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COMPETITIVE ADSORPTION OF CR(VI), K(I) AND NH₄(I) IONS ONTO NATURAL ZEOLITES AND BENTONITES

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ABSTRACT

Chromium, ammonium, and potassium compounds are pollutants in the environment released mainly by industrial wastewater and they can negatively influence the quality of surface water. Zeolites and bentonites are commonly used adsorbents for removal of pollutant from water. In the study, the adsorbents were used in their natural form, without chemical modification for adsorption of Cr(VI), K(I) and $NH_4(I)$ from K_2CrO_4 , $K_2Cr_2O_7$ and $(NH_4)_2CrO_4$ in a single compound system for each adsorbate separately.

The Langmuir isotherm provided the best correlation for the adsorption onto the zeolites and bentonites. The adsorption capacities of bentonites were higher than the adsorption capacities of zeolites from all the used adsorbates. The maximum sorption capacities of K(I) from K_2CrO_4 were approximately the same. The maximum sorption capacities of K(I) from K_2CrO_4 were approximately the same. The maximum sorption capacities of K(I) from K_2CrO_4 were approximately the same. The maximum sorption capacities of K(I) from K_2CrO_4 were higher for zeolites than for bentonites. The adsorption of Cr(VI) in the form of anions is preferred to the adsorption of cations. The zeolites and bentonites were found to be suitable adsorbents for removal of Cr(VI) from aqueous solutions.

Keywords: adsorption, chromium, potassium, ammonium, zeolite, bentonite

INTRODUCTION

Chromium [Cr(VI)] and ammonium [NH₄(I)] are pollutants in the environment and are commonly found mainly in industrial wastewater. Potassium [K(I)] compounds in high concentrations may also cause problems in the environment and their release can negatively influence the quality of surface water. According to the European legislation on the quality of water intended for human consumption the concentrations of Cr and NH₄⁺ should not exceed 0.05 and 0.50 mg.l⁻¹, respectively, in potable water.

Removal of Cr(VI), K(I) and NH₄(I) has been widely studied especially due to toxicity of Cr(VI) in water [1] and soil [2], possible contamination of water by NH₄(I) [3] and K(I) [4]. Several studies concentrated on removal of pollutants from water by different methods. One of the advantageous methods is adsorption. Typically, the adsorption of the elements is studied separately. The adsorption of Cr(VI) by magnetized coconut fibres from agricultural waste was studied by Carvalho Costa et al. [5] who reported a maximum sorption capacity of 87.38 mg.g⁻¹ for the magnetized fibre and 23.87 mg.g⁻¹ for the natural fibre, with an equilibrium time of less than 20 minutes at an optimum pH of 2.

Palm shell activated carbon with polyethyleneimine is also efficient in removal of Cr(VI) with a sorption capacity of 20.5 $mg.g^{-1}$. Zeolite-rich tuff modified maximum by hexadecyltrimethylammonium proved efficient for Cr(VI) removal but with a lower maximum sorption capacity of 0.574 mg.g⁻¹. Removal of K(I) from olive mill wastewater by normal zeolite particles and zeolite clinoptilolite nanoparticles was reported with the best fit of Langmuir isotherm and maximum adsorption capacities of 7.2 and 16.5 mg.g⁻¹, respectively [6]. KOH activated Camellia oleifera shell also proved efficient for Cr(VI) removal [7]. Both $NH_4(I)$ and K(I) removal from wastewater by natural clinoptilolite combined by membrane pre-treatment with Langmuir and Freundlich models fitting best and maximum sorption capacities 19.59 and 34.99 mg.g⁻¹, respectively [4].

A removal capacity of $NH_4(I)$ of 21.96 and 20.71 mg.g⁻¹ was reported from dairy wastewater by zeolites 13X and 4 Å, respectively [8]. The adsorption from piggery water by the clinoptilolite was the best fitted by Langmuir isotherm and pseudo-second order kinetics model with a maximum sorption capacity of 19.7 mg.g⁻¹ [9]. The pseudo-second order kinetics model was confirmed as more suitable by more studies [10,11,12,13].

