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Effect of pH on adsorption of Cr(VI), K(I) and NH_4(I) ions onto natural zeolites and bentonites

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ABSTRACT

Compounds of chromium, ammonium, and potassium are commonly found in the environment due to industrial activities and can negatively influence its quality if occurring in high concentrations. Natural zeolites and bentonites from local sources can be efficiently used for the adsorption of these pollutants from water. In the study, the influence of pH on the adsorption process 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 separately for each adsorbate onto zeolites and bentonites in their natural form, without chemical modification, was studied. The adsorption experiments were carried out in a batch processes in the pH range from 2 to 9. The Langmuir isotherm provided the best correlation for the adsorption onto both the zeolites and bentonites. The maximum sorption capacities for Cr(VI), K(I) and NH_4(I) adsorption were 12.88 mg g^{-1} onto bentonite from $(NH_4)_2CrO_4$, 2.57 mg g^{-1} onto zeolite from K_2CrO_4 and 4.09 mg g^{-1} onto zeolite from $(NH_4)_2CrO_4$, respectively. The adsorption capacities of bentonites were higher than the adsorption capacities of zeolites from all the used adsorbates. There is a strong influence of pH on the maximum sorption capacities of the zeolites and bentonites whereas the optimum pH for the best removal of the pollutants was 5–7. The influence of particle size distribution and the composition of the adsorbents is not as significant as the influence of the counter ion.

Keywords: Adsorption; Chromium; Potassium; Ammonium; Zeolite; Bentonite

1. Introduction

Chromium [Cr(VI)], potassium [K(I)] and ammonium [NH_4(I)] are commonly found in the environment. In higher concentration, they may become toxic. For this reason, it is necessary to remove them from the effluent before it is released into the environment. Chromium exists in various valence states but the most stable and most occurring forms in nature are Cr(III) and Cr(VI) [1] and is naturally found in all components of the environment – soil, water and air [2]. The most toxic for plants and animals is Cr(VI) associated with chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions [3]. Potassium is an essential element for plants, animals and humans [4]. It functions in protein synthesis, activation of enzymes, in solutes it functions in water balance and affects osmosis, operation of stomata. In the deficiency of potassium growth is reduced, curled, leaves are mottled, or spotted, leaf margins are burned, roots and stems are weakened in plants. A high level of potassium increases the requirement for sodium and vice versa and interferes with the absorption of magnesium in plants [5]. The ammonium ion is a source of nitrogen in cellular biosynthesis and is produced in living organisms by several biochemical processes [6]. Its accumulation in cells leads to tissue damage [6] and a high level of ammonium that reduces plant growth, causes changes in roots, decreases in the root/shoot ratio, and leaf chlorosis, among others [7].

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There are a few methods used for the removal of chromium, potassium and ammonium, while recently their adsorption has been widely studied. In a previous study [8], the removal of Cr(VI), K(I) and NH_4(I) by natural zeolites and bentonites has been studied at non-adjusted pH and the maximum sorption capacities were reported 7.5, 2.1 and 3.4 mg g^{-1}, respectively, for zeolites and 12.8, 4.2 and 2.0 mg g^{-1}, respectively, for bentonites. The effect of solution pH on removal of chromium by non-impregnated activated carbon and char derived from South African coal was studied [9] and reported that the maximum adsorption capacities were around 7.0 and 0.3 mg g^{-1}, respectively, at the pH of 7 and 5, respectively. Based on the study of the effect of pH on Cr(VI) removal from $K_2Cr_2O_7$ by carbon waste from thermal power plant [10], the highest removal capacity of about 95% was found at pH = 2. Also, at pH = 2, a removal capacity of 100% and 90% of Cr(VI) from simulated wastewater and wastewater leachate originating from a Cr slag heap-polluted soil, respectively, was found for bentonite-supported zero-valent iron nanoparticles [11]. The effect of pH on K(I) sorption from olive mill wastewater onto $Ca(OH)_2$-treated zeolite was studied [12] and showed that in the case of lower K(I) concentration the highest sorption capacity is for pH = 6 and in the case of higher K(I) concentration, the highest sorption capacity is for pH = 7. The study on the effect of pH solution on NH_4(I) adsorption from ammonium chloride by modified Chinese Medical Stone [13] reported a maximum sorption capacity of about 4.5 mg g^{-1} at pH = 6. The optimum pH for ammonium adsorption onto zeolite P1 synthesized from fluidized bed fly ash was 6.0 [14], onto natural Chinese (Chende) zeolite it was 8.0 [15], onto natural Iranian zeolite it was 7.0 [16], onto zeolite synthesized from fly ash by a fusion method it was 8.0 [17], onto natural Turkish (Yıldızeli) zeolite it was also 8.0 [18]. Natural zeolites and bentonites are also used for the removal of other pollutants, especially metals [19,20].

The sorption of Cr(VI), K(I) and NH_4(I), as presented above, is mostly studied separately. Therefore, this study concentrates on the removal ability of Cr(VI), K(I) and NH_4(I) from the solutions, compared in a single compound system for each adsorbate separately, that is, the competitive adsorption of cations and Cr(VI) in the form of an anion, by natural, locally available material – unmodified zeolites and bentonites from Slovakia and the Czech Republic [21,22] – thus implementing a strategy to greener Europe by lowering the carbon footprint. This study concentrates mainly on the effect of the initial pH of K_2CrO_4, $K_2Cr_2O_7$ and $(NH_4)_2CrO_4$ solutions on the removal of Cr(VI), K(I) and NH_4(I) from the solutions.

The aim of this study is a comparison of adsorption capacities of zeolites from Slovakia and bentonites from the Czech Republic for sorption of Cr(VI), K(I) and NH_4(I) from aqueous solutions of K_2CrO_4, $K_2Cr_2O_7$ and $(NH_4)_2CrO_4$ at different initial pH values. The capacities are compared for each reagent, each adsorbate and each adsorbent separately and together.

2. Materials and methods

Zeolites were taken from ZEOCEM, a.s. (Bystré, Slovakia). Two types of zeolite were used, zeolite Micro 20 (Z-M20), with particle size 0–90 μm and an average particle size of 20 μm, and zeolite Micro 50 (Z-M50), with particle size 0–350 μm and an average particle size of 50 μm. The clinoptilolite content was 60%–65%. Bentonites were taken from KERAMOST, a.s. (Most, Czech Republic). Also, two types of bentonite were used, blue bentonite (B-BL), with particle size 0–250 μm and an average particle size of 50 μm and brown bentonite (B-BR), with particle size 0–250 μm and an average particle size of 180 μm. The montmorillonite content is 75%–80%. The raw solid samples were analyzed by X-ray photoelectron spectroscopy (XPS) performed using PHOIBOS 100 SCD (SPECS Surface Nano Analysis GmbH, Berlin, Germany) and by X-ray fluorescence (XRF) analysis performed using SPECTRO iQ II (SPECTRO Analytical Instruments GmbH, Kleve, Germany) [21].

