

Zeolite Materials Obtained from Fly Ash Used for Removal of Heavy Metals and dye from Complex Wastewaters

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ABSTRACT

Annually huge amounts of fly ash are produced, instead of land filling this waste can be reutilized for obtaining new materials such as zeolites which can be further used in adsorption processes. The fly ash, collected from Power Plant Craiova (Romania) was used for obtaining the zeolites materials with good adsorption capacity for heavy metals and dyes from wastewater.

Fly ashes hydrothermally treated were used as a low cost adsorbents for the removal of Cd²⁺, Cu²⁺ cations and Methylene blue (MB) from synthetic wastewaters containing one, two and three pollutants. The new zeolite materials (ZCRns and ZCRs20) obtained from fly ash Craiova (FACR) has an increased specific surface area which led to good efficiencies. During the adsorption process the parameters: contact time and optimum amount of substrate were optimized for obtaining a maximum efficiency. The adsorption isotherms and kinetics were studied. The obtained results were fitted using Langmuir and Freundlich isotherms. Pseudo-first order, pseudo-second order and interparticle diffusion were employed for analyzing the kinetic data. The new material was characterized in terms of crystallinity (XRD) and surface properties: morphology.

The composite substrate proved good efficiencies for removal of heavy metals cations and methylene blue from the synthetic pollutant systems in adsorption. As the results show, MB removal runs with the highest efficiency in adsorption (93.33%) while heavy metals removal has almost similar values in adsorption processes.

1. INTRODUCTION

The growing need for water in industries has led to many problems like water pollution caused by the discharging of effluents loaded with heavy metals, dyes, surfactants, wax, etc. which poses environmental and health problems. Heavy metals like cadmium,

copper, from these effluents led to groundwater and soil contamination, they are not biodegradable and tend to accumulate in living organisms and their toxicity, even at low concentrations leads to several diseases and disorders [1]. The main resource of heavy metals release in the environment is sewage from different industries such as mining, electroplating, cadmium-nickel batteries, plastic manufacturing [2] melting and casting industries [3] pesticides, petroleum refining processes, photography [4] printed circuit board manufacturing [5]. Cadmium affects mainly the kidneys, the lungs and the liver and it can also lead to bones demineralization [6]. Copper affects in the beginning the liver by disrupting its ability to detoxify, elevated copper level in the body leads to other problems for the nervous, reproductive system. Some of the copper salts are very toxic, like blue vitriol and by taken them in large amounts they cause severe vomiting, pain in the abdomen, severe headaches, diarrhea and paralysis. Nickel mainly affects the skin causing dermatitis; it also causes asthma, conjunctivitis [7]. The maximum acceptable concentration in drinking water declared by World Health Organization (WHO) [8] for these heavy metals is: 0.003 mg/L for Cd^{2+} , 2 mg/L for Cu^{2+} .

Several methods used for the removal of heavy metals and dyes from wastewater are: chemical precipitation [8], coagulation– flocculation, photocatalysis, ion exchange [9,10], nanofiltration membrane technology [11] and adsorption [12]. From all of these, the adsorption is one of the most economical regarding the fact that it uses a variety of adsorbents obtained from the wastes has simple equipment and can be easily operated with it [13]. The most known adsorbent is activated carbon, but it has the production cost and regeneration, because of this it is necessary the development of inexpensive materials.

Zeolites have different applications such as adsorbents [14] catalysts, molecular sieve and can be also used for ion exchange [15]. The synthesis of zeolites from fly ash by some conventional methods include hydrothermal synthesis, microwave heating [16] dry or molten-salt conversion, fusion method [17] and quantum methods [18]. Many researchers have tested the removal efficiency of heavy metals like Cd^{2+} , Pb^{2+} [19], Cu^{2+} [20] Co^{2+} , Cr^{3+} , Ni^{2+} , Zn^{2+} [9] onto zeolites obtained from fly ash.

This paper presents the synthesis, characterization of two zeolites ZCRns and ZCRs20 obtained from fly ash by hydrothermal method, and the results in removal of Cd^{2+} , Cu^{2+} cations and MB from mono-, bi-, and three-component systems by adsorption.

2. EXPERIMENTS

2.1. SUBSTRATE PREPARATION

The material used for zeolites synthesis in this case was fly ash collected from Craiova Central Heat Power Plant, Romania. The composition of ashes depend on the type of fuel, combustion technology applied (type of furnace, the temperature developed and of cooling depends).

The major constituents of the fly ash are oxides: SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O presented in Table 1.