The adsorbents mentioned above were modified by a chemical process or used in a combination with other process. For this reason, the study concentrates on use of locally available natural material, zeolite and bentonite, from Slovakia and Czech Republic, for removal of Cr(VI), K(I) and $NH_4(I)$ from K_2CrO_4 , $K_2Cr_2O_7$ and $(NH_4)_2CrO_4$. The removal ability of the adsorbents is compared in a single compound system for each adsorbate separately, i.e. the competitive adsorption of cations and Cr(VI) in the form of anion.

MATERIALS AND METHODS

Zeolites were acquired from Zeocem, a.s. (Bystré, Slovakia) and were not modified in laboratory condition, they were crushed by the company to average particle size as defined below. Bentonites were acquired from KERAMOST, a.s. (Most, Czech Republic) and were crushed in laboratory conditions as defined below. For analyses the material from below the sieve was used. In the study, two types of zeolite and bentonite were used, namely Zeolite Micro 20 (Z-M20) crushed to 20 μ m of average particle size, Zeolite Micro 50 (Z-M50), crushed to 50 μ m of average particle size, blue bentonite (B-BL) and brown bentonite (B-BR) crushed in ceramic mortar and sieved with 0.25 mm sieve (FRITSCH GmbH - Milling and Sizing, Weimar, Germany). The samples of bentonites and zeolites were analysed for particle size distribution by a particle sizer Analysette 22 (Fritsch, Germany).

The initial solutions were prepared with analytical grade K₂CrO₄, K₂Cr₂O₇, (NH₄)₂CrO₄ provided by ITES Vranov, a.s. (Vranov, Slovakia) dissolved in distilled water and used for adsorption equilibrium experiments. Sets of PET flasks containing 0.1 dm³ (*V*) of solution of different initial concentrations ($C_0 = 1$ to 3000 mg.dm⁻³) prepared from chromium salts and a fixed dosage of sorbent ($C_a = 0.5$ g.dm⁻³) were agitated in a rotary shaker at 200 min⁻¹ with a temperature control at 25 °C for 2 hours. The initial pH of the solution was not adjusted.

The samples were filtered after equilibration and sedimentation and the filtrates were analysed for chromium and potassium content by AAS (using iCE 3300, Thermo Fisher Scientific, Waltham, MA, USA), and for ammonium by colorimetry (using Photometer 7500, Palintest, Tyne and Wear ,UK) where appropriate. The amounts of metals and ammonium adsorbed q_e (mg.g⁻¹) in each flask were determined from the difference between the initial metal concentration C_0 (mg.dm⁻³) and metal concentration at equilibrium C_e (mg.dm⁻³) in the solution and was calculated according to equation

 $q_e = (C_0 - C_e) \cdot V/m_a$

(1)

 m_a (g) is the weight of adsorbent, V (dm³) is the volume of solution

(2)

Adsorption isotherms are crucial for optimization of the use of adsorbents. The isotherms provide a reliable description of metal ions adsorption equilibria on zeolites and bentonites. The Freundlich, Langmuir and Redlich-Peterson isotherms were used for the analysis as follows.

Freundlich [14]:

$$q_e = K_f \cdot C_e^{-1/n}$$

 K_f (mg¹⁻ⁿ.dm³ⁿ.g⁻¹) is a constant related to the adsorption capacity, n (1) is a constant related to the adsorption intensity; the isotherm represents sorption taking place on a heterogeneous surface with interaction between the adsorbed molecules [15]:

Langmuir [16]:

$$q_e = q_m . a_L . C_e / (1 + a_L . C_e)$$
(3)

 q_m (mg.g⁻¹) is maximum sorption capacity, a_L (dm³.mg⁻¹) is adsorption energy; the isotherm represents sorption taking place on a homogenous surface within the adsorbent [17]:

Redlich-Peterson [18]:

$$q_e = K_R \cdot C_e / (1 + a_L \cdot C_e^{\beta})$$
(4)

 K_R (dm³.g⁻¹) and a_R (dm^{3 β}.g^{- β}) are constants, β (1) is exponent; the isotherm is used as a compromise between the Langmuir and Freundlich systems [15].

