorption studies were carried out using 1.0 g of modified zeolite I or modified zeolite II and 20 ml of ten different concentrations (from 0 to 145 ppm) of K₂Cr₂O₇ solution. Samples were shaken in a water bath at 25°C for 24 h. The samples reached at equilibrium after this period and then were centrifuged at 3000 rpm for 10 min. Zeolite was also used for comparison reasons. Hexavalent chromium, Cr(VI), in the supernatant was determined using an atomic absorption spectrometer (Perkin Elmer 3300). The whole procedure was done in triplicate. The adsorbed Cr(VI) from each adsorbent was calculated from the difference between the initial and the final concentration of chromium in the solution. The pH values of Cr(VI) equilibrium solutions were on average 8.03 ± 0.10, 7.95 ± 0.10, and 7.87 ± 0.11 for zeolite, modified zeolite I and II, respectively.

The percentage of chromium adsorption was calculated according to the following equation:

\[ \% Cr_{\text{adsorbed}} = 100 \cdot \frac{Cr_{\text{initial}} - Cr_{\text{solution}}}{Cr_{\text{initial}}} \]  

where \( Cr_{\text{adsorbed}} \) is the adsorbed amount of chromium ions from each adsorbent at time \( t \), \( Cr_{\text{initial}} \) is the initial amount of chromium ions added to the solution and \( Cr_{\text{solution}} \) is the remaining amount of chromium ions in the solution at time \( t \).

2.2. Isotherms
The data obtained concerning the adsorption of chromium ions from their aqueous solutions in correlation with the concentration of chromium ions in equillibrium were fitted to the following isotherm equations: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (Zhang et al., 2010).


2.2.1. Langmuir isotherm

In the Langmuir isotherm, adsorption is characterized by a single binding energy and a maximum adsorption capacity corresponding to monolayer surface coverage. Langmuir expression follows the equation:

\[ \frac{C_e}{X_e} = \frac{1}{K_L \cdot X_m} + \frac{C_e}{X_m} \]  

where: \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of chromium ions, \( X_e \) (mg Cr kg\(^{-1}\)) is the amount of chromium ions adsorbed per unit mass of adsorbent in equilibrium, \( K_L \) (L mg\(^{-1}\)) is a constant related to the energy of adsorption and \( X_m \) (mg Cr kg\(^{-1}\)) is the maximum adsorption of chromium ions per unit mass of adsorbent (Ioannou et al. 2012). Greater values of \( K_L \) indicate the affinity of adsorbent to adsorbate and imply strong bonding of metal ions. The dimensionless separation factor, \( R_L \), was also evaluated using \( K_L \) values according to the following equation:

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

where \( C_0 \) is the initial concentration of adsorbate. The values of \( R_L \) can be used for the interpretation of the adsorption type showing that when \( R_L = 0 \) the adsorption is irreversible, \( R_L > 1 \) the adsorption is unfavorable and \( 0 < R_L < 1 \) the adsorption is favorable (Kim et al., 2003).

2.2.2. Freundlich isotherm

The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. This empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (Ioannou et al., 2012). The initial and linear form of the Freundlich isotherm follows:

\[ X_e = K_F \cdot C_e^n \] or \[ \log(X_e) = \log(K_F) + n \log(C_e) \]

where: \( K_F \) (L mg\(^{-1}\) Cr) is a constant related to the energy of adsorption and \( n \) is a constant with values less than unity indicative of the degree of surface heterogeneity.

2.2.3. Temkin isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given as follows:

\[ X_e = \frac{(RT/b) \cdot \ln(K_T C_0)}{C_e} \] or \[ X_e = \frac{(RT/b) \cdot \ln(K_T) + (RT/b) \cdot \ln(C_e)}{C_e} \]

where \( T \) is the absolute temperature (K), \( R \) is the gas constant, \( K_T \) (L mg\(^{-1}\) Cr) is the equilibrium binding constant corresponding to the maximum binding energy, \( b \) (kJ mol\(^{-1}\)) is Temkin isotherm constant, \( RT/b \) (dimensionless) is related to the heat adsorption (Ioannou et al., 2012). If the adsorption obeys Temkin equation, the variation of adsorption energy and the Temkin equilibrium constant can be calculated from the slope and the intercept of the plot \( X_{eq} \) versus ln \( C_{eq} \). The experiments took place at temperature around 25 °C.