The initial solutions were prepared with analytical grade K_2CrO_4, $K_2Cr_2O_7$, $(NH_4)_2CrO_4$, HCl and NaOH provided by ITES Vranov, a.s. (Vranov, Slovakia) dissolved in distilled water and used for adsorption equilibrium experiments and initial pH adjustment. Sets of chromium solutions (V = 0.1 L) of different initial concentrations (C_0 = 1–3,000 mg dm^{-3}) with adjusted pH (2–9 ± 0.1) and a fixed dosage of sorbent (m_a = 0.5 g) were agitated in a rotary shaker at 200 min^{-1} with a temperature control at 25°C ± 0.1°C for 2 h. The supernatants after equilibration and sedimentation were analyzed 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 adsorbed metals and ammonium amount 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 calculated by the equation.

$$q_e = \frac{\left(C_0 - C_e\right)V}{m_a} \tag{1}$$

One of the tools for optimization of the use of adsorbents are adsorption isotherms which provide a 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 [23]:

$$q_e = K_f C_e^{1/n} \tag{2}$$

where K_f (mg^{1-n} dm^{3n} 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 the interaction between the adsorbed molecules [24]:

Langmuir [25]:

$$q_e = \frac{q_m a_L C_e}{\left(1 + a_L C_e\right)} \tag{3}$$

where q_m (mg g^{-1}) is maximum sorption capacity, a_L (dm^3 mg^{-1}) is adsorption energy; the isotherm represents sorption taking place on a homogenous surface within the adsorbent [26]:

Redlich–Peterson [27]:

$$q_e = \frac{K_R C_e}{\left(1 + a_L C_e^{\beta}\right)} \tag{4}$$

where K_R (dm^3 g^{-1}) and a_R (dm$^{3\beta}$ g$^{-\beta}$) are constants, β (1) is exponent; the isotherm is used as a compromise between the Langmuir and Freundlich systems [24].

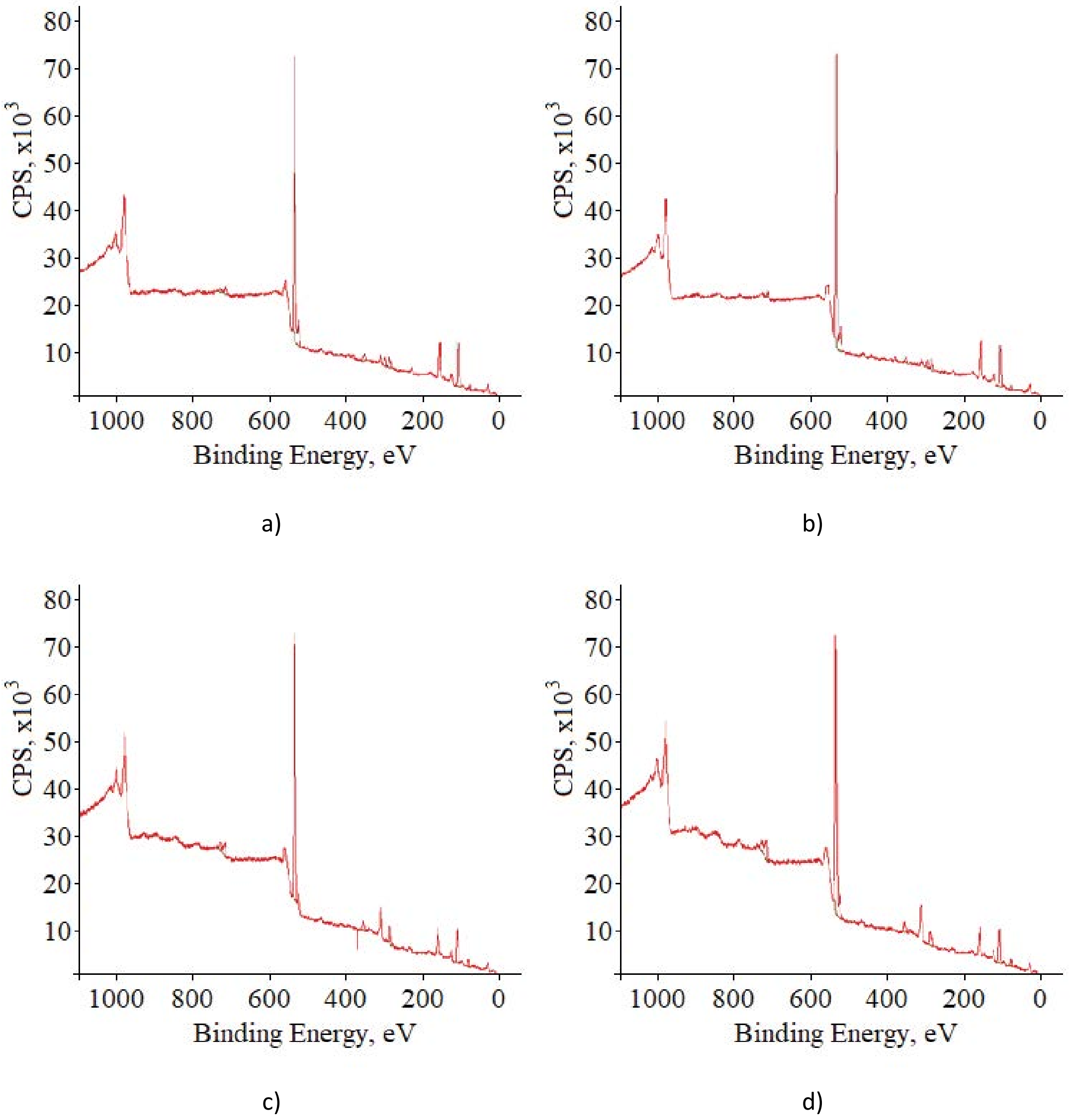
All the experiments were performed in triples and the result was taken as the average value of each experiment. All chemicals and reagents were used with analytical purity (p.a.).

3. Results

The basic chemical composition of raw zeolites and bentonites by XRF are presented in Table 1. The XPS scan spectra are shown in Fig. 1. In the XPS spectra of original Z-M20, Z-M50, B-BL, and B-BR, the highest peak represents the typical dominance of O 1s – oxygen that can be found throughout the zeolite and bentonite structures together with Si 2p – silicon and Al 2p – aluminum. In bentonites, there is also a natural content of Fe 2p – iron with a higher

Table 1
Chemical composition of raw and modified zeolites and bentonites

Compound	Z-M20	Z-M50	B-BL	B-BR
SiO_2 (%)	51.54	53.38	44.78	41.27
Al_2O_3 (%)	8.66	7.13	11.66	10.54
CaO (%)	1.79	0.15	2.53	1.97
K_2O (%)	1.36	0.18	0.00	0.00
Fe_2O_3 (%)	0.83	0.25	2.08	1.50
FeO (%)	0.10	0.10	0.10	0.10
SeO_2 (%)	0.14	0.49	0.39	0.83



a)

b)

c)

d)

Fig. 1. XPS analyses of (a) Z-M20, (b) Z-M50, (c) B-BL, and (d) B-BR.

concentration than Ca 2p – calcium and Se 3d – selenium. The Z-M20 and Z-M50 also contain K 2p – potassium but the content of K 2p – potassium, Ca 2p – calcium and Se 3d – selenium is low.

