Removing metal ions in aqueous solution with zeolites synthesized from fly ashes

Lorena Martínez[1], Gabriel Peña-Rodríguez[2], Fernando Trejo[1,*]
Instituto Politécnico Nacional, CICATA-Legaria. Legaria 694, Col. Irrigación. Ciudad de México 11500, México.
Grupo GIFIMAC, Universidad Francisco de Paula Santander. A.A. 1055, Cúcuta, Colombia.

E-mail: ftrejoz@ipn.mx

Abstract

The removal of metals such as Cr, Ni, Cd, As, Pb, and Cu in water using zeolites synthesized from fly ashes through hydrothermal process was evaluated. NaOH in concentrations of 1.5, 3.0, and 4.5M was used to dissolve the fly ashes. Characterization of zeolites were performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), and nitrogen physisorption. The metal ions removal was evaluated as the percentage of contaminants in polluted water before and after adding zeolites. It was observed that molar concentration of NaOH during the synthesis influences on zeolite types and mostly zeolites P and X were obtained. High removal efficiencies with a zeolite synthesized with NaOH at 4.5M and sample amount of 0.6 g are reported. The metal ions removal follows the order: Ni>Cd>Cu>Pb>As>Cr, and the highest global removal efficiency obtained was 76.3%.

Keywords: Fly ash, hydrothermal process, zeolite P, zeolite X.

Resumen

Se evaluó la remoción de metales como Cr, Ni, Cd, As, Pb y Cu en agua utilizando zeolitas sintetizadas a partir de cenizas volantes mediante procesos hidrotermales. Se utilizó NaOH en concentraciones de 1,5, 3,0 y 4,5 M para disolver las cenizas volantes. La caracterización de las zeolitas se realizó mediante microscopía electrónica de barrido (SEM), difracción de rayos X (XRD), espectroscopía de fluorescencia de rayos X (XRF) y fisisorción de nitrógeno. La eliminación de iones metálicos se evaluó como el porcentaje de contaminantes en el agua contaminada antes y después de agregar zeolitas. Se observó que la concentración molar de NaOH durante la síntesis influye en los tipos de zeolitas y principalmente en las zeolitas P y X. Se informan altas eficiencias de eliminación con una zeolita sintetizada con NaOH a 4,5 M y una cantidad de muestra de 0,6 g. La remoción de iones metálicos sigue el orden: Ni> Cd> Cu> Pb> As> Cr, y la mayor eficiencia de remoción global obtenida fue 76.3%.

Palabras clave: Cenizas volantes, proceso hidrotermal, zeolita P, zeolita X.

I. INTRODUCTION

The contamination of water with metals produced by discharges of factories is a global environmental problem [1], which affects the human health due to its toxicity causing damage in the nervous system, blood, lungs, kidneys, liver, and other organs [2]. Likewise, it impacts negatively on aquatic systems since heavy metals are non-biodegradable and tend to accumulate in aquatic animals [3, 4]. As a result, high cost in terms of investment in purification processes, health systems in countries, among others, is attained [5]. Therefore, metals in water must be removed before discharging.

One of the most striking alternatives for dealing with environmental problems is through using wastes or residues as raw material because pollution is reduced, and energy is saved [6]. In this case, the fly ashes generated as by-product of the coal combustion for electrical energy generation are of special interest [7, 8], since they are mainly composed of aluminum and silicon [9]. Main composition of fly ashes is SiO_2 (60-65 wt%), Al_2O_3 (25-30 wt%), and magnetite (Fe_3O_4, 6-15 wt%) [10], which allows converting them into zeolites by different processes such as hydrothermal via [11, 12].

Zeolites synthesized from fly ashes may be a cheaper alternative to activated carbons or commercial zeolites for metal removal from water. For example, zeolite A synthesized from fly ash showed the following metal removal order: $Cu^{2+}>Cr^{3+}>Zn^{2+}>Co^{2+}>Ni^{2+}$ and fitting well to a Langmuir model [13]. Earlier studies reported that a two-step processes to synthesize zeolite P was carried out and it was able to remove metals from a water treatment plant [14]. In addition, removal of Cu^{2+} and Ni^{2+} over zeolite P from fly ash

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by hydrothermal method was also reported. Higher temperatures enhance the formation of zeolite P; however, sodalite formation is also increased with temperature [15]. Hydrothermal synthesis of zeolite Na-A from fly ash was enhanced through microwave-assisted method and showed good cation-exchange capacity. With this technique, the time of synthesis was reduced compared to conventional hydrothermal method [16]. Adsorption of metal cations such as Zn, Cu, Mn, and Pb was also reported using synthetic zeolites from Brazilian coal fly ash [17]. Both the temperature and time of synthesis influenced on the adsorption capacity, which followed the order: Pb>Cu>Zn>Mn. Due to similarities between natural and synthesized zeolites, the use of fly ashes as source of adsorbent materials may reduce the operation costs in plants of wastewater treatment for example. In addition, the use of residues to obtain materials contribute to diminish the environmental pollution.