Flame atomic absorption spectrometry (AAS) performed using iCE 3300 (Thermo Scientific, USA) was used to determine the concentration of Cr and K in the solutions within 24 hours from the end of the adsorption process.

All the experiments were performed in triples and the result was taken as the average value of each experiment.

RESULTS

The basic properties of the used adsorbents are presented in Table 1. The particle size distributions of used adsorbents are presented in

Figure 1. Though the particle size range of adsorbents is different, the particle size distribution is similar for zeolites and bentonites. The arithmetical mean diameter of adsorbent particles is also similar for zeolites and bentonites.

| | Z-M20 | Z-M50 | B-BL | B-BR | | |
|------------------------------------|-------|-------|-----------|-------|--|--|
| Particle size (µm) | 0-90 | 0-350 | 0-250 | 0-250 | | |
| <i>d</i> ₅₀ (µm) | 3.493 | 9.549 | 19 | 13 | | |
| SiO ₂ (%) | 50.0 | -57.0 | 65-71.3 | | | |
| Al ₂ O ₃ (%) | 15.7 | -17.3 | 11.5-13.1 | | | |
| CaO (%) | 1.7 | -3.1 | 2.7-5.2 | | | |
| K ₂ O (%) | 0.3 | -1.2 | 2.2-3.4 | | | |
| $Fe_2O_3(\%)$ | 8.8- | -17.3 | 0.7-1.9 | | | |
| FeO (%) | 0.1 | -1.0 | 0.1 | | | |

Table 1 The basic physical and chemical properties of zeolites and bentonites.

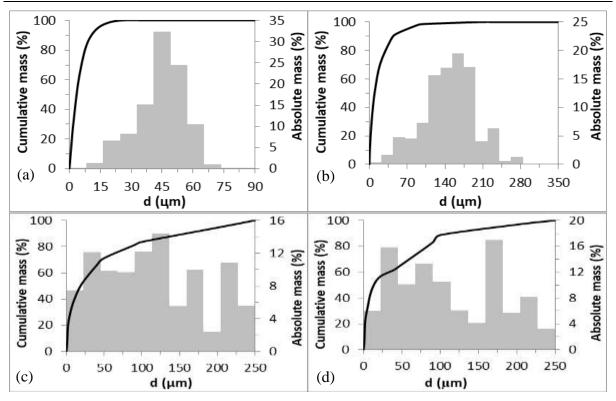


Figure 1 Particle size distribution of (a) Z-M20, (b) Z-M50, (c) B-BL, (d) B-BR.

In the adsorption process of K_2CrO_4 , the maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 0.94 ± 0.04 , 0.82 ± 0.03 , 1.50 ± 0.06 , and 1.64 ± 0.07 mg.g⁻¹, respectively, and for removal of K(I) were 1.58 ± 0.06 , 1.54 ± 0.06 , 1.60 ± 0.06 , and 1.51 ± 0.06 mg.g⁻¹, respectively. The equilibrium data and the fitted data of Cr(VI) and K(I) adsorption by Freundlich, Langmuir and Redlich-Peterson isotherms are presented in Figure 2 and

Table 2, respectively.

The coefficients of determination (R^2) are in the range of 0.59 to 0.99. Based on the regression analysis, the experimental data were the most accurately fit by Langmuir isotherm for adsorption of both Cr(VI) and K(I) onto Z-M50 and Z-M20. For adsorption onto B-BL and B-BR, the experimental data were the most accurately fit by Langmuir isotherm for adsorption of Cr(VI) and by Redlich-Peterson isotherm for adsorption of K(I).