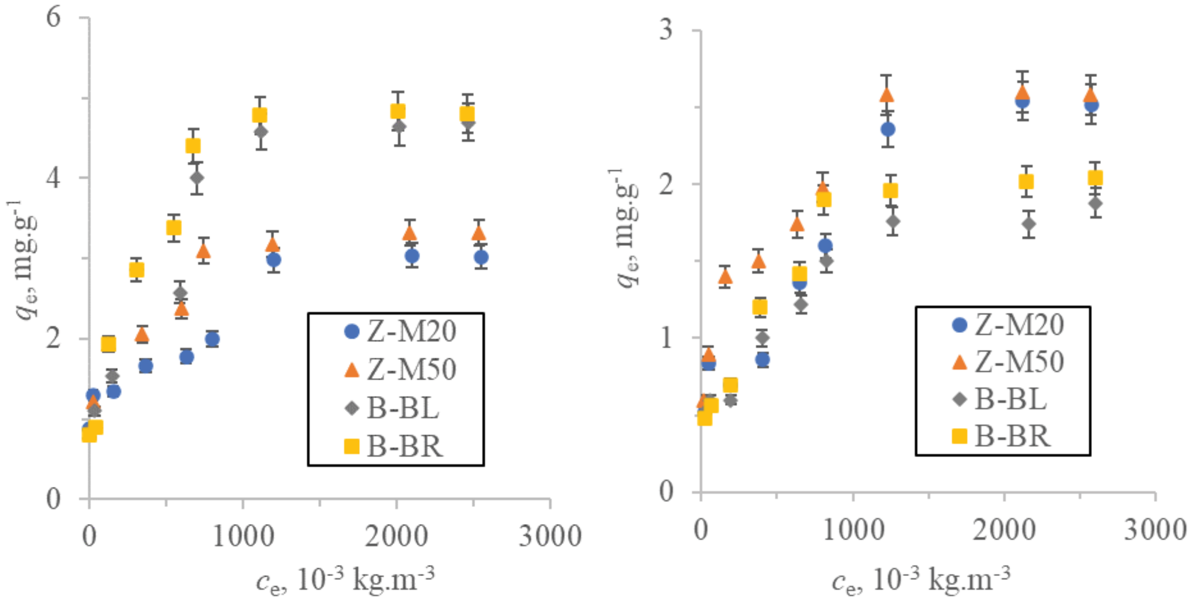
In the adsorption process of K_2CrO_4, the best maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 3.05 ± 0.15 mg g^{-1} at pH = 5, 3.25 ± 0.16 mg g^{-1} at pH = 5, 4.75 ± 0.23 mg g^{-1} at pH = 7, and 4.84 ± 0.24 mg g^{-1} at pH = 7, respectively, and for removal of K(I) were 2.54 ± 0.12 mg g^{-1} at pH = 7, 2.57 ± 0.12 mg g^{-1} at pH = 7, 1.90 ± 0.09 mg g^{-1} at pH = 5, and 2.06 ± 0.10 mg g^{-1} at pH = 5, 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 Fig. 2 and Table 2, respectively, for the best maximum sorption capacities. The coefficients of determination (R^2) are in the range of 0.84 to 0.99. Based on the regression analysis, the experimental data were the most accurate fit by Langmuir isotherm for adsorption of both Cr(VI) and K(I) onto Z-M50, Z-M20, B-BL and B-BR.

In the adsorption process of $K_2Cr_2O_7$, the highest maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 3.20 ± 0.16 mg g^{-1} at pH = 5, 3.06 ± 0.15 mg g^{-1} at pH = 5, 4.60 ± 0.22 mg g^{-1} at pH = 7, and 4.64 ± 0.23 mg g^{-1} at pH = 7, respectively, and for removal of K(I) were 2.50 ± 0.12 mg g^{-1} at pH = 7, 2.39 ± 0.11 mg g^{-1} at pH = 7, 1.80 ± 0.08 mg g^{-1} at pH = 5, and 1.70 ± 0.08 mg g^{-1} at pH = 5, respectively, for the highest maximum sorption capacities. The equilibrium data and the fitted data of Cr(VI) and K(I) adsorption by Freundlich, Langmuir and Redlich–Peterson isotherms are presented in Fig. 3 and Table 3, respectively, for the best maximum sorption capacities. The coefficients of determination (R^2) are in the range of 0.87 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, B-BL and B-BR.

In the adsorption process of $(NH_4)_2CrO_4$, the highest maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 7.45 ± 0.37 mg g^{-1} at pH = 5, 7.52 ± 0.37 mg g^{-1} at pH = 5, 12.19 ± 0.60 mg g^{-1} at pH = 7, and 12.88 ± 0.64 mg g^{-1} at pH = 7, respectively, and for removal of NH_4(I) were 3.46 ± 0.17 mg g^{-1} at pH = 7, 4.09 ± 0.20 mg g^{-1} at pH = 7, 1.39 ± 0.06 mg g^{-1} at pH = 5, and 1.96 ± 0.09 mg g^{-1} at pH = 5, 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 Fig. 4 and Table 4, respectively. The coefficients of determination (R^2) are in the range of 0.91 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 NH_4(I) onto Z-M50 Z-M20, B-BL and B-BR.

The results of the study on the effect of initial pH on the process of Cr(VI) adsorption from K_2CrO_4 are presented in Fig. 5. The best Cr(VI) removal capacities were revealed at pH = 5 for Z-M20 and Z-M50, though the difference in maximum equilibrium capacities was less than 10% for pHs 4, 5 and 6. The best Cr(VI) removal capacities were revealed at pH = 7 for B-BL and B-BR, though the difference in maximum equilibrium capacities was less than 10% for pHs 4, 5 and 6. The best K(I) removal capacities were revealed at pH = 7 for Z-M20 and Z-M50, though the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6 and 7. The best K(I) removal capacities were revealed at pH = 5 for B-BL and B-BR, though the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6, 7 and 8.

The results of the study on the effect of initial pH on the process of Cr(VI) adsorption from $K_2Cr_2O_7$ are presented in Fig. 6. The best Cr(VI) removal capacities were revealed