Therefore, the aim of this work is to synthesize, characterize, and evaluate zeolites obtained from fly ash through hydrothermal synthesis by varying molarity of NaOH at constant temperature and solution-to-ash ratio. Metal ions such as Cu, Cd, Ni, Pb, as, and Cr in aqueous solution were used to evaluate metal removal simultaneously.

II. MATERIALS AND METHODS

Fly ash from combustion in a coal-operated electric plant was used as raw material. Sodium hydroxide was used as such with no further purification (Fermont, Mexico, purity of 99%). Deionized water was used to prepare solutions and to carry out the hydrothermal synthesis of zeolites.

A. Synthesis of zeolites

The ash powders used were sieved with ASTM 200 mesh (size $\leq$ 75μm) for removing impurities like unburnt coal. NaOH at 1.5, 3.0, and 4.5M was used with a solution-to-ash ratio of 6:1 v/w% [18, 19] due to the main objective is reusing the higher amount of fly ash (FA) as possible with decreasing the water consumption [20]. Hydrothermal reaction was carried out in a Teflon vessel of 30 mL at 100°C during 24 h. Under synthesis conditions, crystalline zeolite NaP is obtained [21, 22]. After hydrothermal synthesis, zeolite was washed with deionized water until neutral pH to remove excess of sodium hydroxide and further dried during 4 h at 120°C.

B. Characterization of zeolites

The morphology of zeolites was analyzed with scanning electron microscopy (Jeol JSM-6390, Japan). Samples were covered with gold using a sputtering apparatus (Denton Vacuum, USA). Crystal structure was evaluated by X-ray diffraction (Advanced D8 Discover Bruker diffractometer, USA) at the following operation conditions: CuKα1=1.5406 Å, 40 kV, 20 mA, 2θ range 5-120°, scanning step 0.02°, and scan speed of 2 s/step. Le Bail method for identifying

crystalline phases with the PDF-2 database of the International Center for Diffraction Data and the FULLPROF software to analyze the spectra were used. The chemical composition of zeolites was determined using X-Ray Fluorescence (Bruker S2 Ranger spectrometer, USA) with palladium as radiation source. The specific surface area of the samples was obtained by nitrogen physisorption (Nova Touch 4LX, USA) at degassing temperature of 250°C during 3 h.

The zeta potential was measured with a nano zeta sizer apparatus (Zetasizer Nano ZS, Malvern Panalytical) at various pH values (2-11). Around 0.1 g of zeolite was added to 30 mL of deionized water. By adding HCl, the pH was adjusted to required pH and measurement was carried out.

C. Evaluation of metals ions removal by zeolites

Previously, zeolites were dried at 400°C for 4 h to remove the water from the structure. Three amounts of zeolite were handled (0.15, 0.3, and 0.6 g) and mixed with 30 mL of water (initial pH=2) containing metals ions to be tested (Pb, Cd, Ni, Cu, Cr, and As at 5 ppm each one) at 350 rpm and 35°C during 60 min of contact time. After this time, variations in concentrations were negligible, because it was observed that pH was unchanging at pH=8. Experiments were carried out by triplicate and the average was reported. Subsequently, the mixture was filtered, and water was analyzed with optical emission spectroscopy by inductively coupled plasma (ICP-OES, Perkin Elmer Optima 8000, USA). The metal ions removal efficiency was evaluated with equation (1):

$$Removal\ efficiency,\ \% = (C_i - C_f)/C_i \times 100, \quad (1)$$

where C_i and C_f corresponds to initial and final concentrations of water containing metals ions.

