

REMOVAL OF Zn^{2+} , Cd^{2+} AND Pb^{2+} FROM BINARY AQUEOUS SOLUTION BY NATURAL ZEOLITE AND GRANULATED ACTIVATED CARBON

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The adsorptive removal of Zn^{2+} , Cd^{2+} and Pb^{2+} from single and binary metal ion aqueous solution using natural clinoptilolitic zeolite tuff, a regional low-cost naturally available adsorbent, and granulated activated carbon, an adsorbent conventionally applied in wastewater treatment, was studied. The competitive adsorption equilibrium of three binary mixtures (Cd^{2+}/Zn^{2+} , Zn^{2+}/Pb^{2+} and Pb^{2+}/Cd^{2+}) with different ratios of initial metal ion concentrations, on both adsorbents, was determined in batch mode at 25°C.

Langmuir and Freundlich isotherms were used to interpret the adsorption data of the investigated systems. The results indicate that the Langmuir isotherm fits the data better in both single and binary component systems. Natural zeolite and granulated activated carbon showed similar adsorption capacity for Pb^{2+} , although granulated activated carbon had higher adsorption capacity for Zn^{2+} and Cd^{2+} than natural zeolite. The order of metal ion selectivity on both adsorbents is $Pb^{2+} > Cd^{2+} > Zn^{2+}$.

The binary equilibrium of adsorption showed competitive nature. For all studied metal ions (Zn^{2+} , Cd^{2+} and Pb^{2+}) the natural zeolite and granulated activated carbon metal ion adsorption capacity in the case of binary systems (adsorption) are lower than those obtained for a single metal systems (adsorption), and are significantly influenced by the ratios of initial metal ion concentrations in the binary water solutions.

Key words: heavy metals; adsorption; binary mixture equilibrium; granular activated carbon; natural zeolite

ИЗВЛЕКУВАЊЕ НА Zn^{2+} , Cd^{2+} И Pb^{2+} ОД БИНАРЕН ВОДЕН РАСТВОР СО ПРИРОДЕН ЗЕОЛИТ И ГРАНУЛИРАН АКТИВЕН ЈАГЛЕН

Истражувано е извлекувањето на јоните Zn^{2+} , Cd^{2+} и Pb^{2+} од единичен и бинарен воден раствор со користење на природен клиноптилолитен зеолитен туф, регионален евтин атсорбент, како и со користење на гранулиран активен јаглен што се користи како конвенционален атсорбент при третман на отпадни води. Определени се конкуритивните атсорпциони рамнотежи на три бинарни смеси (Cd^{2+}/Zn^{2+} , Zn^{2+}/Pb^{2+} и Pb^{2+}/Cd^{2+}) со различни односи на почетни концентрации на металните јони врз двата атсорбента во шаржни услови при 25 °C.

За интерпретирање на резултатите на испитуваните системи се користени изотермите на Langmuir и Freundlich. Резултатите покажуваат дека изотермата на Langmuir подобро ги фитира податоците и за единичните и за бинарните системи. Природниот зеолит и гранулираниот активен јаглен покажуваат сличен атсорпционен капацитет за Pb^{2+} , иако гранулираниот активен јаглен има поголем атсорпционен капацитет за Zn^{2+} и Cd^{2+} одошто природниот зеолит. Редот на селективноста на металните јони за двата атсорбента е $Pb^{2+} > Cd^{2+} > Zn^{2+}$.

Студијата за бинарната атсорпција покажа конкуритивна природа. За сите испитувани метални јони (Zn^{2+} , Cd^{2+} и Pb^{2+}) атсорпциониот капацитет на јоните врз двата атсорбента за бинарните системи е помал од оној добиен за единичните системи, при што големо влијание има почетната концентрација на металните јони во бинарните водни раствори.

Клучни зборови: тешки метали; атсорпција; рамнотежа на бинарни смеси; гранулиран активен јаглен; природен зеолит

INTRODUCTION

Heavy metal containing wastes are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even when the heavy metals are present at trace concentrations. Several methods for removal of metal ions from wastewaters have been developed, but most have disadvantages, such as continuous input of chemicals, high cost and even incomplete metal removal [1].

Adsorption is a very effective process for a variety of applications, and now it is considered an economical and efficient method for metal ions removal from wastewaters [2]. The most generally used solid adsorbent is activated carbon which is used as a very efficient solid adsorbent in many different applications [3]. However, activated carbon is expensive and for effluents containing metal ions activated carbon requires chelating agents to enhance its performance, thus increasing treatment cost. Therefore, the need of alternative low-cost adsorbents has prompted the search for new and cheap sorption processes for aqueous effluent treatment, as these materials could reduce significantly the wastewater-treatment cost [4–6].

Recently, there has been a great interest in R&D of low cost alternative adsorbents for treatment of heavy metal wastewaters. These investigations include: removal of Cr(VI) [7], Cu(II) [8, 9], Cd(II) [10,11], Ni(II) [12], Pb (II) [13], Zn(II) [14], Co(II) [15], As(V) [16] and Hg(II) [17] with different low-cost adsorbents such as clinoptilolite [5], coals [8, 11], montmorillonite [10], agricultural waste [14], sepiolite [15], and clay [16].

Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides, are classified as low-cost adsorbents. Natural zeolites also gained a significant interest among scientist, mainly due to their unique properties such as ion exchange capability. Large deposits of natural zeolites in many countries provide local industries some promising benefits, such as cost efficiency, since they are able to treat wastewater contaminated with heavy metal at low cost. For an excellent review regarding the use of this low cost adsorbent, the reader is referred to the articles by Pollard et al. [17] and Sandhya Babel and Tonni Agustiono Kurniawan [18].