2.2.4. Dubinin-Radushkevich (D-R) isotherm

The equilibrium data were tested with the D-R isotherm model in order to distinguish adsorption mechanism between physical and chemical adsorption on the heterogeneous surfaces of adsorbents. The D-R equation has the following form:

\[ \ln(X_e) = \ln(X_m) - \beta \varepsilon^2 \]

where \( \beta \) is the activity coefficient related to the mean adsorption energy and \( \varepsilon \) is the Polanyi potential. The Polanyi potential can be calculated from the following equation:

\[ \varepsilon = R \cdot T \ln(1 + 1/C_0) \]

where \( R \) is the universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)) and \( T \) is the absolute temperature (K). The adsorption energy (E) can be calculated by using \( \beta \) values as expressed in the following equation:

\[ E = 1 / (2\beta)^{1/2} \]
The adsorption energy values (E), calculated from the slope of the plot of $\varepsilon^2$ versus $\ln(X_e)$ (eq. 6) in combination with eq. 7, indicate the nature of adsorption process. When the adsorption energy values were equal to 8-16 kJmol$^{-1}$ then chemisorption is the prevailing mechanism otherwise for adsorption energy values less than 8 kJ mol$^{-1}$ physisorption is the prevailing mechanism [Siyal et al., 2012].

2.2.5. Normalized Standard deviation (NSD)
A normalized standard deviation was used so as to quantitatively compare the applicability of the isotherm models that fit well to the experimental data according to correlation coefficients values, $R^2$. The form of the equation is given below:

$$SD = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left( \frac{X_{e,exp} - X_{e,cal}}{X_{e,exp}} \right)^2}$$

where $X_{e,exp}$ and $X_{e,cal}$ are the experimental and calculated values for the adsorbed amount of chromium ions per gram of adsorptive material at equilibrium and $n$ is the number of data point (Ioannou et al., 2012). The similarity of experimental and calculated data from the model led to small values of standard deviation.

3. RESULTS
The percentage of adsorbed Cr(VI) for each adsorbent in correlation with the initial concentration at temperature equal to 25°C is presented in Fig. 1(a). It seems that modified zeolite I presented higher adsorption of chromium ions than modified zeolite II and zeolite. The percentage of chromium adsorption from the adsorbents followed the order: zeolite < modified zeolite II < modified zeolite I. Furthermore, Figure 1(b) depicts the adsorbed amount of chromium ions per kilogram of adsorptive material in correlation with the concentration of chromium in equilibrium at temperature equal to 25°C. Modified zeolite I presented the maximum adsorption of chromium ions (~2000 mg Cr(VI) kg$^{-1}$), while zeolite presented the minimum adsorption of chromium ions (~35.00 mg Cr(VI) kg$^{-1}$). From the above analysis, it seems that the order of chromium adsorption from the adsorbent increased as follows: zeolite < modified zeolite II < modified zeolite I as it was presented in Fig. 1(a).

![Figure 1](image.png)

**Figure 1.** (a) Percentage of adsorbed Cr(VI) in correlation with the initial concentration of Cr(VI), (b) Adsorption of Cr(VI) per kg of adsorptive material in correlation with the concentration of Cr(VI) in equilibrium for zeolite, modified zeolite I and modified zeolite II at 25 °C.
Figure 2 shows Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms for the adsorption of Cr(VI) from zeolite, modified zeolite I and modified zeolite II. Langmuir isotherm presented linear correlation to the experimental adsorption data derived from all adsorbents with high correlation coefficient factors, $R^2 > 0.97$ (Fig. 1(a)). Moreover, Freundlich and Temkin isotherms presented lower correlation coefficient factors (up to 0.95) than Langmuir isotherm except for modified zeolite I (Fig. 1(c)). Consequently, the experimental adsorption data from all adsorptive materials were best described by Langmuir isotherm while the Cr(IV) experimental adsorption data onto modified zeolite I can also be described by Temkin isotherm. Langmuir isotherm shows monolayer adsorption of Cr(IV) onto zeolitic surface, modified or not, in contrast to Freundlich isotherm which depicts multilayer adsorption. Dubinin-Radushkevich isotherm could not describe the uptake of Cr(IV) ions onto zeolites with a linear correlation and consequently was not applicable. Moreover, the kinetic parameters for all isotherms that fitted linearly to the experimental data are presented in Table 1.