III. ANALYSIS AND DISCUSSION OF RESULTS

A. Characterization of fly ash and zeolites

The collected fly ash corresponds to type F because concentrations of SiO_2, Al_2O_3, and Fe_2O_3 are greater than 70 wt% as shown in Table 1. Fly ash is composed of small particles of spherical shape (cenospheres and pleurospheres) [23] with particle sizes between 1 and 100 μm, unburnt carbon with irregular morphologies and organic matter [24]. In addition, Figure 1(a) shows how the sieving process prior to treatment retains a large amount of these impurities. The effect of hydrothermal process on morphology to obtain zeolites as pseudo spheres is observed in Figure 1(b,c), which are characteristic of zeolite P [25]. Morphology like balls of wool is observed with NaOH at 4.5M (Figure 1d), which are typical of zeolite X [26], likewise morphologies as short needles is showed in Figure 1d that correspond to mullite [27].

In Figure 2, the XRD patterns are depicted for both the fly ash and zeolites synthesized at different NaOH

concentrations. Experimental points are shown in red coloer while diffraction patterns calculated according to Le Bail method are in black color and differences between calculated and experimental patterns are in blue at the bottom of figures.
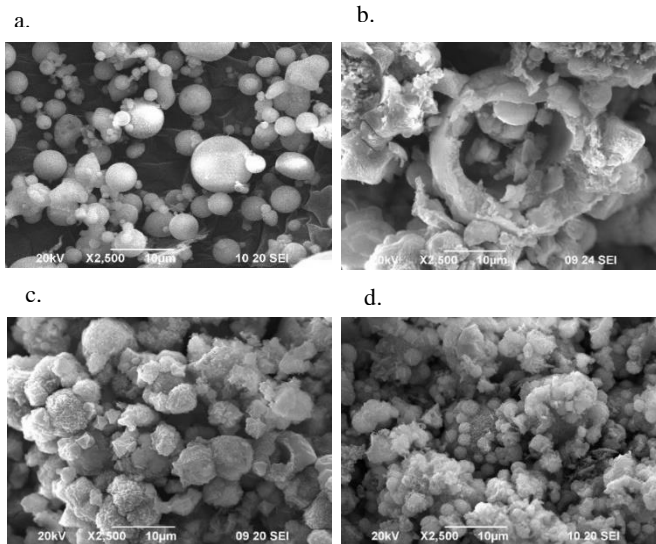

FIGURE 1. Microphotographs at magnification of 2500X from: a) flying ash, b) zeolite synthesized at 1.5M, c) zeolite synthesized at 3.0M, d) zeolite synthesized at 4.5M.

Vertical bars in different colors correspond to Bragg positions. It is observed that crystalline phases present in fly ash are mainly made of quartz and mullite (Figure 2a). Similarly, an amorphous part is observed between 15 and 40° that decreases markedly as the ash was activated with NaOH as consequence of dissolution of aluminosilicate (Figure 2 b,c,d), which forms gels with further creation of zeolite crystals [28].

Zeolites synthesized with NaOH at 1.5 and 3.0M (Figure 2 b,c) showed increased conversion toward zeolites P and X. With NaOH at 1.5M, 61.4% of zeolite P was obtained while with NaOH at 3.0M, conversion was 74% with a mixture of zeolite P (49.7%) and zeolite X (24.3%). Zeolite X (57.2%), zeolite P (6.8%), and sodalite (12.2%) were obtained predominantly with NaOH at 4.5M; however, conversion from fly ash to zeolite diminished compared when using NaOH at 1.5 and 3.0M.

It is observed that zeolite P is obtained mainly with NaOH 1.5M by which it could be stated that low NaOH concentrations enhances the formation of this type of zeolite. However, reaction conditions are not strong enough to convert mullite and silicon oxide into zeolites, because both hardly react [28].