Table 1 Fly ash composition

Major oxides [wt%]							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	% *SiAlFe
46.13	21.39	10.85	10.65	5.24	0.5-2.0	0.2-0.6	78.37

* SiAlFe: % total: (SiO₂ + Al₂O₃ + Fe₂O₃)

The fly ash collected (raw FACR) from the electro-filters of the plant is of F type because the sum of the major compounds, oxides SiO₂ + Al₂O₃ + Fe₂O₃ is over 75% and it doesn't aggregate in water. From this raw fly ash were obtained two types of zeolite materials with washed fly ash and unwashed:

1) A part of the fly ash was washed with ultra pure water by mechanical stirring for 48 h at room temperature (20-22°C). After stirring the washed sample was filtrated, from the filtrated solution were obtained the values of pH (11), conductivity (390µS/cm) and TSD (802mg/L). After filtration the ash was dried in the oven at 105-115°C, the dried substrate was sieved and the 20 µm fraction was selected for further experiments (FAw). For obtaining zeolite materials the washed fly ash was mixed with NaOH solution in autoclave for 5h at 150°C. After running time the material was washed with ultra pure water till constant pH, filtrated and dried over night. This new material (ZCRs20) was used in adsorption experiments.

2) The same amount of raw FACR unmodified by washing was hydrothermally treated with NaOH in the same conditions. This zeolite material was notated ZCRns. The substrates (ZCRns and ZCRs 20) were further used in adsorption experiments for removing heavy metals from synthetic wastewater loaded with: a) Cd²⁺; b) Cd²⁺+Cu²⁺; c) MB+Cd²⁺+Cu²⁺.

2.2. CHARACTERIZATION OF THE SUBSTRATES

The ZCRns and ZCRs20 crystalline structures were evaluated by X-ray diffraction (XRD). By using AFM (Ntegra Spectra, NT-MDT model BL222RNTE) the morphology studies (roughness and macro-pore size distribution) were done. Scanning was conducted on three or more different places with a certain area of 5 µm x 5 µm for each position, chosen randomly at a scanning grate of 1Hz. By using scanning electron microscopy (S-3400N-Hitachi) further surface investigations were done at an accelerating voltage of 20 kV. Surface compositions of zeolites were measured before and after adsorption using energy dispersive X-ray spectroscopy (EDX Thermo Scientific Ultra Dry). By using porosity analysis and BET surface (Autosorb-IQ-MP, Quantachrome Instruments), the characterization of the surface was completed.

2.3. ADSORPTION EXPERIMENTS

The pollutant systems were synthetically prepared using bidistilled water and CdCl₂·2.5 H₂O (Scharlau Chemie S.A., c<98%), CuCl₂·2H₂O (Scharlau Chemie S.A., c<98%) and Metylen Blue (MB) (C₁₆H₁₈N₃S) (Fluka AG, reagent grade). The experiments were

done using heavy metals solutions in concentration range of $C_{Cd^{2+}} = 0, \dots, 560$ mg/L, $C_{Cu^{2+}} = 0, \dots, 330$ mg/L and $C_{MB} = 0,03125$ mMol/L.

For deciding which of the two zeolites materials is more efficient in removing heavy metals and MB from wastewater they were tested in following adsorption experiments:

Three series of experimental test of adsorption were done:

Adsorption on ZCRs20/ ZCRns substrate in solution containing one, two and three pollutants:

- Cd^{2+} / Cu^{2+} from mono-cationic system, under mechanical stirring;
- Cd^{2+} and Cu^{2+} from bi-cationic system, under mechanical stirring;
- MB+ Cd^{2+} + Cu^{2+} from system with three pollutants, under mechanical stirring.

During the batch experiments the kinetic and thermodynamic adsorption parameters of mono-cationic, di-cationic and dye system were evaluated in each experiment. For this 0.1 g of ZCRns substrate or ZCRs20 respectively were stirred (200 rpm) at room temperature (20 - 23°C) with 50 mL solution at initial concentrations ($C_{iCd^{2+}} = 560$ mg/L, $C_{iCu^{2+}} = 330$ mg/L and $C_{iMB} = 0.03125$ mMol/L). For the kinetic studies aliquots were taken each at 10, 15, 30, 45, 60, 90, 120, 150, 180 min., and the substrate was removed by filtration. The supernatant was analyzed using AAS (Analytic Jena, Zeenit 700), at $\lambda_{Cd} = 228.8$ nm, $\lambda_{Cu} = 324.75$ nm, while the dye was analyzed by UV-VIS spectrometry (Perkin Elmer Lambda 25).