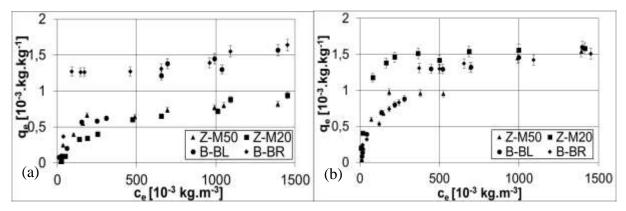


Figure 2 Equilibrium data of (a) Cr(VI) and (b) K(I) adsorption from K₂CrO₄ on Z-M20, Z-M50, B-BL, B-BR.

In the adsorption process of $K_2Cr_2O_7$, the maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 2.71±0.11, 2.82±0.11, 4.21±0.17, and 4.21±0.18 mg.g⁻¹, respectively, and for removal of K(I) were 1.98±0.08, 2.06±0.08, 1.01±0.04, and 0.93±0.04 mg.g⁻¹,

respectively. The equilibrium data and the fitted data of Cr(VI) and K(I) adsorption by Freundlich, Langmuir and Redlich-Peterson isotherms are presented in Figure 3 and Table 3.

| Isotherm | *P. | Z-M20-Cr | Z-M20-K | Z-M50-Cr | Z-M50-K | B-BL-Cr | B-BL-K | B-BR-Cr | B-BR-K |
|------------|-------|-------------|-----------------|-------------|---------------|------------|-----------------|-------------|------------|
| | k_f | 0.97±0.04 | 0.99 ± 0.04 | 0.91±0.04 | 0.95±0.04 | 0.98±0.04 | 0.98 ± 0.04 | 0.85±0.03 | 0.96±0.04 |
| Freundlich | п | 1.10±0.04 | 1.93±0.08 | 1.23±0.05 | 1.12±0.04 | 1.50±0.06 | 0.59±0.02 | 1.27±0.05 | 1.93±0.08 |
| | R^2 | 0.88 | 0.93 | 0.72 | 0.85 | 0.98 | 0.96 | 0.66 | 0.98 |
| | q_m | 0.94±0.04 | 1.58 ± 0.06 | 0.82±0.03 | 1.54 ± 0.06 | 1.57±0.06 | 1.60 ± 0.06 | 1.64±0.07 | 1.51±0.06 |
| Langmuir | a_L | 0.01±0.00 | 0.03 ± 0.00 | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 | 0.01 ± 0.00 | 0.01±0.00 | 0.01±0.00 |
| | R^2 | 0.97 | 0.99 | 0.91 | 0.95 | 0.97 | 0.98 | 0.85 | 0.99 |
| | k_R | 0.33±0.01 | 0.38±0.02 | 0.89±0.04 | 0.03±0.00 | 0.76±0.03 | 0.75±0.03 | 1.31±0.05 | 1.15±0.05 |
| Redlich - | b_R | 152.40±6.10 | 4.22±0.17 | 172.78±6.91 | 4.14±0.17 | 51.48±2.06 | 37.26±1.49 | 100.28±4.01 | 21.96±0.88 |
| Peterson | β | 0.09±0.00 | 0.50 ± 0.02 | 0.18±0.01 | 0.12±0.00 | 0.34±0.01 | 0.31±0.01 | 0.21±0.01 | 0.49±0.02 |
| | R^2 | 0.84 | 0.90 | 0.68 | 0.83 | 0.97 | 0.99 | 0.59 | 0.98 |

Table 2 Adsorption isotherm parameters for K_2CrO_4 adsorption

Note: *P. – parameters, the units are presented in definitions to equations (2)-(4)

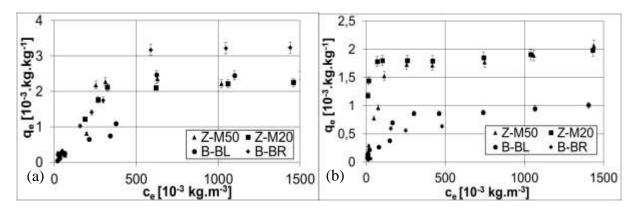


Figure 3 Equilibrium data of (a) Cr(VI) and (b) K(I) adsorption from K₂Cr₂O₇ on Z-M20, Z-M50, B-BL, B-BR.

