

A comparative study on the use of zeolite-like materials in the removal of heavy metals and ammonium from wastewaters

Un estudio comparativo sobre el uso de materiales similares a la zeolita en la eliminación de metales pesados y amonio de las aguas residuales

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Recibido: 02/11/2019

Aceptado: 06/08/2020

Cite this article as: C. A. Ríos Reyes, C. Williams, O. M. Castellanos Alarcón "A comparative study on the use of zeolite-like materials in the removal of heavy metals and ammonium from wastewaters", *Prospectiva*, Vol 18, N° 2, 2020.

<http://doi.org/10.15665/rp.v18i2.2187>

ABSTRACT

The present study aimed at evaluating the use of low-cost sorbents like synthetic (metakaolinite-based Lynde Type A zeolite) and natural (clinoptilolite-rich rhyolite tuft) zeolites to clean-up artificially polluted solutions and to remove heavy metals and ammonium. In order to test their potential applications in the remediation of wastewater, efficiency for heavy metal and ammonium uptake using batch reactions at room temperature was investigated. A specific zeolite dose (g) per effluent volume unit (ml) and reaction time was examined to understand the removal mechanisms involved. pH played a very important role in the sorption/removal of the contaminants and a higher adsorbent ratio in the treatment of AMD promoted the increase of the pH, particularly using Lynde Type A zeolite (9.06) and the reduction of metal concentration. The efficiency shows that the synthetic zeolites may reach a cation exchange capacity appropriate for their application in industrial wastewater treatment. The heavy metal selectivity of zeotypes was determined as Cu>Zn>Cr>Ni>Pb, and it also showed a high affinity for ammonium.

Keywords: Zeolites; Heavy metals; Ammonium; Pollution; Wastewater; Remediation.

RESUMEN

El presente estudio tuvo como objetivo evaluar el uso de sorbentes de bajo costo como las zeolitas sintéticas (zeolita tipo Lynde Tipo A a partir de metacaolinita) y naturales (toba riolítica rica en clinoptilolita) para limpiar soluciones contaminadas artificialmente y eliminar metales pesados y amonio. Con el fin de probar sus aplicaciones potenciales en la remediación de aguas residuales, se investigó la eficiencia de la

absorción de metales pesados y amonio usando reacciones discontinuas a temperatura ambiente. Una dosis específica de zeolita (g) por unidad de volumen de efluente (ml) y el tiempo de reacción se examinó para comprender los mecanismos de eliminación involucrados. El pH desempeñó un papel muy importante en la sorción / eliminación de los contaminantes y una mayor proporción de adsorbente en el tratamiento de AMD promovió el aumento del pH, particularmente usando zeolita Lynde Tipo A (9.06) y la reducción de la concentración de metal. La eficiencia muestra que las zeolitas sintéticas pueden alcanzar una capacidad de intercambio catiónico apropiada para su aplicación en el tratamiento de aguas residuales industriales. La selectividad de metales pesados de los zeotipos se determinó como Cu > Zn > Cr > Ni > Pb, y también mostró una alta afinidad por el amonio.

Palabras claves: Zeolitas; Metales pesados; Amonio; Contaminación; Aguas residuales; Remediación.