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF THE SUBSTRATES

The composition of silicon-aluminous of the fly ash is confirmed by XRD spectra, Fig.1. The major crystalline components of raw fly ash are: αSiO_2 (quartz), hematite (Fe_2O_3), identified by the sharp peaks in the range of $2\theta = 26^\circ$.

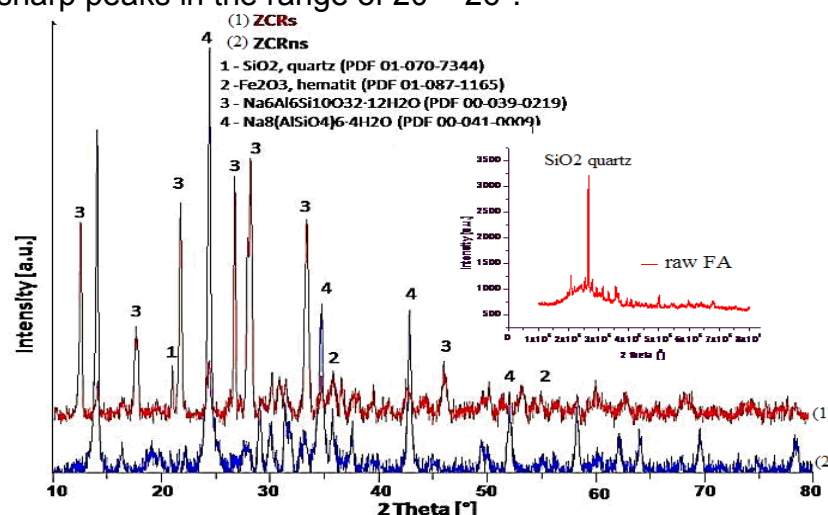


Fig. 1 XRD data of (1) ZCRs20 and (2) ZCRns

The diffractogram (Fig.1) data show that SiO_2 phases of raw FACR and washed fly ash are absent in the new materials (ZCRns and ZCRs 20), while the new crystalline phases are present in zeolites materials: phillipsite ($Na_6Al_6Si_{10}O_{32} \cdot 12H_2O$), sodium aluminum

silicate hydrate $\text{Na}_8(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$, $\text{Na}_8(\text{AlSiO}_4)_6 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (sodium aluminum hydroxide hydrate) and other phases of the aluminosilicates, typical for zeolite materials. The quartz syn, hematite and maghenite are in small proportion in new zeolites while the area picks of new alumino-silicates are higher after treatment. The hydrothermal process of rawFACR or washed fly ash further promotes the surface interactions, including dissolution, re-crystallization processes.

The spherical particles were gradually disappeared and prismatic shape of zeolite occurred and crystalline phases increased in both substrates from 38.5% to 58.5% for ZCRs20 and 41.9% for ZCRns.

The values for both materials ZCRs20 and ZCRns show high conversion of SiO_2 at crystalline zeolite (NaP1) by hydrothermal treatment. The content of quartz and mullite were found to be mainly responsible for hinder formation of zeolite and their activity [21]. The composition of crystalline phases, crystalline degree, and morphological changes are presented in table 2.

Table 2 The characteristics of the raw fly ashes and of the zeolite material

Sample	Crystalline degree		Morphology modifications			
	Composition of crystalline phases	Crystalline degree [%]	R	BETsurfac area [m ² /g]	Micropore volume [cm ³ /g]	Pores diameter [nm]
rawFA	Quartz, SiO_2 , (31.6%) hexagonal Graphite, hexagonal (4.83%) Na/K Aluminosilicate/hydrate (57.45%) Hematite, Fe_2O_3 , romboedric (5.65%), Mn_3O_4 , tetragonal (0.46%)	38.5	-	4.09	0.004	27.2
ZCRs20	Quartz, SiO_2 , (2.56%) hexagonal Na/K Aluminosilicate /hydrate (92.74%) Hematite, Fe_2O_3 , romboedric (4.7%)	49.8	0.08	58.51	0.005	21.36
ZCRns	Quartz, SiO_2 , hexagonal (1.73%) Na/K Aluminosilicate /hydrate (94.45%) Hematite, Fe_2O_3 , romboedric (3.4%) Mn_3O_4 , tetragonal (0.48%)	41.9	0.05	51.68	0.004	19.73

Other information related to the morphology and characteristics of the surface were obtained from the AFM and SEM micrographs (Fig. 2 and Fig. 4).

By washing and hydrothermal treatment, the roughness shows a strong decrease of surface from 74.1 nm to 17.2 nm. The roughness can give information about knowing

the level of investigation (the millimetric scale usually permits one to distinguish the main surface treatments) [22].