| Isotherm | *P. | Z-M20-Cr | Z-M20-K | Z-M50-Cr | Z-M50-K | B-BL-Cr | B-BL-K | B-BR-Cr | B-BR-K |
|------------|----------------|------------|-----------|------------|------------|-------------|------------|------------|-------------|
| isotherm | k _f | 0.97±0.04 | 0.88±0.04 | 0.89+0.04 | 0.99+0.04 | 0.95±0.04 | 0.94±0.04 | 0.98±0.04 | 0.97±0.04 |
| Freundlich | n | 1.42±0.06 | 2.59±0.10 | 1.20±0.05 | 1.50±0.06 | 1.10±0.04 | 1.81±0.07 | 1.33±0.05 | 1.27±0.05 |
| | \mathbb{R}^2 | 0.88 | 0.40 | 0.84 | 0.94 | 0.96 | 0.94 | 0.96 | 0.92 |
| | qm | 2.71±0.11 | 1.98±0.08 | 2.82±0.11 | 2.06±0.08 | 4.21±0.17 | 1.01±0.04 | 4.21±0.18 | 0.93±0.04 |
| Langmuir | aL | 0.01±0.00 | 0.03±0.00 | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 | 0.00±0.00 | 0.01±0.00 |
| | \mathbb{R}^2 | 0.97 | 0.88 | 0.89 | 0.99 | 0.95 | 0.94 | 0.98 | 0.97 |
| | k _R | 0.37±0.01 | 0.85±0.03 | 0.57±0.02 | 0.69±0.03 | 0.79±0.03 | 0.74±0.03 | 0.44±0.02 | 0.75±0.03 |
| Redlich - | b _R | 15.25±0.61 | 3.11±0.12 | 55.68±2.23 | 14.44±0.58 | 173.57±6.94 | 22.86±0.91 | 20.67±0.83 | 105.40±4.22 |
| Peterson | β | 0.30±0.01 | 0.64±0.03 | 0.17±0.01 | 0.34±0.01 | 0.09±0.00 | 0.45±0.02 | 0.25±0.01 | 0.21±0.01 |
| | \mathbf{R}^2 | 0.81 | 0.70 | 0.67 | 0.91 | 0.89 | 0.95 | 0.91 | 0.90 |

Table 3 Isotherm constants for K₂Cr₂O₇ adsorption.

Note: *P. – parameters, the units are presented in definitions to equations (2)-(4)

The coefficients of determination (R^2) are in the range of 0.40 to 0.99. Based on the regression analysis, the experimental data were the most accurately fit by Langmuir isotherm for adsorption of both Cr(VI) and K(I) onto Z-M50, Z-M20, and B-BR. For adsorption onto B-BL, the experimental data were the most accurately fit by Freundlich isotherm for adsorption of Cr(VI) and by Redlich-Peterson isotherm for adsorption of K(I).

In the adsorption process of $(NH_4)_2CrO_4$, the maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 7.52±0.30, 7.45±0.30, 12.08±0.48, and 12.79±0.51 mg.g⁻¹, respectively, and for removal of $NH_4(I)$ were 3.16±0.13, 3.35±0.13, 1.39±0.06, and 1.96±0.08 mg.g⁻¹, respectively.

The equilibrium data and the fitted data of Cr(VI) and $NH_4(I)$ adsorption by Freundlich, Langmuir and Redlich-Peterson isotherms are presented in Table 4.

The coefficients of determination (R^2) are in the range of 0.81 to 0.99. Based on the regression analysis, the experimental data were the most accurately fit by Langmuir isotherm for adsorption of both Cr(VI) and NH₄(I) onto all the studied adsorbents.