It has been reported that zeolites X and A are predominantly obtained at solid/liquid ratio of 0.03 and intervals of temperature between 90-95°C and lower time of synthesis whereas zeolite P is synthesized at times of synthesis higher than 48 h [29].
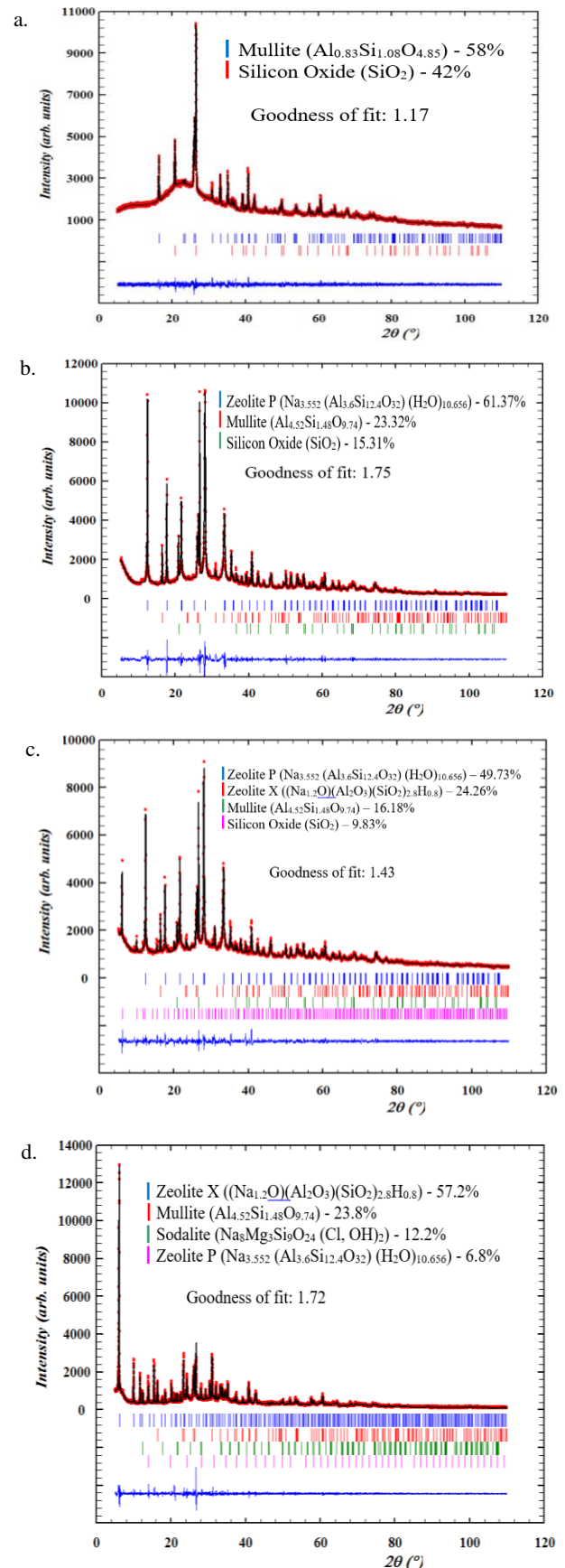

FIGURE 2. DRX patterns of the samples: a) flying ash, b) zeolite synthesized at 1.5M, c) zeolite synthesized at 3.0M, d) zeolite synthesized at 4.5M.

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Nucleation and crystallization to form zeolites are mainly depending on concentration of NaOH, the temperature during hydrothermal process, and reaction time. Needles tend to be thinner as crystallization temperature increased. In addition, higher temperatures also increased the yield of zeolites because of dissolution of Si and Al in fly ashes.

The chemical composition using XRF of both the fly ash and synthesized zeolites is presented in Table 1. Magnesium is not reported in all materials and this fact can be attributed to its low amount contained in the samples, which may be below of the detection limit of the apparatus. During hydrothermal synthesis, SiO_2 content diminished as NaOH molar concentration increased. On the other hand, Al_2O_3 content increased slightly compared to fly ash. Similarly, the Si/Al molar ratio (Table 2) that determines the ion exchange capacity of zeolite, diminished as NaOH concentration increased, which is associated to exchangeable cations. The Na_2O content increased after hydrothermal synthesis that suggests that alkali reacted with fly ash as reported elsewhere [30].

TABLE I. Chemical composition (wt%) of fly ash and zeolites synthesized at different NaOH concentration.

Sample	Fly ash	1.5 Zeolite	3.0 Zeolite	4.5 Zeolite
SiO_2	50.4	44.3	38.9	35
Al_2O_3	20.1	24.4	22.1	23.5
Na_2O	7.6	12.4	18	16.7
Fe_2O_3	8.8	8.5	9.4	10
CaO	3.9	4.2	4.9	5.2
MgO	2	--	--	2.6
TiO_2	1.7	1.9	2.3	2.4
K_2O	1.8	1.6	1.1	0.8
P_2O_5	1.1	0.7	1.1	1.2
SO_3	1.5	0.8	0.9	1.3
Cl	0.5	0.6	0.6	0.5
ZnO	0.1	0.2	0.2	0.2
ZrO_2	0.1	0.1	0.1	0.1

TABLE II. Si/Al molar ratio from fly ash and zeolites synthesized at different NaOH concentration.