In general, contaminated water contains more than one heavy metal. From the point of view of

environmental protection, adsorption studies of multi-metal systems are imperative. Although the number of references in related literature concerning single component systems is rather larger, there are only few studies of multi-component systems. Because of system complexity, a simplification should be introduced in order to make the problem more tractable. Mohan and Sing [14], and Mohan and Chander [19] used Langmuir and Freundlich models to examine the competitive adsorption of metals on activated carbon and agricultural waste in multi-solute systems. Machida et al. [20] used Langmuir equation to predict simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon.

The efficient application of natural zeolites for heavy metal remediation is dependent on the understanding of their capacity and affinity. In this paper, the adsorption ability of local natural zeolite was investigated for removal of Zn(II), Cd(II) and Pb(II) from single (non-competitive) and binary (competitive) aqueous systems. This paper also presents the results of comparative equilibrium studies performed using activated carbon and natural zeolite.

EXPERIMENTAL

Materials and methods

Chemicals

Pb²⁺, Zn²⁺ and Cd²⁺ single and binary ion water solutions were prepared by dissolving respective amount of the metal nitric salts, Pb(NO₃)₂ (Merck-Germany), Zn(NO₃)₂·6H₂O (Fluka, Germany) and Cd(NO₃)₂·4H₂O (Fluka, Germany), in distilled water. The initial total metal ion concentration used in the adsorption equilibrium experiments was in the range between 10 mg/l and 500 mg/l.

Sorbent materials

Natural zeolite tuff (ZEO) and commercial granulated activated carbon (GAC) were used as adsorbents in this study. The natural zeolite was supplied from the Vranjska Banja (Serbia) sedimentary deposit. The granulated activated carbon K-81/B, carbonized coconut shell activated by water steam, was supplied from TRAYAL Corporation (Serbia). The K-81/B granulated activated carbon is commercially applied in filtering systems for water treatment.

The adsorbents were characterized by X-ray diffraction (XRD) using Philips X'pert X-ray diffractometer, and scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using Philips XL 30 CP Scanning Electron Microscope. The ZEO specific surface area, total pore volume, and real density were measured using the multi-point-N₂-BET method, on the Quantachrome NovaWin2 system. The particle density was determined using Hg picnometry analysis.

According to the data from the supplier, the ZEO consists mainly of clinoptilolite (more than 80%), heulandite, and mordenite, with quartz, sanidine, and biotite present in trace quantities. The XRD diffraction pattern of natural zeolite, presented in Figure 1, is in good agreement with the diffraction patterns of clinoptilolite, although some extra peaks corresponding to heulandite and non-zeolite phase (quartz and calcite) were also detected. On the SEM image of ZEO, presented in Figure 2a, typical crystals of clinoptilolite–heulandite family of zeolite were observed. The chemical composition of natural zeolite (ZEO) is presented in Table 1. According to the chemical analysis, the total (or maximum) exchange capacity of ZEO is 2.19 meq/g, calculated as the sum of Mg, Ca, K and Na cations. The Si(mol)/Al(mol) ratio is 4.23. The physical properties of natural zeolite are summarized in Table 2.

The granulated activated carbon (GAC) X-ray diffraction pattern did not show any peak, thereby indicating the amorphous nature of the material. The GAC element composition, calculated from the EDX spectra, in wt% is: 87.67 C, 11.31 O, 0.25 Si, 0.09 S, 0.41 K and 0.28 Ca. The GAC SEM image and physical properties are presented in Figure 2b and Table 2, respectively.

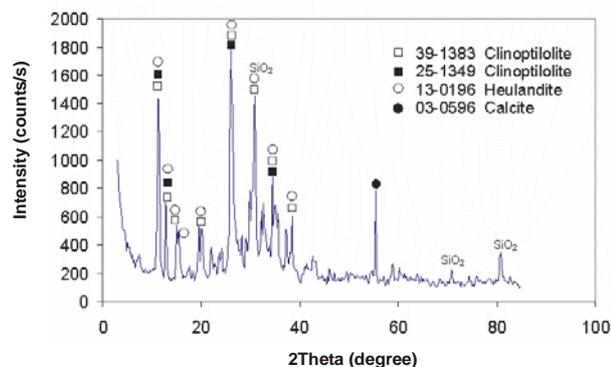
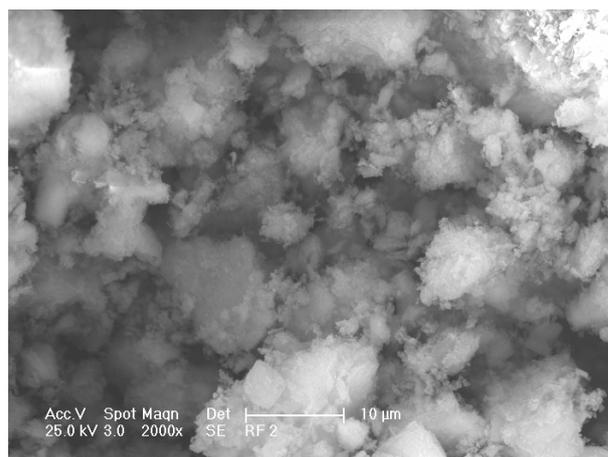
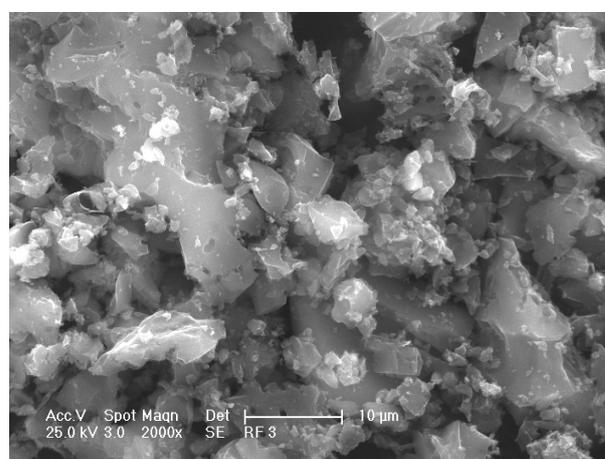