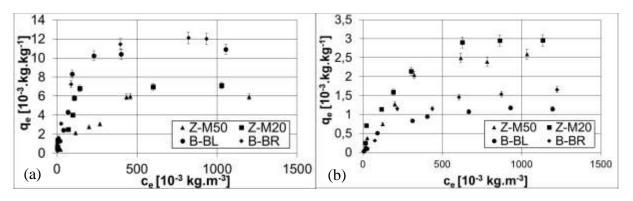


Figure 4 Equilibrium data of (a) Cr(VI) and (b) $NH_4(I)$ adsorption from $(NH_4)_2CrO_4$ on Z-M20, Z-M50, B-BL, B-BR.

| Table 4 Isotherm constants for (NH ₄) ₂ CrO ₄ adsorption. |
|---|
|---|

| Isotherm | *P. | Z-M50-Cr | Z-M50-NH ₄ | Z-M20-Cr | Z-M20-NH ₄ | $B-BL-NH_4$ | B-BL-NH ₄ | B-BR-Cr | B-BR-NH ₄ |
|------------|----------------|------------|-----------------------|-----------------|-----------------------|-----------------|----------------------|---------------|----------------------|
| | k _f | 0.96±0.04 | 0.99±0.04 | 0.94 ± 0.04 | 0.98±0.04 | 0.97 ± 0.04 | 1.00 ± 0.04 | 1.00 ± 0.04 | 0.99±0.04 |
| Freundlich | n | 1.31±0.05 | 1.50±0.06 | 1.98 ± 0.08 | 1.92±0.08 | 1.54 ± 0.06 | 1.37±0.05 | 1.98 ± 0.08 | 1.36±0.05 |
| | \mathbb{R}^2 | 0.94 | 0.96 | 0.90 | 0.91 | 0.90 | 0.93 | 0.96 | 0.96 |
| | qm | 7.52±0.30 | 3.16±0.13 | 7.45±0.30 | 3.35±0.13 | 12.08 ± 0.48 | 1.39±0.06 | 12.79±0.51 | 1.96±0.08 |
| Langmuir | a_L | 0.01±0.00 | 0.01±0.00 | 0.02 ± 0.00 | 0.01±0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 | 0.02 ± 0.00 | 0.01±0.00 |
| | \mathbb{R}^2 | 0.96 | 0.99 | 0.94 | 0.98 | 0.97 | 0.99 | 0.99 | 0.99 |
| | k _R | 0.60±0.02 | 0.47±0.02 | 0.73±0.03 | 0.49±0.02 | 1.13±0.05 | 0.40 ± 0.02 | 0.79±0.03 | 0.28±0.01 |
| Redlich - | b _R | 13.18±0.53 | 14.00±0.56 | 1.32 ± 0.05 | 4.81±0.19 | 4.58±0.18 | 39.50±1.58 | 1.07±0.04 | 21,70±0,87 |
| Peterson | β | 0.24±0.01 | 0.34±0.01 | 0.56 ± 0.02 | 0.49±0.02 | 0.36±0.01 | 0.27±0.01 | 0.56±0.02 | 0.27±0.01 |
| | \mathbb{R}^2 | 0.85 | 0.95 | 0.88 | 0.97 | 0.81 | 0.92 | 0.96 | 0.93 |
| | 1 | 0.05 | 0.75 | 0.00 | 0.77 | 0.01 | 0.72 | 0.70 | 0.75 |

Note: *P. – parameters, the units are presented in definitions to equations (2)-(4)

DISCUSSION

According to the results presented in

Table 2 – Table 4, the prevailing adsorption isotherm is the Langmuir isotherm which assumes that the Cr(VI) and K(I) ions are adsorbed on a fixed number of sites, each site occupied by one adsorbed ion, all the sites are energetically equivalent, the adsorption is monolayer, and the adsorbed molecules do not interact [19]. There is an exception of K_2CrO_4 and $K_2Cr_2O_7$ adsorption onto B-BL – the adsorption of Cr(VI) is characterized by the Freundlich adsorption isotherm and the adsorption of K(I) is characterized by the Redlich-Peterson isotherm.

The Freundlich isotherm is applicable to adsorption processes occurring on heterogonous surfaces and defines the surface heterogeneity and the exponential distribution of active sites and their energies. The Redlich-Peterson isotherm combines elements from both Langmuir and Freundlich equations; therefore, the mechanism of adsorption is a mix and does not follow ideal monolayer adsorption and is applicable in either homogenous or heterogeneous systems because of its versatility [20].