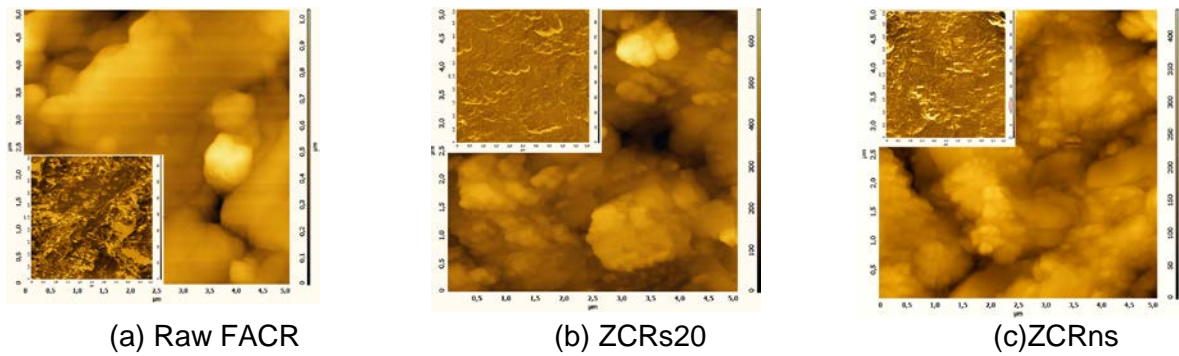


Fig.2 The AFM topography and phase distribution

The chemical report (Si/Al) and structural changes are mirrored in morphology modifications, Fig. 2 (a,b,c) resulting large differences in the substrates' affinity for heavy metals. On phase's distributions, it can be seen more agglomerates in the new material adsorbent, so more macro-pores and meso-pores are ready to lodge the cations of heavy metals. These AFM images were used to characterize the surface morphology: the uniformity, grain size and pore size distribution [23] of the samples Fig.3.

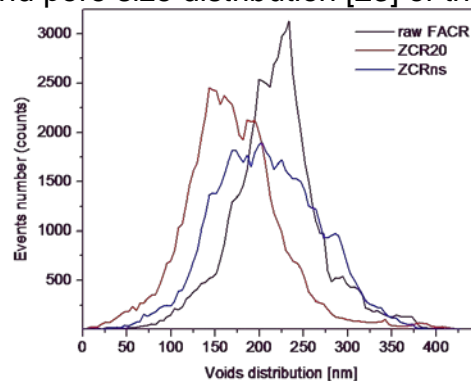


Fig. 3. The interparticle voids distribution

The raw FACR, ZCRs20 and ZCRns have a rough surface with larger pores/voids heterogeneously distributed, confirmed by the pores/voids distribution curves with two or three maxima.

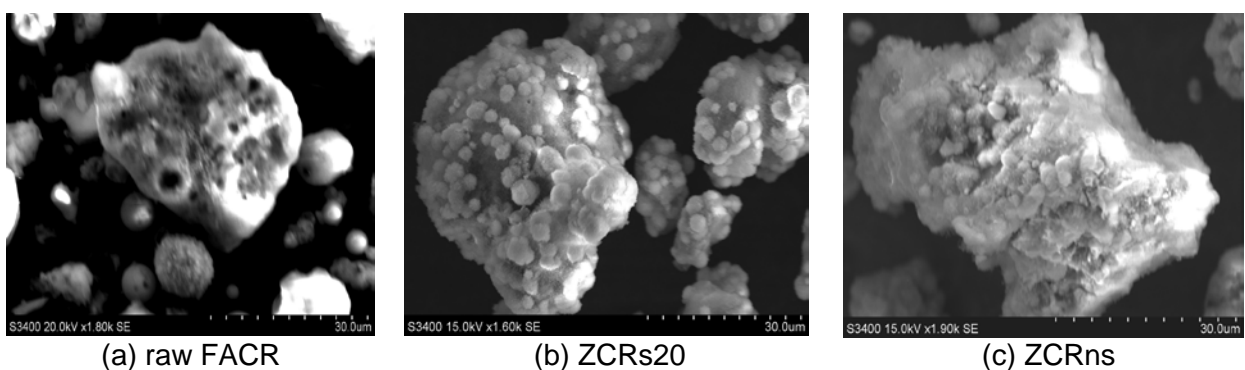


Fig. 4. Scanning Electron Microscopic images (a) rawFACR; (b) ZCRs20; (c) ZCRns

The SEM images Fig. 4 show significant modifications during the fly ashes processing. Most raw FACR particles are spherical with particles size from 7.94 μm to 44.1 μm while in zeolite materials large agglomerates (18.8 μm) are formed from mostly spherical and minority prismatic particles (3.47 μm average) Fig.4. Surface compositions (Si, Al, Fe, Mn, Ti) of raw fly ash and of ZCRs20, ZCRns zeolites were evaluated using energy dispersive X-ray spectroscopy (EDX), Table 3.