1. INTRODUCTION

Currently, the contamination of water resources constitutes a serious problem facing humanity, making it difficult to control and manage water consumption, therefore, it is necessary to take measures to reduce environmental pollution. Wastewater contains several contaminants, including heavy metals, plant nutrients, pathogenic microorganisms, and organic and inorganic pollutants, which can cause adverse effects on the health and environment. Globally, wastewater treatment represents a challenge to address the scarcity of water resources and reduce their negative impact. Large amounts of wastewater containing heavy metals and/or ammonium are produced and discharged from domestic, stormwater runoff, industrial and agroindustrial sources (Figure 1). The presence of heavy metal ions in wastewater is of great concern due to its toxicity, high solubility persistence and not biodegradable nature, causing numerous diseases and disorders [1-2]. On the other hand, ammonium is an important nutrient, which, however, can contribute to undesirable changes in water quality [3] and can cause diverse problems such as toxic algal blooms, loss of oxygen, fish kills, loss of biodiversity, loss of aquatic plant beds and coral reefs, and other problems [4]. Therefore, wastewaters containing heavy metals and/or ammonium are required to be treated prior to discharge into receiving environments. Removal of heavy metals and/or ammonium from polluted effluents is a challenging task all over the world regarding the correct management of wastewater for a sustainable future. If not carefully managed, however, wastewater may produce both short- and long-term effects on the health and environment. Wastewater treatment is the last line of defense against water pollution. Globally, despite efforts to improve water quality, there is a significant deficit in wastewater treatment, with a high percentage of the world population without access to an adequate wastewater treatment system, which is a consequence of the demographic explosion, the water crisis and the high costs of the facilities to carry out its treatment. There are different procedures for removal of heavy metals from wastewater, including chemical precipitation [5-7], electrodeposition [8], ion exchange [9-10], membrane separation [11-12] and adsorption [13-15] have been developed, although adsorption has been the preferred method for heavy metal removal, because it is considered to be a particularly effective technique. There are several methods have been applied to remove ammonium from wastewaters including ion exchange or adsorption [16-18], membrane processes [19-20], break-point chlorination [21], biological treatment [22-24], chemical precipitation [4,25], reverse osmosis [26-27], microwave radiation [28-29], supercritical water oxidation [30-31] and air stripping [32-33]. Adsorption is usually quite a complex process, generally involving much more than simple ion exchange into the pore openings of the ion exchanger. Factors such as pH, nature and concentration of the ionic species, ion hydration, varying metal solubilities, presence of competing and complexing ions, all affect the amount of metal ion to be adsorbed [34] and therefore the sorbent selectivity. Activated carbon is considered to be a particularly competitive and effective sorbent for the removal of heavy metals and/or ammonium. However, may not be suitable due to high costs associated with production and regeneration of spent carbon [35]. Therefore, alternative low-cost liming substitutes are constantly sought. Such adsorbents should be readily available, economically feasible and easily regenerated. Zeolites are well-known crystalline microporous materials with a three-dimensional structure composed by $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, which corner-share to form different open structures with an overall negative

charge, which is balanced by cations which move freely in and out of their frameworks. At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes [36]. Owing to the framework characteristics of zeolites and their adsorbent properties, they have been mainly applied in adsorption. Synthetic Lynde Type A (LTA) and natural clinoptilolite (HEU) zeolite have a large selectivity for NH_4^+ [37-39] and heavy metal ions [40-42]. The structural and physicochemical properties of zeolites make them very effective for the removal of heavy metals and ammonium from wastewaters. There are increasing demands for a healthy environment, particularly with regards to high-quality drinking water and removal of pollutants from industrial, agricultural and municipal wastewaters. Most technologies using zeolites for water purification are based on their unique cation-exchange behavior through which dissolved cations are removed from water by exchanging with cations on a zeolite exchange sites. The current study focused on the efficiency and affinity of zeolites LTA and HEU to remove heavy metals and ammonium from wastewaters, taking into account the zeolite's behavior toward divalent cations in competition with each other. For this purpose, we used synthetic (metakaolinite-based Lynde Type A zeolite) and natural (clinoptilolite-rich rhyolite tuft) zeolites and artificially polluted solutions with low pH and high heavy metal and ammonium concentrations. On the other hand, we investigate the relevant mechanisms for metal ion removal by equilibrium studies and kinetic studies. These zeotypes were chosen to be utilized in batch reaction experiments, taking into account their cation exchange capacity (CEC) and low Si/Al ratio. Such a low Si/Al ratio means that higher concentration of terminal Al-OH groups can be expected at the mineral/solution interface, as well as a zeolite with a more hydrophilic nature [43], which consequently leads to a greater capacity for ligand exchange and thus better performance during decontamination experiments [44-45].

Figure. 1. Sources of wastewater.

Figura. 1. Fuentes de aguas residuales.



Source: Authors.