Owlad et al. [21] found the Freundlich isotherm to be the most suitable isotherm for removal of Cr(VI) by modified activated carbon. Et al. found that Langmuir isotherm well described the experimental data of Cr(VI) adsorption from $K_2Cr_2O_7$ by hexadecyltrimethylammonium-modified zeolite-rich tuff, which complies with the results of this study.

By a comparison of Cr(VI), K(I) and $NH_4(I)$ maximum adsorption capacities (

Figure 5), the highest Cr(VI) capacity was recorded for adsorption of $(NH_4)_2CrO_4$ onto B-BR. In general, the adsorption capacities of bentonite were higher than the adsorption capacities of zeolites

from all the used adsorbates. The maximum sorption capacities of K(I) from K_2CrO_4 were approximately the same.

The maximum sorption capacities of K(I) from $K_2Cr_2O_7$ and $NH_4(I)$ from $(NH_4)_2CrO_4$ were higher for zeolites than for bentonites. A comparison of maximum sorption capacities of selected sorbents is presented in Table 5.

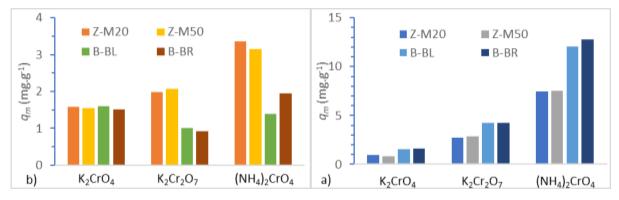


Figure 5 A comparison of a) Cr(VI), and b) K(I) and NH₄(I) maximum adsorption capacities.

The different sorption capacity might be caused by different initial pH. At pH 2 to 6, HCrO₄⁻ and Cr₂O₇²⁻ are in equilibrium, above pH 6, the dominant species are CrO_4^{2-} [22,23]. Below pH 1, the dominant species are $HCr_2O_7^{-}$. Depending on pH, the $HCrO_4^{-}$, $Cr_2O_7^{2-}$, CrO_4^{2-} and HCr_2O^{7-} forms displace the surfactant counter ions from the exchange sites on the clays [24]. At lower pH, with univalent form ($HCrO_4^{-}$) prevailing, it requires one exchange site for one molecule of Cr(VI) species; however, at higher pH, with divalent forms ($Cr_2O_7^{2-}$, CrO_4^{2-}) prevailing, two exchange sites are requires from zeolite or bentonite for the adsorption to take place [25].

In the present study the solution pH values ranged from 8.74 to 9.34 for K_2CrO_4 indicating that $CrO_4^{2^-}$ was predominant, from 3.74 to 4.06 for $K_2Cr_2O_7$ indicating that $HCrO_4^-$ was predominant with minor $Cr_2O_7^{2^-}$ and from 5.05 to 5.43 for $(NH_4)_2CrO_4$ indicating that $HCrO_4^-$ was predominant with minor $Cr_2O_7^{2^-}$ and $CrO_4^{2^-}$. Another approach to chromium adsorption claims that the uptake depends on the availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the Cr(VI) which leads to the formation of Cr(III). The reduction of Cr(VI) and the following sorption of Cr(III) cations was claimed the leading mechanism for chromium uptake on char from coal and on granular activated carbon at pH below 3 [26].