Table 3. Surface compositions of raw fly ash and ZCRs20, ZCRns zeolites

Sample	Si [%]	Al [%]	Fe [%]	Mn [%]	Ti [%]
Raw FACR	21.36	6.72	5.17	0.1	0.18
ZCRs20	14.92	10.87	1.16	0.00	0.11
ZCRns	14.6	13.71	0.8	0.03	0.04

The polar and disperse contributions to the surface energy of ZCRs20 and ZCRns were calculated according to the model developed by Owens, Wendt, Robel and Kaelble and are presented in Table 4.

Table 4. Surface energy data for the substrates

Substrate	Surface Energy [mN/m]	Disperse contribution [mN/m]	Polar contribution [mN/m]
ZCRs20	21.58	8.51	13.07
ZCRns	80.15	0.32	79.83

The data show a large polar component, recommending the zeolites materials as a good adsorption substrate. The hydrothermal processes developed in autoclave with NaOH solution include changes in various chemical and physical properties such as surface structure (roughness), crystal structure and cation exchange capacity.

The mechanism of zeolite crystallization and the role of alkali solution on the synthesis reaction were considered. Three steps exist in alkali hydrothermal reaction of zeolite NaP1 synthesis: (1) the dissolution of Si^{4+} and Al^{3+} in coal fly ash, (2) the condensation of silicate and aluminate ions in alkali solution to make aluminosilicate gel, (3) the crystallization of aluminosilicate gel to make zeolite crystal. The OH^- in alkali solution remarkably contributes to the dissolution step of Si^{4+} and Al^{3+} in coal fly ash, while Na^+ in alkali solution makes a contribution to the crystallization step of zeolite.

3.2. ADSORPTION OF HEAVY METALS ON ZCRs20 and ZCRns SUBSTRATES

The zeolite materials obtained from fly ash were tested for heavy metals removal. The experiments were done on synthetic solutions containing one cation Cd^{2+} or Cu^{2+} , two cations $\text{Cd}^{2+} + \text{Cu}^{2+}$ and two cations with Methylene Blue ($\text{MB} + \text{Cd}^{2+} + \text{Cu}^{2+}$). The parameters of the process such as contact time, substrate's dosage and initial cation's concentration were optimized considering the maximum efficiency of heavy metals cations, $[\text{I}]$, on ZCRns and ZCRs 20, which was calculated using the following eq. (2):

$$\eta = \frac{(c_{cation/MB}^i - c_{cation/MB}^t) \cdot 100}{c_{cation/MB}^i} \quad (2)$$

- where c^i and c^t are the initial and at a given time cations concentrations (mg/L). The contact time effect on heavy metals adsorption efficiency is presented in Fig. 6 ...8b. The adsorption of one heavy metal cation is efficient using zeolite materials even at 30 min. contact time for Cu^{2+} cation. In the same conditions cooper and cadmium cations are adsorbed better on ZCR20 with surface area larger than ZCRns. In all cases, the working pH was the natural value of the solutions, pH = 6.9.

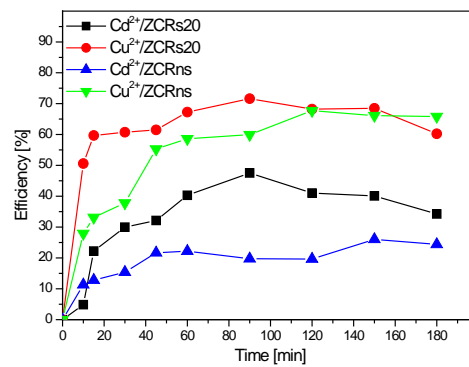


Fig.6. Adsorption efficiency vs. contact time in solutions containing one heavy metal

- b) The system containing two heavy metals cadmium and cooper was chosen because the most toxic heavy metal is cadmium and it accumulates in the human body.