Fuente: Autores.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Raw materials

The raw materials used as sorbents in this study correspond to a synthetic zeolite LTA and a natural zeolite HEU. The zeolite LTA was synthesized following the method described in detail by Ríos [43]. Kaolinite ($\leq 2 \mu\text{m}$), $\text{Al}_2\text{SiO}_5(\text{OH})_4$, distributed under the name Supreme Powder and supplied by ECC International was thermally treatment at $600 \text{ }^\circ\text{C}$ for 1 h to obtain metakaolinite, which was used as starting material for zeolite LTA synthesis. Reagents used in the activation of metakaolinite were: sodium hydroxide, NaOH, as

pellets (99.99%, Aldrich Chemical Company, Inc.) and distilled water using standard purification methods. The synthesis of zeolite LTA was carried out under hydrothermal conditions in alkaline medium using metakaolinite as SiO_2 and Al_2O_3 sources. A calculated amount of alkali hydroxide pellets was added to distilled water in reaction plastic beakers (150-250 mL) to prepare a 1.33 M NaOH solution; the starting materials were then mixed with an alkaline solution to produce a reaction gel. The progressive addition of reagents was carried out under stirring conditions until they dissolved to homogenize the reaction gels. Crystallization was carried out under static conditions in PTFE vessels of 65 mL at 100 °C for 52 h. Once the activation time was reached, reactors were removed from the oven and quenched in cold water to stop the reaction. After hydrothermal treatment, reaction mixtures were filtered and washed with distilled water. Then, samples were oven dried at 80 °C overnight. Dried samples were weighted and kept in plastic bags for characterization. The zeolite HEU - rich rhyolite tuft was obtained from the Miocene volcanic area of Tokaj Mts. (Hungary). It was prepared by grinding with a SpectroMill Ball Pestle Impact grinder and sieved size 200 mesh and then ground and particles of $< 75 \mu\text{m}$. Synthetic polluted solutions were prepared using the following compounds: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Scientific & Chemical Supplied Ltd, general purpose), $\text{Pb}(\text{NO}_3)_2$ (BDH Laboratories Supplies, general purpose, 99%), $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Hopkins & Williams AnalaR, laboratory reagent), $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Hopkins & Williams AnalaR, laboratory reagent) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Hopkins & Williams AnalaR, 98%), ammonium chloride - NH_4Cl (Scientific & Chemical Supplied Ltd, general purpose), and distilled water using standard purification methods.

2.2 Characterization of zeolite sorbents

Mineral phases in zeolites LTA and HEU were studied by X-ray powder diffraction (Philips PW1710) diffractometer operating in Bragg-Brentano geometry with $\text{Cu-K}\alpha_1$ radiation (40 kV and 40 mA) and secondary monochromation. Data collection was carried out in the 2θ range 3-50°, with a step size of 0.02°. Phase identification was made by searching the ICDD powder diffraction file database, using JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds. The morphology of zeolites LTA and HEU was studied with a ZEISS EVO50 scanning electron microscope, under the following analytical conditions: I probe 1 nA, EHT = 20.00 kV, beam current 100 μA , Signal A = SE1, WD = 8.0 mm. Fourier transform infrared (FT-IR) spectroscopy was carried out by using a Mattson Genesis II FT-IR spectrometer in the 4000-400 cm^{-1} region. However, it is discussed only the 1200-400 cm^{-1} region, because it is where spectra showed remarkable changes. Thermogravimetric and differential thermal analyses were performed on a Mettler Toledo TG 50 thermobalance. Samples of 15-20 mg were heated under nitrogen gas flow (20ml/min) between 25-700 °C at a rate of 20 °C/min.

2.3 Preparation of synthetic solutions

Synthetic polluted solutions were prepared weighting 50 mg l^{-1} of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 25 mg l^{-1} of NH_4Cl , which were dissolved in distilled water to formulate artificially polluted stock solutions (1000 mg l^{-1}) used to make up solutions containing the selected metals.