Fig. 1. XRD spectrum of natural zeolite



a)



b)

Fig. 2. SEM images of (a) natural zeolite (clinoptilolite) and (b) granulated activated carbon

Table 1

Chemical composition of natural zeolite (ZEO)

Oxide	wt%
SiO ₂	64.88
Al ₂ O ₃	12.99
Fe ₂ O ₃	2.00
TiO ₂	0.37
CaO	3.26
MgO	1.07
Na ₂ O	0.95
K ₂ O	0.89
H ₂ O	13.59

Table 2

Physical properties of natural zeolite (ZEO) and granulated activated carbon (GAC)

Property	Natural zeolite	Granulated activated carbon
Particle size (mm)	1–2	0.5–1.6
Particle density (g/cm ³)	1.425	
Real density (g/cm ³)	2.246	
Bulk density (g/cm ³)	0.70–0.75	0.44–0.48
BET area m ² /g	17.83	1200
Pore volume (cm ³ /g)	0.01597*	0.8–1.0
Micropore volume (cm ³ /g)		0.45–0.50
CEC (meq/g)	2.19	
Hardness (Moss scale)	3–3.5	
Ballpan hardness	96–9%	
Iodine number AWWA (mg/g)		1150–1250
Ash content (%)		3–5

*Pores smaller than 269.8 Å

Prior to the experiments, the ZEO was washed with distilled water in order to remove the surface dust and possible impurities, and dried at 350°C for 48 hours. GAC was repeatedly washed with distilled water to remove any leachable impurities and adherent powder, and then dried to constant weight at 120 °C for 24 hours. After the treatment, both materials were stored in well closed glass bottles.

Equilibrium of adsorption

The single and binary equilibrium of adsorption of Zn²⁺, Cd²⁺ and Pb²⁺ on ZEO and GAC was determined at 25°C in batch mode. The competitive adsorption equilibrium of three binary mixtures (Cd²⁺/Zn²⁺, Zn²⁺/Pb²⁺ and Pb²⁺/Cd²⁺), with different ratios of initial metal ion concentrations, were studied. Three different metal ion initial concentration ratios were used in the determination of the binary adsorption equilibrium: Cd²⁺:Zn²⁺ = 2.5:1, 1:1, 0.45:1; Zn²⁺:Pb²⁺ = 2:1, 1:1, 0.5:1 and Pb²⁺:Cd²⁺ = 7.4:1, 2.2:1, 0.43:1. The purpose of the use of different ratios of initial metal ion concentrations is to determine the effect of the second metal ions on the adsorption of Zn²⁺, Cd²⁺ and Pb²⁺ on ZEO and GAC.

A 100 ml of solution with selected metal ion/s concentration (10–500 mg/l) and mass of adsorbent (1–4 g) were placed in 250 ml Erlenmeyer flask and shaken for a predefined time period needed for reaching an equilibrium (3 days for GAC and 4 days for ZEO) in vertical rotary shaker

(150 turns/min), at constant temperature. The pH of the solution was not adjusted. After an equilibrium has been established, the mixture was separated by filtration, the filtrate was acidified with HNO₃, and the concentration of the filtrate was measured on ARL 3520 atomic absorption spectrophotometer (ARL, Ecublens, Switzerland).

RESULTS AND DISCUSSION

Single adsorption isotherms

The equilibrium of adsorption of Zn²⁺, Cd²⁺ and Pb²⁺ on natural zeolite (ZEO) and granulated activated carbon (GAC) was determined at 25°C. The adsorption equilibrium isotherms of Zn²⁺, Cd²⁺ and Pb²⁺ on ZEO and GAC are presented in Figure 3a and Figure 3b, respectively. The GAC has higher adsorption capacity for Zn²⁺ and Cd²⁺ than ZEO. Both adsorbents showed similar adsorption capacity for Pb²⁺.

The experimental adsorption equilibrium data were described by the Langmuir and Freundlich equations.

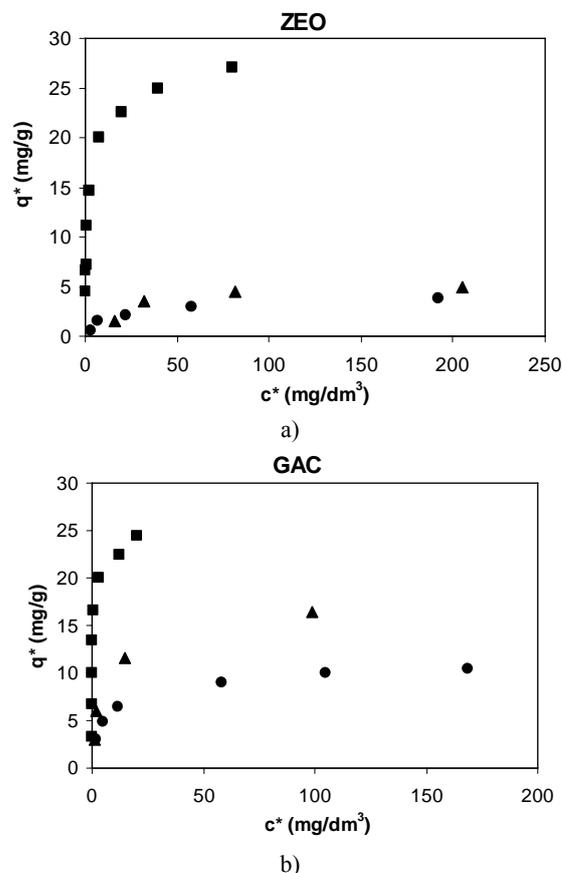


Fig. 3. Equilibrium of adsorption of Zn²⁺, Cd²⁺ and Pb²⁺ at 25°C on (a) natural zeolite (clinoptilolite) and (b) granulated activated carbon. ● (Zn²⁺) ▲ (Cd²⁺) and ■ (Pb²⁺)