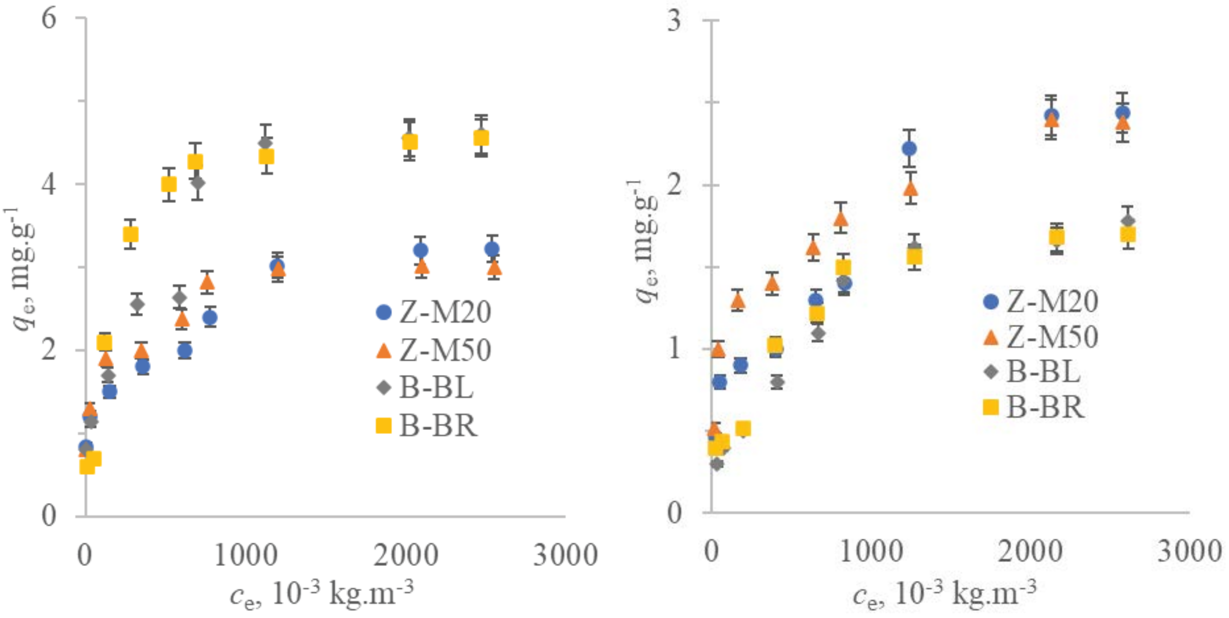
a) b)

Fig. 2. Equilibrium data of (a) Cr(VI) adsorption on Z-M20 and Z-M50 at pH = 5, on B-BL, B-BR at pH = 7 and (b) K(I) adsorption on Z-M20 and Z-M50 at pH = 7, on B-BL, B-BR at pH = 5, from K_2CrO_4.

Table 2
Adsorption isotherm parameters for K_2CrO_4 adsorption

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
Freundlich	K_f	0.77 ± 0.03	0.19 ± 0.01	0.64 ± 0.03	0.29 ± 0.01	0.55 ± 0.02	0.18 ± 0.01	0.38 ± 0.02	0.98 ± 0.04
	n	6.33 ± 0.25	3.07 ± 0.12	4.60 ± 0.18	3.50 ± 0.14	3.67 ± 0.15	3.38 ± 0.14	2.91 ± 0.12	1.46 ± 0.06
	R^2	0.84	0.84	0.97	0.94	0.89	0.90	0.92	0.94
Langmuir	q_m	3.05 ± 0.12	2.54 ± 0.10	3.25 ± 0.13	2.57 ± 0.10	4,75 ± 0.19	1.90 ± 0.08	4.84 ± 0.19	2.06 ± 0.08
	a_L	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
	R^2	**0.91**	**0.94**	**0.99**	**0.95**	**0.95**	**0.95**	**0.98**	**0.96**
Redlich–Peterson	K_R	2.03 ± 0.08	1.08 ± 0.02	1.00 ± 0.04	1.86 ± 0.07	1.81 ± 0.07	1.10 ± 0.04	1.61 ± 0.06	0.99 ± 0.04
	b_R	1.58 ± 0.06	5.80 ± 0.17	1.65 ± 0.07	6.15 ± 0.25	2.64 ± 0.11	5.88 ± 0.24	3.89 ± 0.16	6.61 ± 0.26
	β	0.88 ± 0.04	0.68 ± 0.02	0.78 ± 0.03	0.72 ± 0.03	0.76 ± 0.03	0.71 ± 0.03	0.67 ± 0.03	0.65 ± 0.03
	R^2	0.85	0.92	0.97	0.90	0.94	0.94	0.96	0.95

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



a) b)

Fig. 3. Equilibrium data of (a) Cr(VI) adsorption on Z-M20 and Z-M50 at pH = 5, on B-BL, B-BR at pH = 7 and (b) K(I) adsorption on Z-M20 and Z-M50 at pH = 7, on B-BL, B-BR at pH = 5, from $K_2Cr_2O_7$.

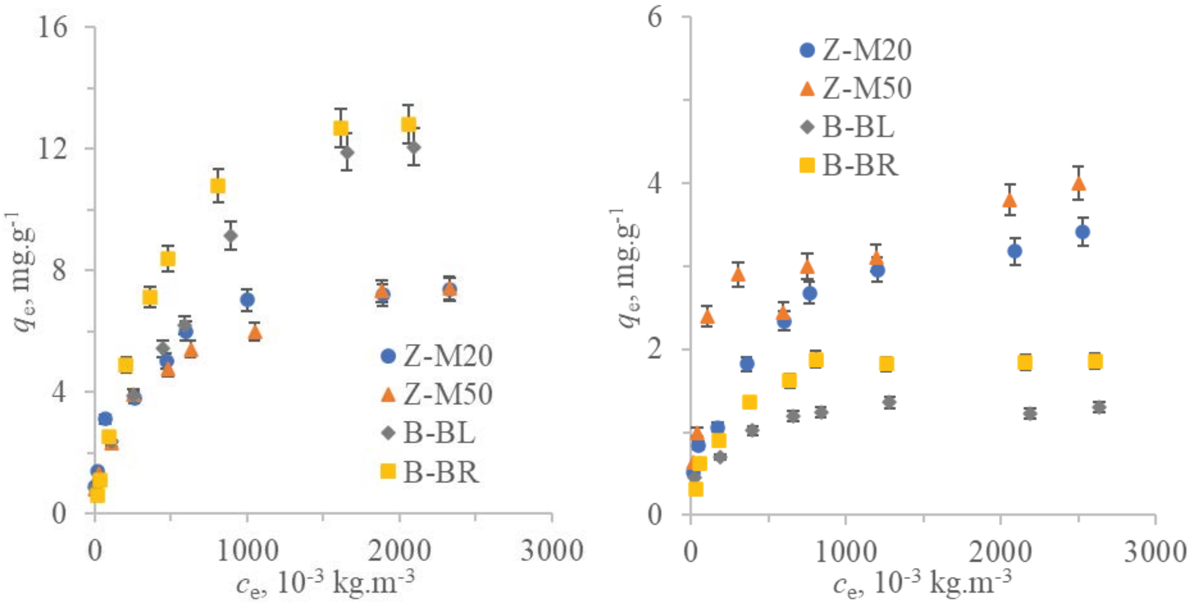
at pH = 5 for Z-M20 and Z-M50, but for Z-M20 the difference in maximum equilibrium capacities was less than 10% for pHs 5 and 6 and for Z-M50 the difference in maximum equilibrium capacities was less than 10% for pHs 4 and 5. The best Cr(VI) removal capacities were revealed at pH = 7 for B-BL and B-BR, but the difference in maximum equilibrium capacities was less than 10% for pHs 4, 5, 6 and 7. The best K(I) removal capacities were revealed at pH = 7 for Z-M20 and Z-M50, but the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6 and 7. The best K(I) removal capacities were revealed at pH = 5 for B-BL and B-BR, but for B-BL the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6, 7, 8 and 9 and for B-BR the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6, 7 and 8.