Except for the correlation coefficient factors, the SD value (Eq. 9) was used so as to compare quantitatively the applicability of the isotherm models that fitted well to the experimental data. The higher correlation coefficient values and the lower SD values showed that Langmuir isotherm fitted well to the experimental adsorption data of Cr(IV) by modified zeolite II and zeolite while Langmuir and Temkin isotherms were ideal for the uptake of Cr(IV) by modified zeolite I. Other researchers have shown similar results (Thanos et al. 2012; Leyva-Ramos et al. 2008; Li and Bowman 1997). The values of $R_L$ in Langmuir isotherm between 0.06 and 1 showed that the adsorption of Cr(IV) onto the adsorbents is favorable.

Chromate ions exist in an aqueous solution in different ionic forms. The pH and concentrations are important factors showing which particular chromate species will predominate. The bichromate ions ($Cr_2O_7^{2-}$) dominate in acidic environments for chromium concentrations higher than 500 mg/L, while the $HCrO_4^-$ and $CrO_4^{2-}$ oxyanions dominate at concentrations below 500 mg/L.
Figure 2. Langmuir (a), Freundlich (b), Temkin (c) and D-R (d) isotherms for the adsorption of Cr(VI) from zeolite (Z), modified zeolite I (MOD. ZEOL. I), and modified zeolite II (MOD. ZEOL. II), at 25 °C, where $C_e$ is the concentration of chromium in solution at equilibrium (mg L$^{-1}$), and $X_e$ is the adsorbed amount of chromium per kilogram of adsorptive material (mg kg$^{-1}$).

In the present study chromium concentrations were below 500 mg/L and subsequently HCrO$_4^-$ and CrO$_4^{2-}$ oxyanions dominated. The Cr(VI) species may be presented in various forms such as H$_2$CrO$_4$, HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ in the solution phase as a function of pH according to the following reactions (Yusof and Malek, 2009):

$$
\text{HCrO}_4^- \leftrightarrow \text{CrO}_4^{2-} + \text{H}^+ \quad (1),
\text{H}_2\text{CrO}_4 \leftrightarrow \text{HCrO}_4^- + \text{H}^+ \quad (2),
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCrO}_4^- \quad (3)
$$

According to literature (Baes and Mesmer, 1976) between pH 2 and 6, HCrO$_4^-$, and dichromate ion, Cr$_2$O$_7^{2-}$, are in equilibrium while above pH 6, the dominant species are CrO$_4^{2-}$. Below pH 1, the Cr(VI) species are presented as HCrO$_4^-$ ions. According to the solution pH, the HCrO$_4^-$, Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$ and HCrO$_4^-$ ions displace the surfactant counter ion from the exchange sites on the clays forming Cl$^{-}$-HDTMA-HCrO$_4$, (Cl$^{-}$-HDTMA)$_2$-Cr$_2$O$_7$, (Cl$^{-}$-HDTMA)$_2$-CrO$_4$, or Cl$^{-}$-HDTMA-HCrO$_4$-Cr$_2$O$_7$ respectively, where Cl$^{-}$-HDTMA is the modified clinoptilolite with HDTMA-$\text{Br}$ exchanging Br$^-$ ions with the different species of chromate ions (Krishna et al., 2001). In the present study the pH solution values range from 7.8 to 8.0 for all adsorbents indicating that CrO$_4^{2-}$ are predominant. It is known (Yusof and Malek, 2009) that at lower pH, the Cr(VI) species are mostly in the univalent form (HCrO$_4^-$) and thus require one exchange site for one molecule of Cr(VI) species at that pH while at higher pH, the divalent form of Cr(VI) species (Cr$_2$O$_7^{2-}$,CrO$_4^{2-}$) are mostly present and need two exchange sites from modified zeolite for the adsorption to take place. This resulted in higher removal capacity of Cr(VI) species by modified zeolite at lower pH than that at higher pH. In addition, the lower affinity of Cr(VI) sorption at pH 10 may also be influenced by the strong competition from OH$^-$ with Br$^-$ or chromate anion for the sorption sites since more OH$^-$ anions are present at high pH. At pH values greater than 6, the presence of OH$^-$ ions forms the hydroxyl complexes of chromium. The Cr(VI) species are very soluble in aqueous solutions and their solubility increase with pH. Consequently, these experiments were practical to take place in solutions with pH values of 8 and below. The pH solution values for all adsorbents ranged from 7.8 to 8.0 indicating that CrO$_4^{2-}$ were predominant in the solution and were adsorbed by modified zeolites in the form of (Cl$^{-}$-HDTMA)$_2$-CrO$_4$. 
Table 1. Langmuir, Freundlich and Temkin parameters for heavy metal sorption by zeolite, modified zeolite I and modified zeolite II at temperature equal to 25°C