Langmuir isotherm

$$q^* = \frac{Q_0 b c^*}{1 + b c^*} \quad (1)$$

linear form

$$\frac{c^*}{q^*} = \frac{1}{Q_0 b} + \frac{c^*}{Q_0} \quad (2)$$

where c (mg/dm³) is the equilibrium concentration, q (mg/g) is the amount adsorbed at equilibrium, b (dm³/mg) is the "affinity" parameter or the Langmuir constant, and Q_0 (mg/g) is the maximum adsorption capacities.

Freundlich isotherm

$$q^* = K_F c^{*(1/n)} \quad (3)$$

linear form

$$\log(q^*) = \log(K_F) + \frac{1}{n} \log(c^*) \quad (4)$$

where c and q have the same definitions presented for the Langmuir isotherm. K_F and n are the constants that can be related to the adsorption capacity and the adsorption intensity, respectively.

The Langmuir and Freundlich isotherm parameters for Zn²⁺, Cd²⁺ and Pb²⁺ adsorption on ZEO and

GAC are presented in Table 3 and Table 4, respectively. The Langmuir isotherm gives better fitting of the experimental adsorption isotherms for all metal ions on both adsorbents. The Zn²⁺, Cd²⁺ and Pb²⁺ maximum (monolayer) adsorption capacities on ZEO are: 3.93 mg/g, 5.18 mg/g and 27.17 mg/g, respectively, and on GAC are: 10.70 mg/g, 17.15 mg/g and 24.27 mg/g, respectively. Oren and Kaya [21], Zamzow and Murphy [22], Alvarez-Ayuso et al, [23] and Athanasiadis and Helmreich [24] obtained similar adsorption capacity of Zn²⁺ on clinoptilolite form of natural zeolite. The Cd²⁺ adsorption capacity obtained in our study is similar to those determined by Sprynskyy et al. [25] and Alvarez-Ayuso et al. [23]. The ZEO adsorption capacity for Pb²⁺ is similar to that obtained by Sprynskyy et al. [25], in the other studies the obtained values are much lower or much higher than 27.17 mg/g. There are several possible reasons for the difference in clinoptilolite metal ion adsorption capacity presented in the literature: the mineralogical composition of natural zeolite from different deposits, the initial metal ion concentration range, pH and mass of adsorbent used in the adsorption equilibrium experiments, etc.

Table 3

Comparison of adsorption capacities in single and binary systems for natural zeolite (ZEO)

	Q_0 (mg/g)	K (dm ³ /mg)	R (-)	Q_0/Q_{0bin} (-)	K_F (mg/g(dm ³ /mg) ^{1/n})	n (-)	R (-)	K_F/K_{F0} (-)
Zn alone	3.926	0.041	0.996	–	0.546	2.78	0.975	–
Zn:Cd (2.2:1)	3.667	0.011	0.828	0.93	0.125	1.74	0.949	0.23
Zn:Cd (1:1)	2.02	0.015	0.974	0.51	0.118	2.06	0.988	0.22
Zn:Cd (0.4:1)	1.109	0.035	0.773	0.28	0.103	2.09	0.817	0.19
Zn:Pb (2:1)	1.201	0.073	0.992	0.31	0.416	5.33	0.898	0.76
Zn:Pb (1:1)	0.881	0.112	0.988	0.22	0.188	3.21	0.687	0.34
Zn:Pb (0.5:1)	0.604	0.091	0.977	0.15	0.227	3.21	0.869	0.42
Cd alone	5.157	0.05	0.997	–	0.962	3.38	0.669	–
Cd:Zn (2.5:1)	4.64	0.007	0.812	0.9	0.128	1.78	0.96	0.13
Cd:Zn (1:1)	3.804	0.009	0.818	0.74	0.149	1.94	0.966	0.15
Cd:Zn (0.45:1)	2.037	0.02	0.634	0.39	0.093	1.67	0.91	0.1
Cd:Pb (2.3:1)	2.601	0.133	0.978	0.5	0.411	2.06	0.897	0.43
Cd:Pb (0.5:1)	2.314	0.1	0.967	0.45	0.248	1.62	0.897	0.26
Cd:Pb (0.14:1)	1.326	0.172	0.906	0.26	0.216	1.81	0.937	0.22
Pb alone	27.174	0.644	0.998	–	11.752	5.56	0.887	–
Pb:Cd (7.4:1)	21.739	0.498	0.937	0.80	5.951	1.68	0.832	0.51
Pb:Cd (2.2:1)	18.622	0.349	0.723	0.69	4.448	1.36	0.857	0.38
Pb:Cd (0.43:1)	12.3	0.246	0.77	0.45	2.127	1.3	0.872	0.18
Pb:Zn (2:1)	26.316	0.125	0.994	0.97	3.38	1.9	0.827	0.29
Pb:Zn (1:1)	24.51	0.168	0.987	0.90	3.718	1.93	0.926	0.32
Pb:Zn (0.5:1)	13.928	0.324	0.944	0.51	3.126	1.96	0.842	0.27

Table 4

Comparison of adsorption capacities in single and binary systems for granulated activated carbon (GAC)