Ratio	Fly ash	1.5 Zeolite	3.0 Zeolite	4.5 Zeolite
Si/Al	2.13	1.82	1.49	1.26

The specific surface area, average pore volume, and average pore diameter determined by nitrogen physisorption are reported in Table 3 where mesoporous materials are mainly observed (pores from 2 to 50 nm). In addition, it is observed that there is not significant change in textural properties as function of synthesis conditions; however, the specific surface area increases significantly when comparing the fly ash to the synthesized material.

TABLE III. Textural properties of fly ash and zeolites synthesized at different NaOH concentration.

Sample	Specific surface area, m^2/g	Average pore volume, cm^3/g	Average pore diameter, nm
Fly ash	1.0	0.01	3.6
1.5 zeolite	30	0.07	2.9
3.0 zeolite	33	0.09	3.2
4.5 zeolite	34	0.10	3.3

B. Evaluation of metals ions removal by zeolites

Figure 3 shows the pH at point of zero charge (pH_{pzc}) for synthesized zeolite to be 2.5. Initial pH of aqueous solution containing all metal ions was 2 and it increased around pH~8 as tests were carried out. When pH value of aqueous solution is below than pH_{pzc}, the zeolite surface is positively charged allowing interactions with negative metal species while at pH value higher than pH_{pzc}, the material is negatively charged by which interactions with positive metal species are to be expected [23]. The pH value in aqueous solution increased rapidly during the first five minutes until reaching an equilibrium value of pH around 8 by which the main removal process is adsorption by interaction of zeolite surface negatively charged with positively charged metal ions in solution. In addition, at pH>0 values the solution is alkaline, and some hydroxide species are prone to precipitate.
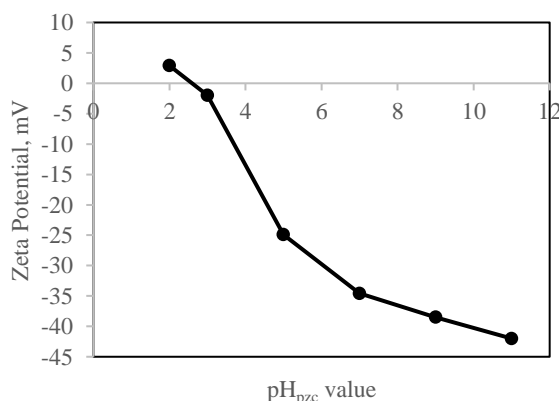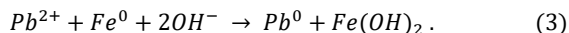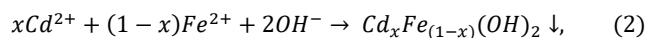

FIGURE 3. Zeta potential of synthesized zeolite to obtain the pH_{pzc} value.

Adsorption of metals ions using 0.3 g of zeolite synthesized with NaOH 1.5M is depicted in Figure 4. Contact time is plotted up to 60 min at which equilibrium was reached. It is observed that Pb removal was higher than 99% after 5 min of contact time. Cu removal was 99% at 5 min while practically all cupper ions were removed at 10 min. A similar trend was observed for Cd. Nickel, chromium, and arsenic were removed at lesser extent compared to Pb, Cu, and Cd.

Removal efficiency of Ni, Cr, and As reached 97%, 61%, and 58%, respectively. As aforementioned, zeolites obtained almost completely removed Pb, Cd, and Cu, regardless the molarity used during the synthesis as observed in Table 4. For these metal ions, the Fe present in fly ash contributed to form

hydroxides and then precipitated over the external surfaces of zeolites like showed as follows [31]:

$$xCd^{2+} + (1-x)Fe^{2+} + 2OH^- \rightarrow Cd_xFe_{(1-x)}(OH)_2 \downarrow, \qquad (2)$$