The results of the study on the effect of initial pH on the process of Cr(VI) adsorption from $(NH_4)_2Cr_2O_7$ are presented in Fig. 7. The best Cr(VI) removal capacities were revealed at pH = 5 for Z-M20 and Z-M50, though the difference in maximum equilibrium capacities was less than 10% for pHs 5 and 6. The best Cr(VI) removal capacities were revealed at pH = 7 for B-BL and B-BR, though the difference in maximum equilibrium capacities was less than 10% for pHs 5, 6 and 7. The best NH_4(I) removal capacities were revealed at pH = 7 for Z-M20 and Z-M50, but for Z-M20 the difference in maximum equilibrium capacities was less than 10% for pHs 4, 5, 6, 7 and 8 and for B-BR the difference in maximum equilibrium capacities was less than 10% for pHs 7 and 8. The best NH_4(I) removal capacities were revealed at pH = 5 for B-BL and B-BR, but the difference in

Table 3
Adsorption isotherm parameters for $K_2Cr_2O_7$ adsorption

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
Freundlich	K_f	0.60 ± 0.02	0.17 ± 0.01	0.62 ± 0.02	0.29 ± 0.01	0.43 ± 0.02	0.06 ± 0.00	0.19 ± 0.01	0.10 ± 0.00
	n	4.83 ± 0.19	3.02 ± 0.12	4.68 ± 0.19	3.69 ± 0.15	3.20 ± 0.13	2.30 ± 0.09	2.25 ± 0.09	2.72 ± 0.11
	R^2	0.95	0.92	0.97	0.96	0.95	0.96	0.87	0.92
Langmuir	q_m	3.20 ± 0.13	2.50 ± 0.10	3.06 ± 0.12	2.39 ± 0.10	4,60 ± 0.18	1.80 ± 0.07	4.64 ± 0.19	1.70 ± 0.07
	a_L	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
	R^2	**0.96**	**0.96**	**0.98**	**0.98**	**0.96**	**0.97**	**0.99**	**0.97**
Redlich–Peterson	K_R	2.19 ± 0.09	1.14 ± 0.05	0.93 ± 0.04	1.80 ± 0.07	1.72 ± 0.07	1.02 ± 0.04	1.61 ± 0.06	0.90 ± 0.04
	b_R	3.23 ± 0.13	6.46 ± 0.26	1.26 ± 0.05	6.00 ± 0.24	3.69 ± 0.15	15.91 ± 0.64	8.17 ± 0.33	8.41 ± 0.34
	β	0.81 ± 0.03	0.67 ± 0.03	0.81 ± 0.03	0.73 ± 0.03	0.70 ± 0.03	0.57 ± 0.02	0.56 ± 0.02	0.64 ± 0.03
	R^2	0.94	0.93	0.98	0.96	0.95	0.96	0.89	0.96

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



a) b)

Fig. 4. Equilibrium data of (a) Cr(VI) adsorption on Z-M20 and Z-M50 at pH = 5, on B-BL, B-BR at pH = 7 and (b) NH_4(I) adsorption on Z-M20 and Z-M50 at pH = 7, on B-BL, B-BR at pH = 5, from $(NH_4)_2Cr_2O_7$.

maximum equilibrium capacities was less than 10% for all the studied pHs.

4. Discussion

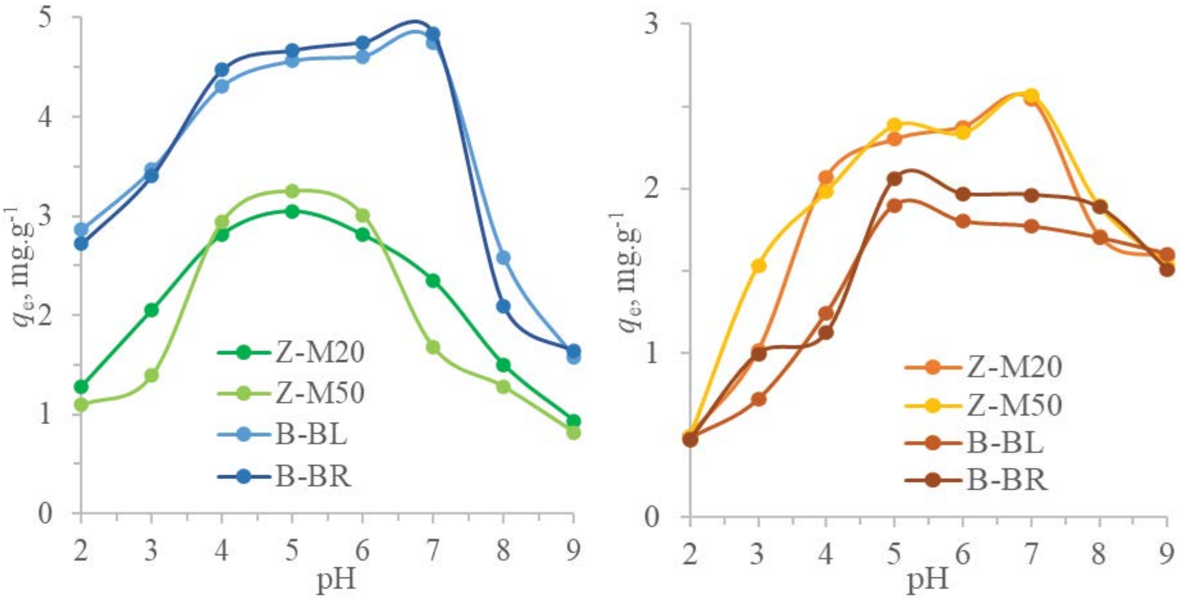
There is a difference in the composition of the zeolites and bentonites based on the results of XRF analyses (Table 1). The zeolites contain higher amount of SiO_2, but lower amount of Al_2O_3, CaO, and Fe_2O_3 than bentonites. The bentonites contain no potassium. The difference in composition is also between different types of zeolites and bentonites. Z-M20 has a significantly higher content of CaO and K_2O, but lower content of SeO_2 than Z-M50. B-BL has a significantly higher content of CaO and Fe_2O_3, but lower content of SeO_2 than B-BR. There is no significant difference in the elemental composition of the surface layer determined by XPS (Fig. 1) and the bulk (Table 1) [21] of both zeolites and bentonites.