	Q_0 (mg/g)	K (dm ³ /mg)	R (-)	Q_0/Q_{0bin} (-)	K_F (mg/g(dm ³ /mg) ^{1/n})	n (-)	R (-)	K_F/K_{F0} (-)
Zn alone	10.695	0.15	0.999	–	3.047	3.88	0.947	–
Zn: Cd (2.2:1)	6.911	0.4	0.988	0.65	2.437	4.03	0.907	0.8
Zn: Cd (1:1)	6.502	0.169	0.979	0.61	2.055	4.28	0.955	0.67
Zn: Cd (0.4:1)	3.052	0.337	0.987	0.29	1.15	4.35	0.934	0.38
Zn: Pb (2:1)	3.358	0.111	0.989	0.31	1.477	7.02	0.966	0.48
Zn: Pb (1:1)	2.061	0.752	0.998	0.19	1.383	9.65	0.8	0.45
Zn: Pb (0.5:1)	1.208	1.36	0.999	0.11	0.852	10.18	0.93	0.28
Cd alone	17.153	0.203	0.999	–	4.065	3.52	0.861	–
Cd: Zn (2.5:1)	6.09	0.668	0.999	0.36	2.358	4.83	0.903	0.58
Cd: Zn (1:1)	3.324	13.611	0.999	0.19	2.075	9.42	0.777	0.51
Cd: Zn (0.45:1)	2.023	2.85	0.999	0.12	1.112	5.38	0.835	0.27
Cd: Pb (2.3:1)	6.878	1.634	0.997	0.4	1.894	3.43	0.807	0.71
Cd: Pb (0.5:1)	5.066	2.924	0.999	0.3	2.486	4.67	0.537	0.61
Cd: Pb (0.14:1)	1.708	17.268	0.999	0.1	1.029	4.13	0.651	0.25
Pb alone	24.272	3.646	0.997	–	17.964	3	0.803	–
Pb: Cd (7.4:1)	23.148	1.778	0.947	0.95	14.898	1.5	0.846	0.83
Pb: Cd (2.2:1)	22.779	0.876	0.978	0.94	8.25	1.72	0.747	0.46
Pb: Cd (0.43:1)	11.148	4.172	0.873	0.46	11.701	1.5	0.923	0.65
Pb: Zn (2:1)	22.371	0.878	0.992	0.92	7.986	2.08	0.934	0.44
Pb: Zn (1:1)	21.739	1.162	0.995	0.90	8.198	2.35	0.93	0.46
Pb: Zn (0.5:1)	16.464	1.457	0.947	0.68	6.859	2.49	0.996	0.38

The order of metal ion selectivity on both adsorbents is $Pb^{2+} > Cd^{2+} > Zn^{2+}$. The same order of ZEO selectivity was determined by Zamzow and Murphy [22] and Kesraoui-Ouki et al. [26]. In the following section the relation between adsorbents metal ion selectivity series ($Pb^{2+} > Cd^{2+} > Zn^{2+}$) and Zn^{2+} , Cd^{2+} and Pb^{2+} characteristic properties (Table 5) are discussed.

Table 5

Metal ion characteristic parameters

Metal	Ionic radius (pm)	Hydrated radius, (pm)	Electronegativity (Pauling)	Hydratation entalpy (KJ/mol)
Zn^{2+}	88 ^a	430 ^b	1.65 ^a	-2044 ^a
Cd^{2+}	109 ^a	426 ^b	1.69 ^a	-1806 ^a
Pb^{2+}	133 ^a	401 ^b	2.33 ^a	-1480 ^a

^aWulfsberg, 1987; ^bNightingale Jr., 1959

The metal ions with larger ionic radius have lower charge density and lower electrostatic attraction that limits the interaction of the metal ions with the adsorption sites. Thus metals with higher electronegativity adsorb more readily. The obtained selectivity series is in agreement with the metal ions electronegativity, namely $Pb^{2+}(2.33) > Cd^{2+}(1.69) > Zn^{2+}(1.65)$. Also, with an increase of the ionic size, the absolute value of enthalpy of hydration decreases. The enthalpy of hydration of an ion is the amount of energy released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution. According to the values of enthalpy of hydration (Table 3), the Pb^{2+}_{aq} ions will have a greater accessibility to the adsorbent surface, followed by Cd^{2+}_{aq} and Zn^{2+}_{aq} , which would lead to the following order $Pb^{2+} > Cd^{2+} > Zn^{2+}$ in the extent to the adsorption process.

Binary adsorption equilibrium

The competitive adsorption equilibrium of three binary mixtures, Cd^{2+}/Zn^{2+} , Zn^{2+}/Pb^{2+} and Pb^{2+}/Cd^{2+} were studied at 25°C. For each binary system three different ratios of the initial metal ion concentration were used in order to determine the effect of the second metal ions on the adsorption of Zn^{2+} , Cd^{2+} and Pb^{2+} on ZEO and GAC. The following metal ion initial concentration ratios were used: $Cd^{2+}:Zn^{2+} = 2.5:1, 1:1, 0.45:1$; $Zn^{2+}:Pb^{2+} = 2:1, 1:1, 0.5:1$ and $Pb^{2+}:Cd^{2+} = 7.4:1, 2.2:1, 0.43:1$. The total metal ion concentration in all studied binary systems was between 10 and 500 mg/l, and the pH of the metal ions aqueous solutions was not adjusted.

The binary adsorption isotherms were fitted with the Langmuir (Eq. 2) and Freundlich isotherm (Eq. 4). The Langmuir and Freundlich parameters for binary adsorption isotherms on ZEO and GAC are presented in Tables 3 and 4, respectively. Once again, the Langmuir isotherm fits better the experimentally obtained binary adsorption isotherms. The calculated Langmuir adsorption isotherms and experimental data of Zn^{2+} , Cd^{2+} and Pb^{2+} single and binary adsorption on ZEO and GAC are presented in Figures 4, 5 and 6, respectively. It was observed that the Pb^{2+} adsorption on both natural zeolite and activated granulated carbon (Fig. 6) is less affected by the presence of second metal ion (Zn^{2+} or Cd^{2+}).