$$Pb^{2+} + Fe^0 + 2OH^- \rightarrow Pb^0 + Fe(OH)_2. \qquad (3)$$

In the case of Ni, the lower the amount and molarity, the lower metal ion removal efficiency. Functional groups attached to the surface influence on Ni removal [32, 33]. In addition, Ni removal is dependent on pH, i.e., the higher the pH, the higher the Ni removal, because at pH alkaline allows easier combination between HO$^-$ groups with Ni^{2+} to form Ni(OH)$_2$ and precipitate [34]. When pH>8.5, Ni removal keeps as constant. Competition between cations also affects Ni sorption at lower pH but its influence is not observed at higher pH values due to complexation is attained [35, 36]. At the highest amount of material, as removal was carried out almost completely and diminished when decreasing the amount of zeolite. It has been reported that arsenic may be adsorbed onto zeolites through aluminol or silanol groups on the edges of material. Better dispersion of material into aqueous solution was observed at the highest amount of zeolite (0.6 g) compared to the lowest one (0.15 g). In addition, H$_2$AsO$_4^-$ species is present at lower pH (pH<7) while HAsO$_2$ is commonly observed as pH value increases [37, 38]. At higher pH values there is less iron oxyhydroxide species dissolved compared with acid medium, thus As^{3+} may form complexes with Fe^0 and metal ion removal through precipitation may proceed [39].

TABLE IV. Removal efficiency of different metals with fly ash and zeolites synthesized at different NaOH concentration.

Sample	Amount g	Removal efficiency of different metals, %					
		As	Cd	Cr	Cu	Ni	Pb
Fly ash	0.15	0.1	1.6	4.0	0.9	1.4	34.1
	0.30	29.3	1.6	13.5	0.9	1.4	47.1
	0.60	73.9	1.6	21.8	0.9	1.4	77.8
1.5 zeolite	0.15	24.0	71.9	1.7	82.1	8.7	98.9
	0.30	63.2	99.5	0.2	99.2	91.7	98.7
	0.60	91.4	98.4	0.2	98.8	98.5	98.0
3.0 zeolite	0.15	12.0	96.9	1.2	98.5	56.9	98.2
	0.30	27.0	98.4	1.0	98.6	98.1	97.0
	0.60	84.2	97.8	0.9	98.0	97.7	96.1
4.5 zeolite	0.15	33.1	99.1	0.8	99.0	57.1	95.0
	0.30	40.8	99.8	3.5	99.7	99.8	94.4
	0.60	93.4	99.8	6.0	98.6	99.9	93.8

Finally, the synthesized materials do not remove Cr effectively since the highest efficiency found was 6% as an effect of pH in the solution. It is assumed that Cr may form several complexes or species as pH varies [40, 41] while Cr removal is maximum at low pH values and depends on temperature by which at higher temperature the Cr removal

is enhanced [42]. Literature reports have stated that Cu, Pb, and Zn tends to reduce the Cr adsorption where the effective metal radii play an important role [43]. In the case of trivalent chromium ion, adsorption by zeolites is strongly influenced by pH while Cr is better removed by fly ash compared to zeolites, which is attributed to the high CaO content in fly ashes [44]. In addition, different chromium species are observed as pH varies from 1 to 7, i.e., Cr^{3+} hydrolyzes to Cr(OH)$^{2+}$ and Cr(OH)$_2^+$ showing strong dependence on pH.

Considering zeolite synthesized with NaOH at 4.5M and sample of 0.6 g as shown in Table 4, the metal ions removal follows the order: Ni>Cd>Cu>Pb>As>Cr. Since pH of water increased after metal ions removal, Cr was not adsorbed in high amount due to its dependence on pH. On the other hand, Ni, Cd, and Cu, were removed almost similarly as well as Pb and As do. Energy of hydration and hydrated radii of metal ions may be responsible of this trend. Hydrated radii of metal ions have been reported elsewhere [18, 45, 46] to be 4.04Å (Ni^{2+}), 4.26Å (Cd^{2+}), 4.19Å (Cu^{2+}), 4.01Å (Pb^{2+}), 2-2.2Å (for As^{5+} in arsenate ion HAsO$_4^{2-}$), and 4.61Å (Cr^{3+}). In this case, Cr^{3+} has the higher hydrated radii by which it is to be expected that its adsorption was the lowest one compared with other ions. According to hydrated radii, the sequence of adsorption should be as follows (excluding As ion): Pb>Cd>Cu>Ni>Zn. However, in this study the observed trend decreased as: Ni>Cd>Cu>Pb>As>Cr. Taking into consideration the energy of hydration, the higher values imply that ions remain in solution instead of being adsorbed on zeolite. Energy of hydration values reported elsewhere [47] are: -1481 kJ/mol for Pb^{2+}, -1807 kJ/mol for Cd^{2+}, -2100 kJ/mol for Cu^{2+}, and -2105 kJ/mol for Ni^{2+}. Pb ion has the lower value of energy of hydration, and it may explain why it is readily adsorbed during the first minutes as shown in Figure 4. In fact, according to energies of hydration values, Cd ions are adsorbed almost completely at lower contact time as Pb ions do. Some competition for adsorption sites is carried out at lower pH values due to H$_3$O$^+$ ions are abundant when having acid solution [13]; however, some functional groups from zeolite may dissociate at higher pH values turning the zeolite surface into anionic influencing on metal removal.
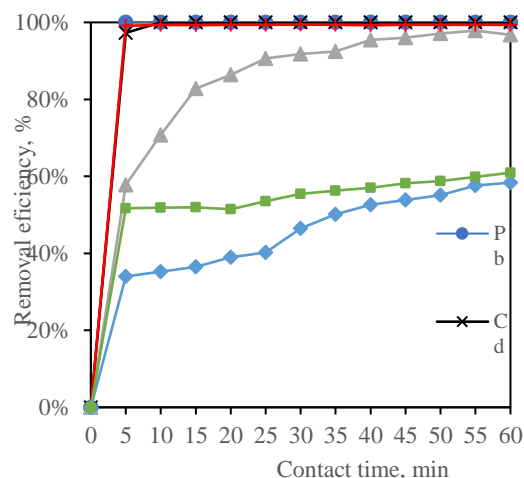