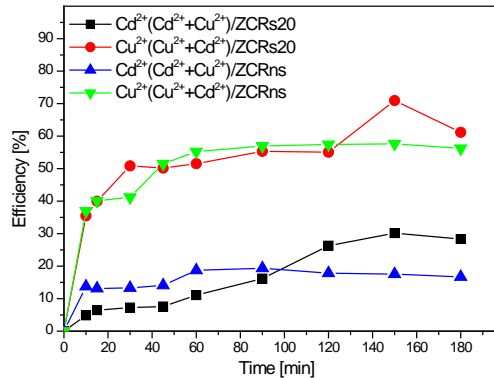
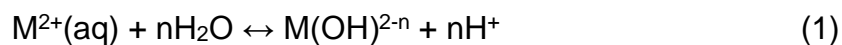


Fig.7. Adsorption efficiency vs. contact time in solutions with two heavy metals

The same numbers of active sites are occupied simultaneously by different cations so there is a competition between Cu^{2+} and Cd^{2+} cations hydrated with 4...6 water molecules. In aqueous solutions hydrated heavy metal ions can be subject of hydrolysis, according to the reaction (1), written for divalent metals:



Methylen Blue has different adsorption efficiencies on the same amount of adsorbents in present of one or two heavy metals Fig. 8.

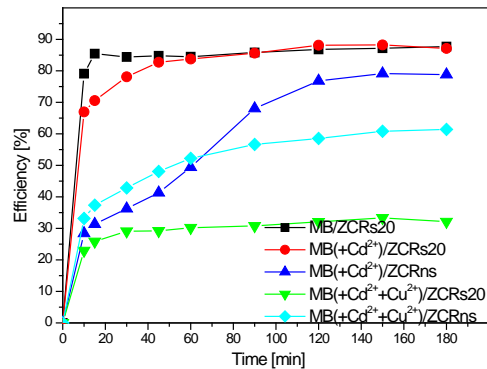


Fig. 8. Adsorption efficiency vs. contact time in three -pollutants system

The planar structure of Methyl blue with two aromatic rings can act as an electron donor in the interaction with Cd^{2+} cation, specific. The alkali form of MB may act as a supplementary complexing agent, which adsorbed heavy metals by terminal group $-SO_3^-$. By increasing the substrate mass the adsorption efficiency is better because on the substrate exist more active sites available for adsorption. A sharp increase in the percentage uptake of copper cations can be seen until a maximum value (97.79 - 99.51%). In adsorption process in all cases the cations prefer substrate ZCRs20 with the largest BET surface. The affinity of new zeolites obtained from this fly ash for heavy metals depends on many factors for example:

- a) the properties of substrate (composition in aluminosilicates (Si/Al), surface area, the electrical charge of surface, types of exchangeable ions) [24];
- b) the properties of cations (hydrated ionic radius, hydrolysis constant, electronegativity value of the metal);
- c) the properties of wastewater (solutions) (pH, pollutant concentration and presence of other compounds (dyes, surfactants etc.)

Adsorption is a surface process, as consequence, not only the surface morphology and crystallinity, but also the surface charge is important. The surface charge depends on the pH solution and it must be discussed based on the value(s) of the point of zero charge (PZC), Fig.9.

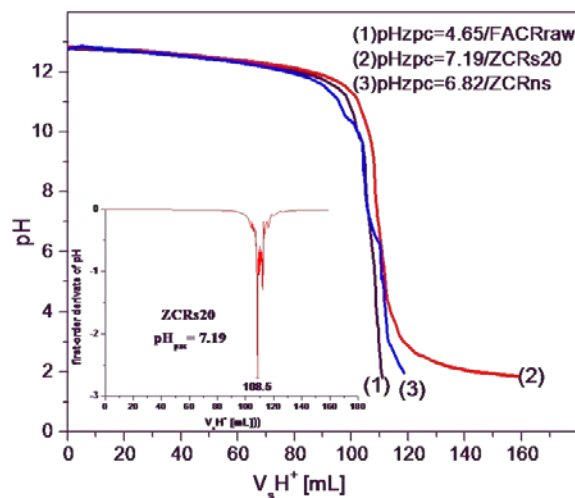


Fig.9. The PZC determination is represented

According to the Pourbaix diagram, the copper ions can exist in aqueous solutions as $(\text{CuOH})^+$ at $\text{pH} > 6.8$ and as neutral hydroxide as precipitate, at $\text{pH} > 7.5$ [34]. Thus, to avoid copper precipitation the experiments should run in weak acidic media or close to the neutral pH. The channels of the lattice and they can replace the exchangeable Na^+ , K^+ , Ca^{2+} cations. As evidenced in the previous step, on the surface of zeolite materials new types of active centres were developed ($\equiv \text{SiO}^-$), ($\equiv \text{SiONa}$) and ($\equiv \text{AlO}^-$) complex structures were formed with metal cations according to reactions (2, 3). During the adsorption process the heavy metal cations have to move through the pores.