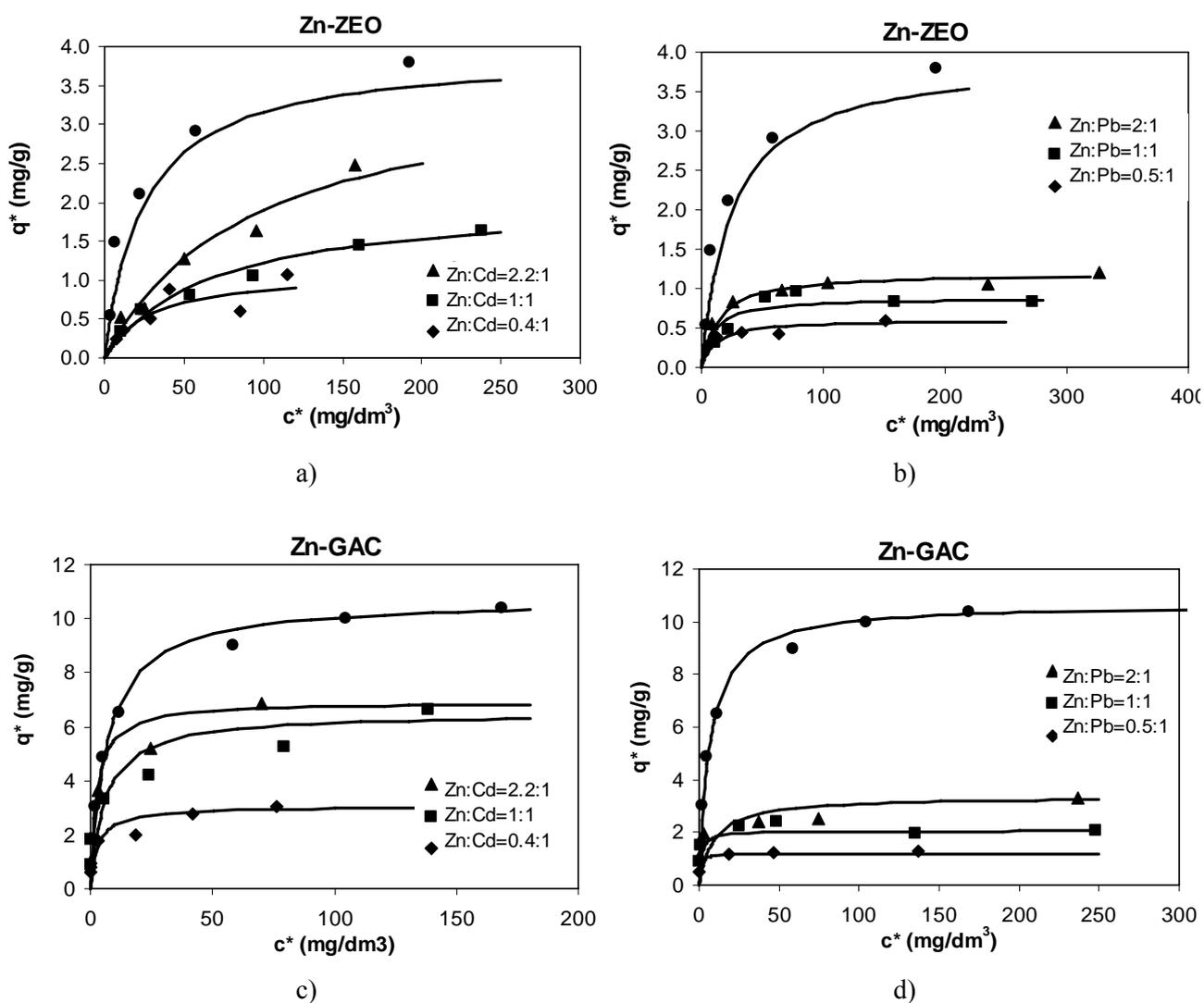


Fig. 4. Zn^{2+} single and binary equilibrium isotherms at 25°C. a) Zn^{2+}/Cd^{2+} – ZEO; b) Zn^{2+}/Pb^{2+} – ZEO; c) Zn^{2+}/Cd^{2+} – GAC; d) Zn^{2+}/Pb^{2+} – GAC. ● (Zn^{2+}) – single adsorption isotherm (the solid lines represent the fitting of data by Langmuir isotherms)