The removal of Cr(VI), K(I) and NH_4(I) by Z-M20, Z-M50, B-BL, and B-BR was studied at pH that was not modified [8]. In the adsorption process of K_2CrO_4 at pH = 8.74–9.34, 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. In the adsorption process of $K_2Cr_2O_7$ at pH = 3.74 – 4.06, 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

Table 4
Adsorption isotherm parameters for $(NH_4)_2Cr_2O_7$ adsorption

Isotherm	*P.	Z-M20-Cr	Z-M20-NH_4	Z-M50-Cr	Z-M50-NH_4	B-BL-Cr	B-BL-NH_4	B-BR-Cr	B-BR-NH_4
Freundlich	K_f	0.78 ± 0.03	0.17 ± 0.01	0.41 ± 0.02	0.35 ± 0.01	0.55 ± 0.02	0.24 ± 0.01	0.12 ± 0.00	0.12 ± 0.00
	n	3.33 ± 0.13	2.53 ± 0.10	2.60 ± 0.10	3.10 ± 0.12	3.67 ± 0.15	4.33 ± 0.17	1.54 ± 0.06	2.63 ± 0.11
	R^2	0.96	0.97	0.98	0.88	0.89	0.92	0.97	0.91
Langmuir	q_m	7.45 ± 0.30	3.46 ± 0.14	7.52 ± 0.30	4.09 ± 0.16	12.19 ± 0.49	1.39 ± 0.06	12.88 ± 0.52	1.96 ± 0.08
	a_L	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.02 ± 0.00	0.00 ± 0.00	0.01 ± 0.00
	R^2	**0.97**	**0.98**	**0.99**	**0.96**	**0.98**	**0.97**	**0.99**	**0.99**
Redlich–Peterson	K_R	2.18 ± 0.09	0.99 ± 0.04	0.93 ± 0.04	1.72 ± 0.07	2.12 ± 0.08	0.98 ± 0.04	1.17 ± 0.05	0.99 ± 0.04
	b_R	1.96 ± 0.08	5.67 ± 0.23	1.88 ± 0.08	4.14 ± 0.17	4.28 ± 0.17	4.03 ± 0.16	9.04 ± 0.36	8.19 ± 0.33
	β	0.76 ± 0.03	0.61 ± 0.02	0.64 ± 0.03	0.68 ± 0.03	0.60 ± 0.02	0.77 ± 0.03	0.35 ± 0.01	0.62 ± 0.02
	R^2	0.97	0.97	0.98	0.94	0.97	0.93	0.95	0.91

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

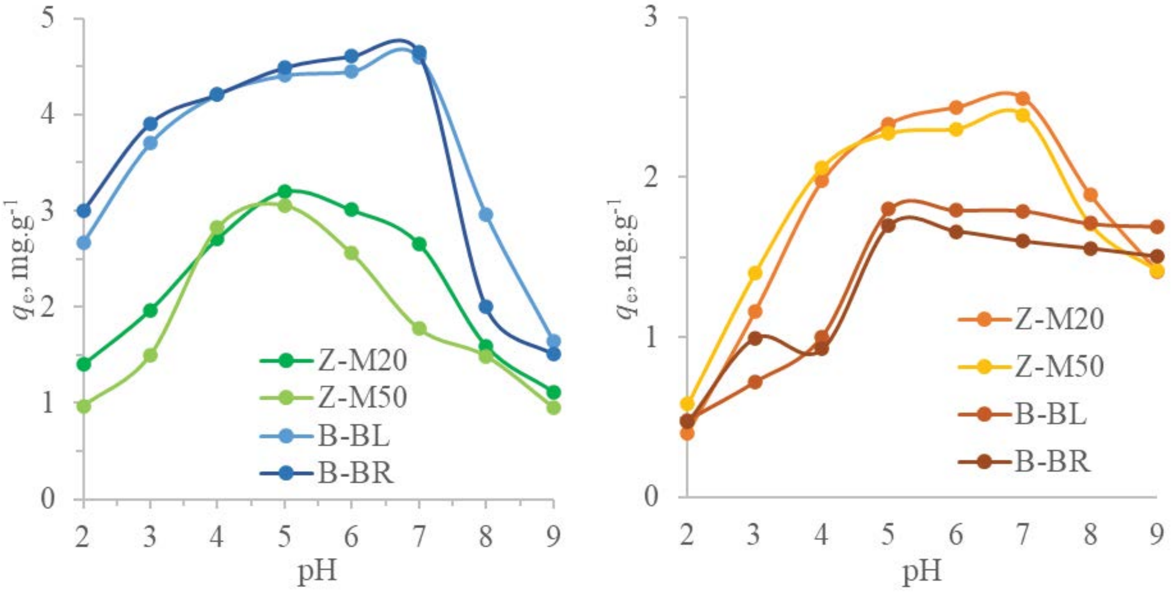


(a) (b)

Fig. 5. Effect of initial pH on the maximum equilibrium capacity of (a) Cr(VI) and (b) K(I) adsorption from K_2CrO_4.

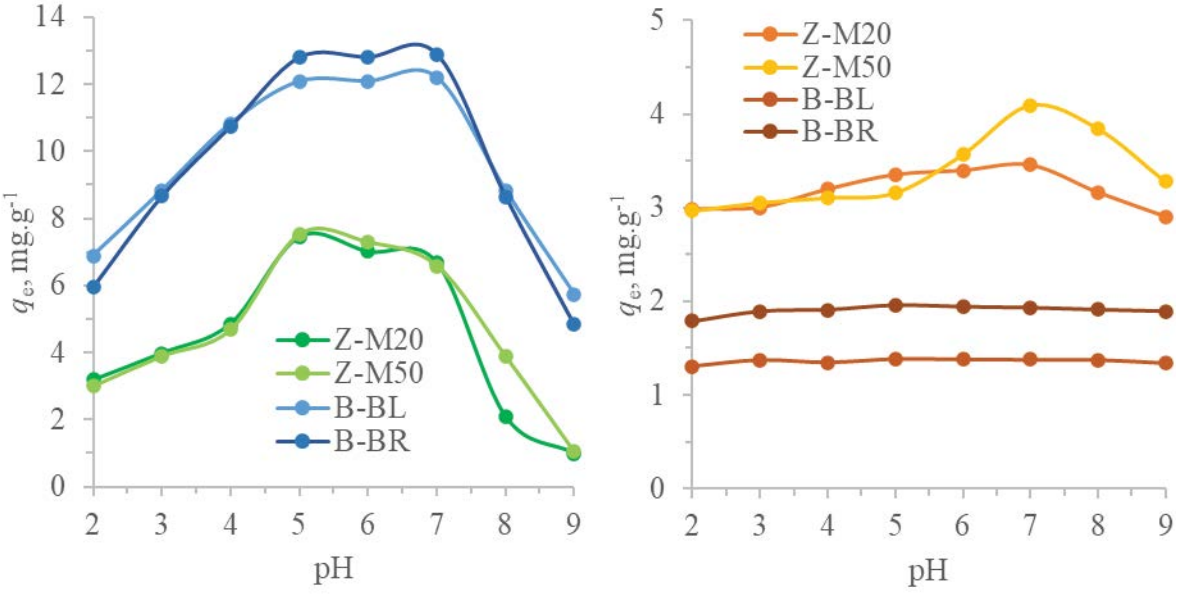
removal of K(I) were 1.98 ± 0.08, 2.06 ± 0.08, 1.01 ± 0.04, and 0.93 ± 0.04 mg g^{-1}, respectively. In the adsorption process of $(NH_4)_2CrO_4$, at pH = 5.05–5.43 the maximum adsorption capacities for removal of Cr(VI) by Z-M20, Z-M50, B-BL, and B-BR were 7.52 ± 0.30, 7.45 ± 0.30, 12.08 ± 0.48, and 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. These results correspond to the results of the study with initial pH modified. The comparisons of maximum equilibrium capacities based on pH are presented in Fig. 8 for zeolites and in Fig. 9 for bentonites. Both zeolites and bentonites proved efficient in the removal of Cr(VI), K(I) and NH_4(I).