Heavy metals adsorption onto zeolites is an ion-exchange. Different stages are observed in the ion-exchange adsorption of the heavy metals: fast adsorption on the zeolite microcrystal surfaces during the first 30 min; then the inversion stage has a short-time prevalence of the desorption process connected with the diffusion flow from the zeolite microcrystal's interior and is the moderate adsorption in the microcrystal's interior [26].

3.3. THE ADSORPTION KINETIC

The metal uptake q_e (mg/g) was evaluated for the kinetic studies by using the initial and current, t , heavy metal concentrations (c_{cation}^i and c_{cation}^t) in a given solution volume ($V = 50$ mL) for a given amount of ZCRns, respectively ZCRs 20 substrate ($m_s = 0.1$ g) as given in eq. (3):

$$q_e = \frac{(c_{\text{cation}/\text{MB}}^i - c_{\text{cation}/\text{MB}}^t) \cdot V}{m_s} \quad (3)$$

By using the following equations (4) and (5) the kinetics of the heavy metals adsorption were modeled:

- The pseudo first-order equation Lagergren 1989 [27]:

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303} t \quad (4)$$

where K_L is the Lagergren constant, q_e is the equilibrium uptake value and q_t the current metal uptake.

- The pseudo-second order kinetic equation Ho Y.S, McKay 1999 [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 is rate constant.

The interparticle diffusion is another possible kinetic model that can be applied in adsorption processes eq. (6) [29].

$$q = k_{id} t^{1/2} + C \quad (6)$$

where k_{id} is the rate constant and C is the intercept at the ordinate. If the plot of q_t vs. $t^{1/2}$, according to eq. 6, gives a straight line, then intraparticle diffusion was involved in the adsorption process; in addition, if the straight line passes through the origin, then

the intra-particle diffusion was the rate-limiting step [30]. Generally, the intercept, C, gives an idea about boundary layer thickness: the larger value of intercept, the greater the boundary layer diffusion effect is [31]. The kinetic parameters are presented in table 6

Table 6 Kinetic parameters of heavy metals adsorption

Substrate	Pseudo first-order kinetics		Pseudo second-order kinetics			Interparticle diffusion		
	K_L [min ⁻¹]	R^2	k_2 [g/mg·mi]	q_e [mg/]	R^2	K_{id} (mg/gmin ^{1/2})	C	R^2
Cd²⁺								
ZCRns	-	0.702	0.093	54.945	0.988	-	-	0.73
ZCRs20	-	0.66	0.065	93.458	0.919	9.906	17.70	0.824
Cu²⁺								
ZCRns	0.005	0.968	0.151	153.846	0.969	6.539	53.015	0.902
ZCRs20	0.022	0.962	0.367	95.593	0.956	4.708	17.737	0.977
Cd²⁺(Cd²⁺+Cu²⁺)								
ZCRns	-	0.382	0.025	40.650	0.937	-	-	0.313
ZCRs20	0.0037	0.893	0.176	23.148	0.966	2.553	6.239	0.883
Cu²⁺(Cd²⁺+Cu²⁺)								
ZCRns	0.015	0.827	0.095	98.039	0.982	-	-	0.658
ZCRs20	0.009	0.815	0.080	78.740	0.999	0.406	3.888	0.852
Cd²⁺(Cd²⁺+Cu²⁺+MB)								
ZCRns	-	0.433	0.01	26.738	0.932	-	-	0.651
ZCRs20	-	0.542	0.096	30.769	0.948	2.7209	55.17	0.845
Cu²⁺(Cd²⁺+Cu²⁺+MB)								
ZCRns	0.01	0.829	0.051	80.65	0.999	1.824	58.83	0.866
ZCRs20	0.023	0.953	0.08	108.69	0.999	5.992	47.01	0.903

The pseudo-second order kinetics fitted the adsorption kinetics much better than the pseudo-first-order model for both adsorbents and supports the chemisorption process on these zeolite materials. Like in most other investigations, the adsorption capacity was the highest for Cu²⁺ for both zeolites. There are some cases where correlation coefficient R^2 is not close to 1, which indicates departure from the pseudo first-order kinetics or intraparticle diffusion model. They are mainly in the case of cadmium, because the affinities of the adsorbents for nickel and cadmium are the smallest. On both zeolite materials the order is: Cu²⁺ > Cd²⁺ > MB which follows the order size of the hydrated ions [nm]: 0.29, 0.43 and 0.25.