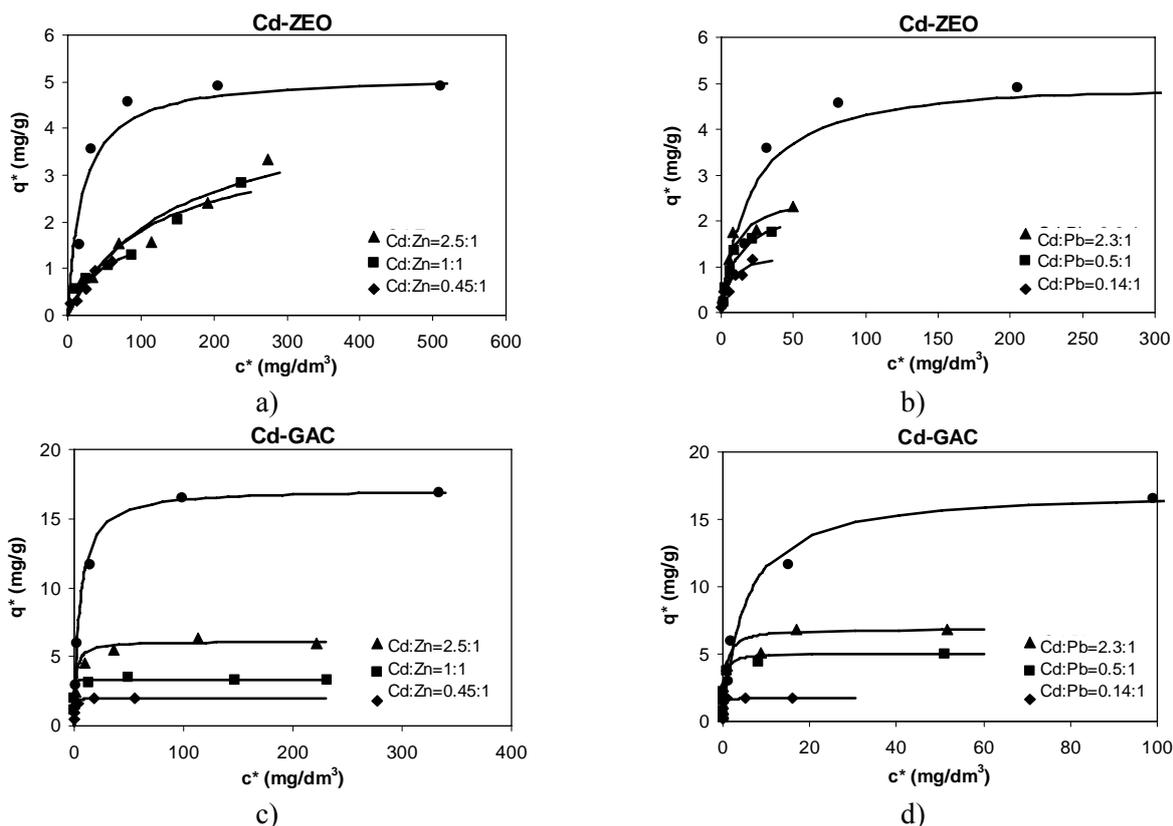


Fig. 5. Cd^{2+} single and binary equilibrium isotherms at 25°C . a) $\text{Cd}^{2+}/\text{Zn}^{2+}$ – ZEO; b) $\text{Cd}^{2+}/\text{Pb}^{2+}$ – ZEO; c) $\text{Cd}^{2+}/\text{Zn}^{2+}$ – GAC; d) $\text{Zn}^{2+}/\text{Pb}^{2+}$ – GAC. ● (Cd^{2+}) – single adsorption isotherm (the solid lines represent the fitting of data by Langmuir isotherms)

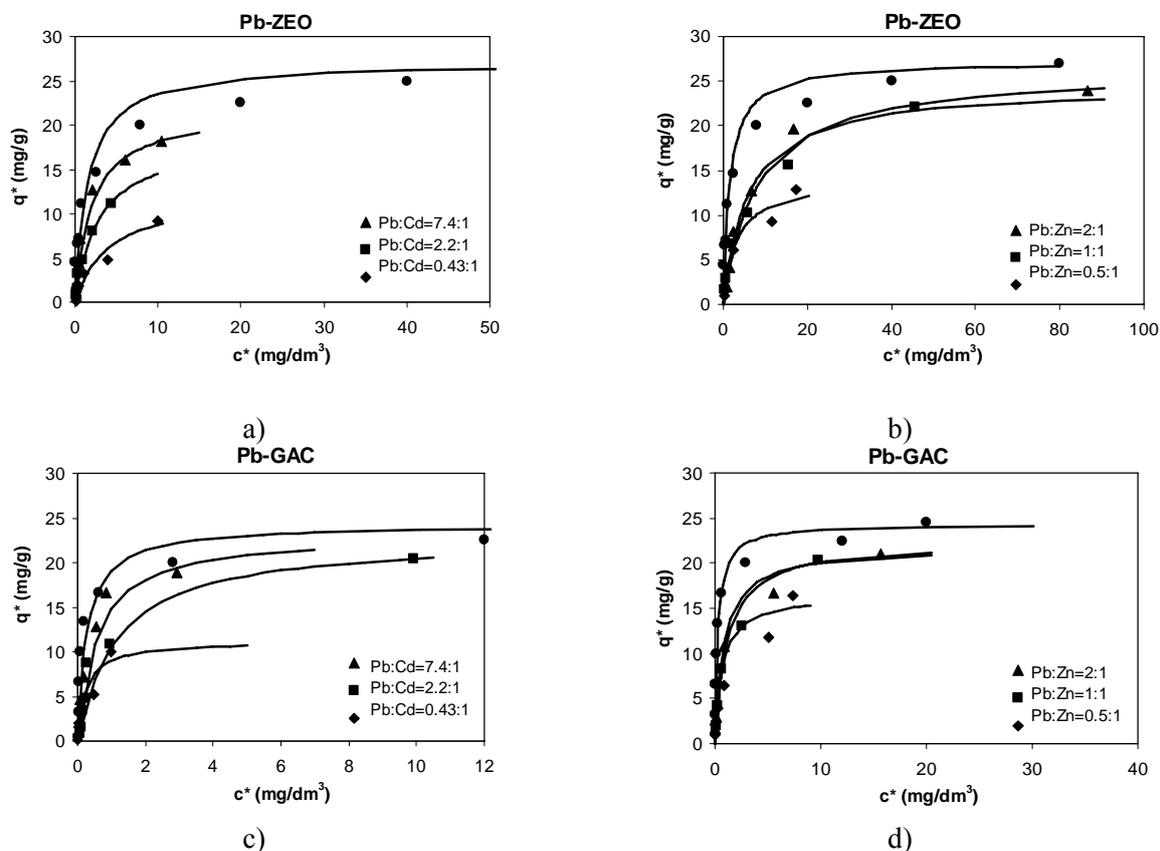


Fig. 6. Pb^{2+} single and binary equilibrium isotherms at 25°C . a) $\text{Pb}^{2+}/\text{Cd}^{2+}$ – ZEO; b) $\text{Pb}^{2+}/\text{Zn}^{2+}$ – ZEO; c) $\text{Pb}^{2+}/\text{Cd}^{2+}$ – GAC; d) $\text{Pb}^{2+}/\text{Zn}^{2+}$ – GAC. ● (Pb^{2+}) – single adsorption isotherm (the solid lines represent the fitting of data by Langmuir isotherms)