<table>
<thead>
<tr>
<th>Isotherms/Minerals</th>
<th>ZEOL.</th>
<th>MOD. ZEOL. II</th>
<th>MOD. ZEOL. I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L$ (L mg$^{-1}$)</td>
<td>0.118</td>
<td>0.027</td>
<td>0.302</td>
</tr>
<tr>
<td>$X_m$ (mg kg$^{-1}$)</td>
<td>35.050</td>
<td>379.855</td>
<td>2000.017</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.055-1.000</td>
<td>0.055-1.000</td>
<td>0.055-1.000</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.997</td>
<td>0.972</td>
<td>0.997</td>
</tr>
<tr>
<td>SD</td>
<td>0.086</td>
<td>0.084</td>
<td>0.095</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (L mg$^{-1}$)</td>
<td>18.828</td>
<td>24.221</td>
<td>506.616</td>
</tr>
<tr>
<td>$n$</td>
<td>0.128</td>
<td>0.543</td>
<td>0.451</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.932</td>
<td>0.948</td>
<td>0.927</td>
</tr>
<tr>
<td>SD</td>
<td>0.028</td>
<td>0.114</td>
<td>0.227</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b (kJ mol$^{-1}$)</td>
<td>0.632</td>
<td>0.029</td>
<td>0.006</td>
</tr>
<tr>
<td>$K_T$ (L mg$^{-1}$)</td>
<td>58.137</td>
<td>0.249</td>
<td>4.746</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.919</td>
<td>0.945</td>
<td>0.991</td>
</tr>
<tr>
<td>SD</td>
<td>0.873</td>
<td>1.044</td>
<td>1.044</td>
</tr>
</tbody>
</table>

In order to sorb negatively charged chromate, the sorbed HDTMA layer must make use of its positively charged head group. This can only happen when the sorbed HDTMA molecules form bilayers or patchy bilayers and chromate has a stronger affinity for the positively charged HDTMA head group than for the counter-ions already sorbed. The bilayer coverage is most complete when Br$^-$ is the counterion than other counter-ions such as Cl$^-$, HSO$_4^-$ (Li and Bowman,1997). Modified zeolite I presents a higher ratio of Clin to HDTMA than modified zeolite II indicating that the sorbed HDTMA molecules form probably bilayer on modified zeolite I surface and patchy bilayer on modified zeolite II surface resulting to a higher adsorption of anions on modified zeolite I surface than II.

5. CONCLUSIONS

-Clinoptilolite was modified with hexadecyltrimethylammonium-bromide solution (HDTMA-Br) in two different proportions (modified zeolite I and II) so as to obtain its surface positively charged exchange sites for the adsorption of chromate anions from aqueous solutions.

- The initial Cr(VI) concentration was below 500 mg/L and the pH solution values ranged from 7.8 to 8.0 for the adsorbents indicating that CrO$_4^{2-}$ were predominant in the solution and were adsorbed by modified zeolites in the form of (Clin-HDTMA)$_2$-CrO$_4$.

- The maximum adsorbed amount of chromate anions was equal to 35.05, 2000.01 and 379.86 mg Kg$^{-1}$ for zeolite, modified zeolite I and II, respectively.

- The chromate anions adsorption capacity of adsorbents followed the order: modified zeolite I>modified zeolite II>clinoptilolite.

- Isotherm studies showed that the adsorption data from zeolite and modified zeolite II are best described by Langmuir isotherm while the adsorption data from modified zeolite I are best described by Langmuir and Temkin isotherm.

REFERENCES