3.4. ADSORPTION ISOTHERM

The adsorption isotherm data were experimentally obtained based on the optimized contact duration (90 min for ZCRns and 60 min for ZCRs20) and substrate amount (0.2 g ZCRns/ZCRs20 in 50 mL solution). The adsorption parameters were calculated considering the Langmuir and Freundlich equations (7) and (8) [32]:

- the Langmuir isotherm – linearization:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{max} \cdot a} + \frac{C_{eq}}{q_{max}} \quad (7)$$

- where q_{max} (mg/g) represents the maximum monolayer adsorption capacity, a is a constant related to the adsorption free energy, q_{eq} is the amount of metal ions adsorbed from the solution with the equilibrium concentration, C_{eq} .
- the Freundlich isotherm – linearization:

$$\ln q_{eq} = \ln k_f + \frac{1}{n} \ln C_{eq} \quad (8)$$

- where k_f is Freundlich constant, an indicator of the adsorption capacity, and the $1/n$ dimensionless parameter is a measure of the adsorption density. The adsorption parameters are presented in table 7.

Table 7 Adsorption isotherm parameters

Substrate	Langmuir parameters			Freundlich parameters		
	q_{max} [mg/g]	a [L/mg]	R^2	n	K_F	R^2
Cd²⁺						
ZCRns	58.823	0.0002	0.949	6.896	48.843	0.821
ZCRs 20	69.44	0.0001	0.966	-	-	0.748
Cu²⁺						
ZCRns	36.764	0,0002	0,999	-	-	0,536
ZCRs 20	59.505	0,016	0,920	-	-	0,657
Cd²⁺(Cd²⁺+Cu²⁺)						
ZCRns	16.129	0.021	0.989	5.628	1.284	0.827
ZCRs 20	32.895	0.001	0.978	3.284	15.975	0.833
Cu²⁺(Cd²⁺+Cu²⁺)						
ZCRns	58.139	0.002	0.918	4.482	12.3327	0.914
ZCRs 20	66.667	0.0003	0.975	2.989	19.436	0.942
Cd²⁺(Cd²⁺+Cu²⁺+MB)						
ZCRns	35.211	0.006	0.994	-	-	0.738
ZCRs 20	26.316	0.016	0.979	5.695	0.740	0.916
Cu²⁺(Cd²⁺+Cu²⁺+MB)						
ZCRns	69.444	0.001	0.982	2.629	3.579	0.923
ZCRs 20	35.842	0.0002	0.999	3.271	29.530	0.939
MB(Cd²⁺+Cu²⁺+MB)						
ZCRns	22.472	0.013	0.971	3.254	0.035	0.880
ZCRs 20	3.175	1.482	0.919	-	-	0.538

The Langmuir model fits the equilibrium data much better than the Freundlich model for both adsorbents table 7. The Freundlich model can be fitted for cooper and cadmium on these substrates. Accordingly with data table the adsorption was rather homogeneous than heterogeneous and rather monolayer than multilayer.

The SEM images after adsorption of cations from bi-component solution present the competition between copper and cadmium cations. The percentages of cadmium and copper on surface scanned are: Cu (atom %) = 93.55 and Cu (atom %) = 6.45.

Conclusions

Adsorption efficiency of cadmium, copper cations is reduced compared to the adsorption efficiencies of mono-cationic systems, indicating the competition on similar active centers of powder zeolites (homogeneity substrates).

The competition between the different metal ions for surface sites of powder zeolites occurs and is dependent on the characteristics of the ions, substrate (crystalline phases, and morphological, surface area, changes), respectively.

The adsorption isotherms and kinetic data fitted well the Langmuir and pseudo-second order kinetic models, respectively. The order of affinities of ZCRs20 > ZCRns for the divalent metal ions reported is $\text{Cu}^{2+} > \text{Cd}^{2+}$ at optimized contact time 60 min. for ZCRs20 and substrate amount 4g/L multicomponent solution.

Three stages exist in alkali hydrothermal reaction of zeolite NaP1 synthesis: (1) the dissolution of Si^{4+} and Al^{3+} in coal fly ash; (2) the formation sodium aluminosilicate gel as zeolite precursor; (3) the crystallization of aluminosilicate gel to make zeolite crystal.

The zeolitic material ZCRs20 with high degree of crystallinity and specific surface area greater than ZCRns can be recommended for technologic adsorption process.

Two environmental problems are solved using zeolite materials obtained from fly ash: removing pollutants from wastewater and reducing huge amounts of fly ash.

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