The best maximum equilibrium adsorption capacities were recorded for Cr(VI) removal from $(NH_4)_2CrO_4$ at all studied pHs, except sorption onto zeolites at pH = 9. There was no statistical difference in adsorption of Cr(VI) from K_2CrO_4 and $K_2Cr_2O_7$ onto zeolites and bentonites, but the equilibrium adsorption capacities significantly depend on the initial solution pH. This fact may be caused by prevailing Cr(VI) species in the solution as, depending on pH, the $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} and HCr_2O^{7-} ion species displace the surfactant counter ions from the exchange sites on the clays [28]. At lower pH, with prevailing monovalent form ($HCrO_4^-$), one exchange site is required for one ion of Cr(VI) species; however, at higher pH, with prevailing divalent forms ($Cr_2O_7^{2-}$,CrO_4^{2-}), two exchange sites are required from zeolite or bentonite for one ion of Cr(VI) species for the adsorption to take place [29]. Another approach claims that the uptake of chromium depends on the availability of chromium ions in solution and on the incidence of redox reactions between the surfactant ion groups and the Cr(VI) which leads to the creation of Cr(III). The reduction of Cr(VI) cations and the following sorption of Cr(III)



(a) (b)

Fig. 6. Effect of initial pH on the maximum equilibrium capacity of (a) Cr(VI) and (b) K(I) adsorption from $K_2Cr_2O_7$.

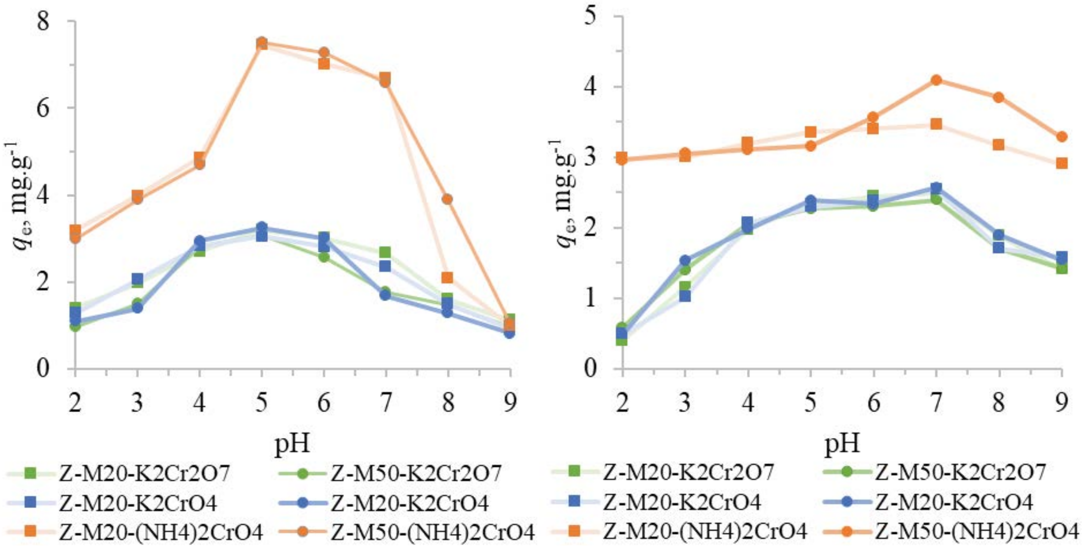


(a) (b)

Fig. 7. Effect of initial pH on the maximum equilibrium capacity of (a) Cr(VI) and (b) NH_4(I) adsorption from $(NH_4)_2CrO_4$.

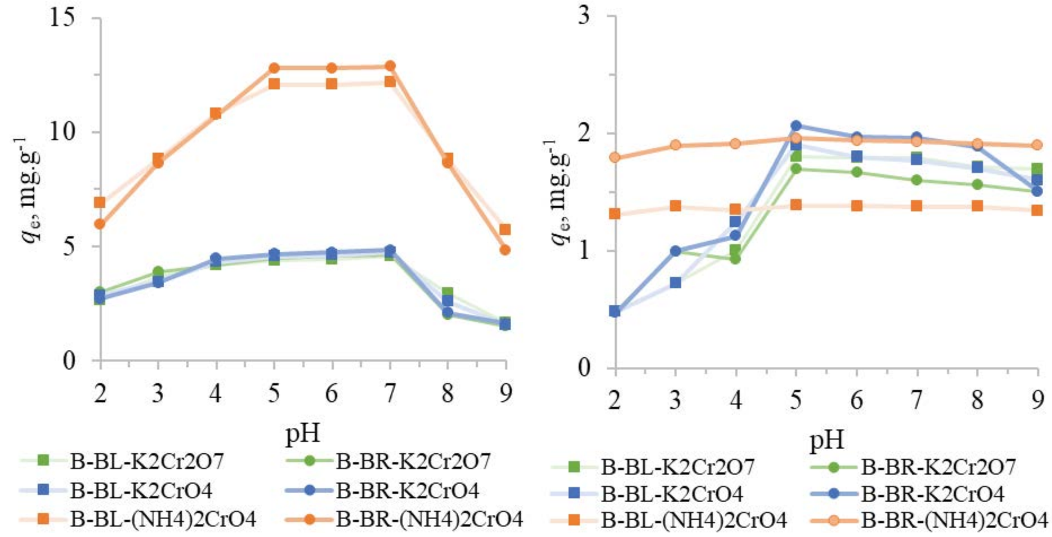
cations was claimed the leading mechanism for chromium uptake on char from coal and on granular activated carbon at pH below 3 [9]. Based on the results, regardless of the source of Cr(VI) – chromate or dichromate – the best maximum equilibrium capacities of Cr(VI) were at pH 5–7, where there is no dominant species as the $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} are present in the solution, while below pH 5, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are in equilibrium and no CrO_4^{2-} are present [30,31], in contrast at pH above 8 only CrO_4^{2-} is present [31].

The adsorption capacity of Cr(VI) is not only affected by the pH but is significantly affected by the counter ion for both the bentonites and zeolites. For adsorption of Cr(VI) from all the studied sources K_2CrO_4, $K_2Cr_2O_7$ and $(NH_4)_2CrO_4$, the best maximum adsorption capacities were revealed at pHs 5 and 7 for the zeolites and bentonites, respectively, but there is only a difference of up to 10% for the maximum adsorption capacities pHs in the range 5–7. Nevertheless, the maximum adsorption capacities at pH range 5–7 for Cr(VI) adsorption from $(NH_4)_2CrO_4$ is about three time



a) b)

Fig. 8. Comparison of maximum sorption capacities of (a) Cr(VI) and (b) K(I) or NH_4(I) adsorption onto zeolites.



a) b)

Fig. 9. Comparison of maximum sorption capacities of (a) Cr(VI) and (b) K(I) or NH_4(I) adsorption onto bentonites.

higher than from K_2CrO_4 and $K_2Cr_2O_7$ for both the zeolites and bentonites. This implies that the effect of ionic strength and the kind of counter ion should also be considered when studying the adsorption of Cr(VI) and further studied.