Adsorption in multi-component systems is complicated because of the fact that solute–surface interactions are involved. The second metal ion present in the water solution competes with the single metal (Zn²⁺, Cd²⁺ and Pb²⁺) ions adsorption. The influence of the ionic interaction of the second metal ion present in the binary metal ion mixture can also be evaluated by the ratio of the sorption capacity for the particular metal ion in the presence and absence of the second metal ion in the solution:

$$\frac{Q_{0bin}}{Q_0}$$

where Q_{0bin} is the metal ion adsorption capacity in presence of second metal ion in the aqueous solution, and Q_0 is the sorption capacity for the same metal ion when it is present alone in the aqueous solution. They are three possible cases of metal ions interaction, namely:

$$\frac{Q_{0bin}}{Q_0} > 1$$

which indicates that the presence of the second metal ion in the solution promotes the sorption, i.e. increases the metal ion adsorption capacity.

When

$$\frac{Q_{0bin}}{Q_0} = 1$$

there is no interaction of the metal ions during the adsorption process.

And the last case:

$$\frac{Q_{0bin}}{Q_0} < 1$$

which suggest that the metal ions interact during the adsorption and compete for the same adsorption sites. In this case the sorption is suppressed by the presence of the second metal ion, leading to lower adsorption capacity as compared to the case when the particular ion was the only ion present in the aqueous solution.

The values of $\frac{Q_{0bin}}{Q_0}$ for Zn²⁺, Cd²⁺ and Pb²⁺

on natural zeolite (ZEO) and granulated activated carbon for all studied binary mixtures are presented in Table 3 and Table 4, respectively. The

$\frac{Q_{0bin}}{Q_0}$ are higher than 1 for all binary adsorption isotherms obtained on both adsorbents. The

$\frac{Q_{0bin}}{Q_0}$ should be used only as an indicator of the

nature of the metal ion interaction during their binary (competitive) adsorption, since some of the single and binary isotherms do not cover the same concentration range, as is the case of the Cd²⁺/Zn²⁺ and Cd²⁺/Pb²⁺ adsorption on natural zeolite (Figs. 5a and 5b).

The influence of the second metal ion in the mixtures on the single metal ion adsorption capacity increases as its concentration in the binary mixtures increases. For example, in the case of the system Zn²⁺/Pb²⁺ – ZEO, the Zn²⁺ adsorption capacity obtained for the single component (Zn²⁺ only) decreases as the quantity of the Pb²⁺ in the initial binary mixture increases (Table 3). Namely, in the case when the zinc concentration in the mixture is two times higher than the lead concentration (Zn²⁺: Pb²⁺ = 2:1) the $\frac{Q_{0bin}}{Q_0}$ is 0.31 and drops

to 0.15 when the zinc concentration is two times lower than the lead concentration in the mixture (Zn²⁺: Pb²⁺ = 0.5:1).

Generally, it can be also concluded that the single component metal ion adsorption capacity is more affected by the presence of metal ions with higher single component adsorption capacity than by the metal ions with lower single component adsorption capacity. Namely, the Zn²⁺ (or Cd²⁺) single component adsorption capacity is much more affected by the presence of Pb²⁺ than by the presence of Cd²⁺ (or Zn²⁺) in the binary solution.

CONCLUSIONS

The equilibrium of adsorption of Zn²⁺, Cd²⁺ and Pb²⁺ on regional low-cost natural clinoptilolite containing zeolite tuff (ZEO) and commercial granulated activated carbon (GAC) was studied for single and binary systems (Cd²⁺/Zn²⁺, Zn²⁺/Pb²⁺ and Pb²⁺/Cd²⁺). The adsorption equilibrium was determined in batch mode at 25°C, without adjustment of metal ion water solution pH. Langmuir and Freundlich isotherm were used to interpret the adsorption data of the investigated single and binary systems. The following general conclusions may be deduced from this study:

- The Langmuir isotherm gives better presentation of the single and binary metal ion experimentally determined adsorption isotherms.

- The GAC has around three time higher adsorption capacity for Cd^{2+} and Zn^{2+} , then ZEO; and almost the same adsorption capacity for Pb^{2+} as ZEO.
- The same metal ion selectivity series, $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$, was obtained for both adsorbents. The metal ion selectivity series is in agreement with the metals ionic radius, electronegativity, and hydration enthalpy.
- The binary adsorption isotherms show competitive nature of the adsorption process. The adsorption capacity of natural zeolite and granulated activated carbon for given metal ion obtained from single adsorption isotherms decrease when the second metal ion is present in the solution.
- The adsorption of a metal ions in binary systems is affected by the concentration of the second ion present in the solution.
- The lead, as the most selectively adsorbed component, is less affected by the presence of zinc and cadmium in the binary solutions.

Acknowledgements: Mirjana Minčeva gratefully acknowledges the financial support of NATO Security through Science Programme – Reintegration grant (EAP.RIG.981814).

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