FIGURE 4. Profiles for adsorption of different metal ions (T=35°C, t=60 min, stirring speed=350.

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Since polluted water contains several metal ions as contaminants, the global removal efficiency was evaluated considering the initial and final ions concentration measured by ICP. Some metal ions are easily removed whereas other ones remain in water. Taking into consideration the presence of all metal ions in aqueous solution: Cd, Cr, Cu, Ni, and Pb, the influence of fly ash and zeolites as well as the amount of material was plotted as shown in Figure 5. The highest removal efficiency (76.3%) was obtained with 0.3 g of zeolite synthesized using NaOH at 1.5M. Zeolites synthesized with NaOH at 3.0 and 4.5M have similar textural properties as shown in Table 3.
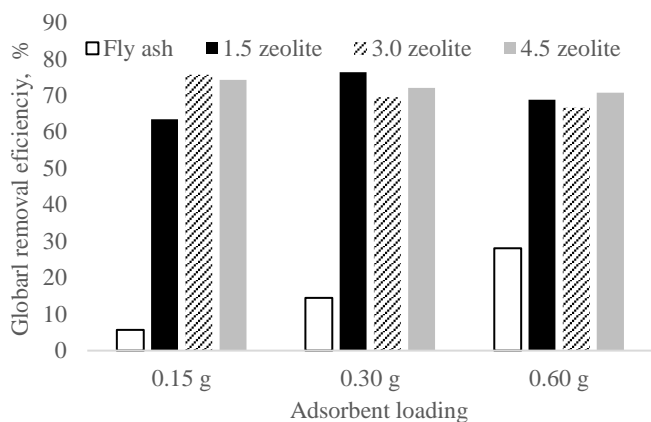

FIGURE 5. Global removal efficiency of mixed metal ions with fly ash and zeolites synthesized at different NaOH concentration.

V. CONCLUSIONS

The concentration of NaOH used in the synthesis directly influences on morphology of zeolites from fly ashes. As concentration of NaOH increases, zeolite X is more abundant and sodalite is also formed. Fly ashes conversion toward zeolite (including all types such as P, X, and sodalite) varied as function of NaOH concentration as follows: 61.37% (1.5M), 73.99% (3.0M), 76.20% (4.5M). The higher the NaOH concentration, the higher the fly ashes conversion.

On the other hand, with lower concentrations of NaOH, zeolite P is predominant. However, conversion of fly ashes is not carried out completely because aluminosilicate glasses are hard to be converted into zeolites and they are observed in diffraction patterns as amorphous components. The Si/Al ratio was influenced by the alkali concentration by which the higher the NaOH molarity, the lower the Si/Al ratio. The highest specific surface area of zeolites was 34 m^2g^{-1} and formed mainly by mesopores. During the removal process, two processes were identified to occur: 1) adsorption during the first minutes of contact between zeolite and aqueous solution, and 2) precipitation as hydroxides as pH increased.

The zeolites effectively removed metals ions such as Pb, Cd, Ni, and Cu. To remove As, amounts of material of 0.6 g is preferable. Chromium was hardly removed in all cases due to its higher metal ion radii.

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