The sorption of K(I) is not supposed to be significantly affected by the pH [12]. The results of this study indicated that the sorption of K(I) is not significantly affected at pH ranging 5–7 onto zeolite and at pH ranging 5–8 onto bentonite, regardless of the source. In the adsorption process of Cr(VI) and K(I) there is a significant mutual effect and the effect of pH. At lower pH below 5 and higher pH above 8 the sorption capacity of zeolites and bentonites for both Cr(VI) and K(I) is significantly lower than at pH ranging 5–8. Nevertheless, the effect of particle size distribution and composition of the adsorbents is negligible.

The adsorption of NH_4(I) is significantly different from the adsorption of K(I). The optimum pH values for NH_4(I) adsorption by zeolite are in the range 5–8 [15–17]. At pH below 6, there is a competition between H_3O^+ and NH_4^+ in solution for the limited exchange sites of zeolite, which accounts for the decline of NH_4^+ removal under acidic conditions [32]. Moreover, if the pH is below 4, the structure of zeolites starts to collapse (or dissolve) in the solution [17]. At pH above 7, the decline is probably due to the increase of free NH_3 molecules, which cannot enter the zeolite by ion exchange [17,18]. The adsorption of NH_4(I) was better than the adsorption of K(I) by zeolite. By the zeolites, the maximum equilibrium capacity of NH_4(I) was the best at pH = 7 and it was higher than the maximum equilibrium capacity of K(I) adsorption at the same pH. The effect of pH on the maximum equilibrium capacity is not significant, only for Z-M20 there is a peak at pH 7, otherwise the difference in the equilibrium capacity is less than 10%. By the bentonites, the maximum equilibrium capacity of NH_4(I) was the best at pH = 5 but it was not higher than the maximum equilibrium capacity of K(I) adsorption at the same pH. The effect of pH on the maximum equilibrium capacity is not significant as the difference in the equilibrium capacity is less than 5% (except for pH 2). The competitive adsorption of K(I) is stronger than the competitive adsorption of NH_4(I) and the adsorption of Cr(VI) in the form of anions is preferred to the adsorption of cations.

Carvalho Costa et al. [33] reported a higher maximum sorption capacity for the magnetized fiber than for the natural fiber, with an equilibrium time of less than 20 min at an optimum pH of 2 for the adsorption of Cr(VI) by magnetized coconut fibers from agricultural waste. Khezami and Capart [34] studied the effect of pH (3, 6 and 9) on adsorption of Cr(VI), prepared by dissolving CrO_3 in distilled water, onto activated carbons and reported that the maximum equilibrium adsorption capacity was at pH = 3 and the capacity was increasing with decreasing pH. Guo et al. [35] studied the effect of pH (6 and 9) on adsorption of K(I) and NH_4(I), prepared by dissolving KCl and NH_4Cl powder, respectively, in deionized water, onto natural clinoptilolite and reported no effect of pH. Both Liu et al. [14] – studied the effect of pH (in the range of 2–8) on adsorption of NH_4(I), prepared by dissolving anhydrous NH_4Cl in deionized water, onto zeolite P1 synthesized from fly ash under solvent-free conditions – and Tang et al. [36] – studied the effect of pH (2, 4, 6, 8, 10) on adsorption of NH_4(I) onto biochar, produced from the pyrolysis of digested sludge – reported maximum adsorption capacity at pH = 6. Tang et al. [36] also concluded that biochar ammonium adsorption capacity in municipal wastewater was lower than that found in experiments with ammonium solution prepared in the laboratory. Fan et al. [37] reported the maximum adsorption capacity at pH = 5 for ammonium ions adsorption onto bamboo biochar (studied at pH = 3, 5 and 7), with a conclusion that solution pH is important for ammonium adsorption but particle size of adsorbent did not have a significant influence on the process. These results are consistent with the findings of this study. The maximum sorption capacities are presented in Table 5.

The studies discussed above also confirmed that the Cr(VI), K(I) and NH_4(I) adsorption onto natural or synthesized adsorbent is strongly affected not only by pH but also by the source of adsorbate and therefore by the ionic strength and by the adsorbent, but the particle size distribution is negligible. The future study should concentrate on completing the results with other available methods, for example, scanning electron microscopy, Brunauer–Emmett–Teller, adsorption kinetics, etc.

Table 5
Comparison of maximum sorption capacities

Adsorbent	Adsorbate	pH	Temperature, (°C)	q_m, (mg g^{-1})	Source
Zeolite-rich tuff modified by hexadecyltrimethylammonium	Cr(VI)	3	Room	0.574	[31]
Acid-modified bentonite	Cr(VI)	1–3	n/a	10.55	[38]
Natural coconut fibres	Cr(VI)	2	28	23.87	[33]
Magnetized coconut fibres	Cr(VI)	2	28	87.38	[33]
Granular activated carbon	Cr(VI)	5.8	n/a	7.00	[9]
Char of South African coal	Cr(VI)	5.8	n/a	0.30	[9]
KOH-activated carbon	Cr(VI)	3	40	315.6	[34]
H_3PO_4-activated carbon	Cr(VI)	3	40	186.1	[34]
Fly ash	Cr(VI)	1–3	n/a	0.57	[38]
Pine nut shells	Cr(VI)	1–3	n/a	6.06	[38]
Normal zeolite	K(I)	25	4.5	7.20	[39]
Zeolite clinoptilolite nanoparticles	K(I)	25	4.5	16.50	[39]
Natural clinoptilolite with membrane pre-treatment	K(I)	6	19–21	34.99	[35]
Zeolite 4 Å	NH_4(I)	n/a	n/a	20.71	[40]
Zeolite 13X	NH_4(I)	n/a	n/a	21.96	[40]
Clinoptilolite	NH_4(I)	8.3	n/a	19.7	[41]
Activated carbon	NH_4(I)	6.0	22	4.48	[42]
Sodiumdodecyl sulfate modified activated carbon	NH_4(I)	6.0	22	6.67	[42]
Sodiumdodecyl benzene sulfonate modified activated carbon	NH_4(I)	6.0	22	4.87	[42]
Sodium octanoate modified activated carbon	NH_4(I)	6.0	22	3.87	[42]
Natural clinoptilolite with membrane pre-treatment	NH_4(I)	9	19–21	19.59	[35]
Synthetized zeolite from fly ash	NH_4(I)	6	25	22.9	[14]
Biochar	NH_4(I)	6	20	1.4	[36]

Note: n/a – data not available

5. Conclusion

The ability of studied natural zeolites and bentonites from local sources to adsorb chromium, ammonium and potassium was investigated and was proved efficient in adsorption 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). The pH study demonstrated a strong influence of pH on the maximum sorption capacities of the zeolites and bentonites whereas the best efficiency was found for pH in the range 5–7. It was also documented that the influence of particle size distribution and the composition of the adsorbents is not so significant as the influence of the counterion, which should be further studied.

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