Table 5 A comparison of maximum sorption capacities

| Adsorbent | Adsorbate | Comp. | pH | Temp., °C | q_m mg.g ⁻¹ | |
|--|-----------|---|-----|--------------|--------------------------|------|
| natural coconut fibres | Cr(VI) | $K_2Cr_2O_7$ | 2 | 28 | 23.87 | [5] |
| magnetized coconut fibres | Cr(VI) | $K_2Cr_2O_7$ | 2 | 28 | 87.38 | [5] |
| granular activated carbon | Cr(VI) | K ₂ Cr ₂ O ₇ | 5.8 | | 7.00 | [26] |
| char of South African coal | Cr(VI) | K ₂ Cr ₂ O ₇ | 5.8 | | 0.3 | [26] |
| AC from palm shell modified by Low Molecular Weight Polyethyleneimine | Cr(VI) | K ₂ Cr ₂ O ₇ | 5.7 | | 20.50 | [21] |
| zeolite-rich tuff modified by hexadecyltrimethylammonium | Cr(VI) | Na ₂ CrO ₄ | 3 | room | 0.504 | [23] |
| zeolite-rich tuff modified by hexadecyltrimethylammonium | Cr(VI) | K2Cr2O7 | 3 | room | 0.574 | [23] |
| fly ash | Cr(VI) | Cr solution | 1-3 | | 0.57 | [13] |
| pine nut shells | Cr(VI) | Cr solution | 1-3 | | 6.06 | [13] |
| acid-modified bentonite | Cr(VI) | Cr solution | 1-3 | | 10.55 | [13] |
| zeolite | K(I) | olive mill wastewater | | | 7.20 | [6] |
| zeolite nanoparticles | K(I) | olive mill wastewater | | | 16.50 | [6] |

| natural clinoptilolite with membrane pre- treatment | K(I) | K ⁺ solution | 6 | 19-21 | 34.99 | [4] |
|--|---------------------|---------------------------|-----|-------|-------|------|
| zeolie 13X | NH4(I) | dairy wastewater | | | 21.96 | [8] |
| zeolite 4 Å | NH ₄ (I) | dairy wastewater | | | 20.71 | [8] |
| clinoptilolite | NH4(I) | piggery wastewater | 8.3 | | 19.7 | [9] |
| activated carbon | NH4(I) | NH4 ⁺ solution | | 22 | 4.48 | [10] |
| sodiumdodecyl sulfate modified activated carbon | NH4(I) | NH4 ⁺ solution | | 22 | 6.67 | [10] |
| sodiumdodecyl benzene sulfonate modified activated carbon | NH4(I) | NH4 ⁺ solution | | 22 | 4.87 | [10] |
| sodium octanoate modified activated carbon | NH4(I) | NH4 ⁺ solution | | 22 | 3.87 | [10] |
| tricalcium aluminate | NH4(I) | NH4 ⁺ solution | | 25 | 155.4 | [3] |
| natural clinoptilolite with membrane pre- treatment | NH4(I) | NH4 ⁺ solution | 9 | 19-21 | 19.59 | [4] |

Based on the above it can be concluded that for K₂CrO₄, that took place at alkaline pH with predominant ion form of $CrO_4^{2^-}$, the adsorption capacities of zeolites for K(I) were almost double the adsorption capacities for Cr(VI) and the adsorption capacities of bentonites for K(I) were almost the same as the adsorption capacities for Cr(VI) with a difference less than 10%. For K₂Cr₂O₇ and (NH₄)₂CrO₄, that took place at acidic pH with predominant ion form of HCrO₄⁻, the adsorption capacities of both zeolites and bentonites for K(I) and NH₄(I), respectively, were lower than the adsorption capacities for Cr(VI). The highest sorption capacities were reached for adsorption of Cr(VI) from (NH₄)₂CrO₄ for both bentonites and zeolites implying that the competitive adsorption of K(I) is stronger than the competitive adsorption of NH₄(I). The results also imply that the adsorption of Cr(VI) in the form of anions is preferred to the adsorption of cations.

CONCLUSION

The ability of natural zeolites and bentonites to sorb chromium, ammonium and potassium was studied. The zeolites and bentonites were found to be suitable adsorbents for removal of Cr(VI) from aqueous solutions based on the results of the adsorption experiments. The Langmuir isotherm provided the best correlation for the adsorption of Cr(VI) onto the zeolites and bentonites. The adsorption of Cr(VI) is preferred to adsorption of K(I) or $NH_4(I)$. Additional studies should be conducted on kinetic studies and the influence of pH, on the adsorption behaviour accompanied by the study of surface by XPS.

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