2.4 Batch experiments and water analysis

Adsorption of heavy metals and ammonium onto different inorganic exchangers (zeolites LTA and HEU) were conducted to investigate their efficiency to clean-up wastewater effluents. Sorption tests were carried out in high density plastic polyethylene containers with a volume capacity of 100 ml through batch type reactions at room temperature, by using a given sorbent dose (sorbent:solution mixture of 0.25 g/20 ml) and the suspension was kept in a rotary shaker with a constant agitation speed of 150 rpm for a given time interval. In these experiments the sorbent:liquid ratio was varied to investigate effects of variation of sorbent dose on the metal retention of selected metals with the sorbent. Each sorbent/solution sample was

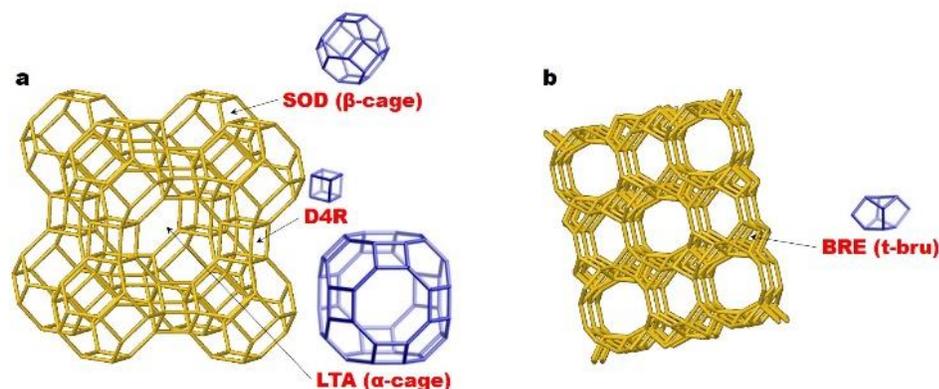
individually placed in separate containers and at scheduled times each container was removed from the shaker and the filtrate collected by filtering the suspension with a 0.45 μm membrane filter, and finally pH and EC measured. Resultant leachates were kept in a refrigerator at 4 $^{\circ}\text{C}$ for ICP-AES. All measurements were done according to Standard Methods for the Examination of Water and Wastewater. Analysis of synthetic solutions and leachates obtained after batch experiments were initially performed using pH (pH 211 Autocalibration bench pH/mV meter - Hanna instruments) and electrical conductivity - EC (Conductivity meter - version Cond 315i - WTW). Dilutions were made using distilled water depending on the original EC of each sample. The equilibrium concentration of heavy metal ions was measured by using a Spectro Ciros ICP-AE Spectrometer. A Photometer 7100 fully integrated with the Palintest water test system was used to measure ammonium over ranges 0-1.0 mg/l N.

3. RESULTS AND DISCUSSION

As shown in Figure 2a, zeolite LTA has a three-dimensional pore structure, which is composed of SOD (β -cages) connected through double four-membered rings (D4Rs) of $[\text{SiO}_4]_4^-$ and $[\text{AlO}_4]_5^-$; by this connection, three cages are present: D4Rs, SOD (β -cages), and LTA (α -cages) [47]. The pore diameter is defined by an eight member oxygen ring and is small at 4.2 \AA , which leads into a larger cavity of minimum free diameter 11.4 \AA [48]. The general chemical formula of zeolite LTA is $\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})27\text{H}_2\text{O}$ [49], with a cubic unit cell, space group Pm-3m [50] and Si/Al ratio ranging from 1.0 to 1.7 [51]. As shown in Figure 2b, zeolite HEU possesses a two-dimensional structure [52], which is characterized by tetrahedral SiO_4 and AlO_4 units and contains three sets of intersecting channels; two channels are parallel to the c-axis (A channels are formed by strongly compressed 10-rings (M10Rs) - aperture 3.1x7.6 \AA and B channels are confined by 8-rings (M8Rs) - aperture 3.6 x 4.6 \AA), whereas C channels are parallel to the a-axis and they are also formed by M8Rs - aperture 2.6x4.7 \AA) [53]. The general chemical formula of zeolite HEU is $(\text{Na},\text{K})_6\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 20\text{H}_2\text{O}$ [50], with a monoclinic unit cell, space group C2/m [50] and Si/Al ratio ranging from 4.0 to 5.3 [54].

Figure 2. The structural frameworks of zeolites (a) LTA and (b) HEU, showing their characteristic cages and channels (adapted and modified after Baerlocher et al. [50]).

Figura 2. Las estructuras de las zeolitas (a) LTA y (b) HEU, mostrando sus jaulas y canales característicos (adaptado y modificado después de Baerlocher et al. [50]).



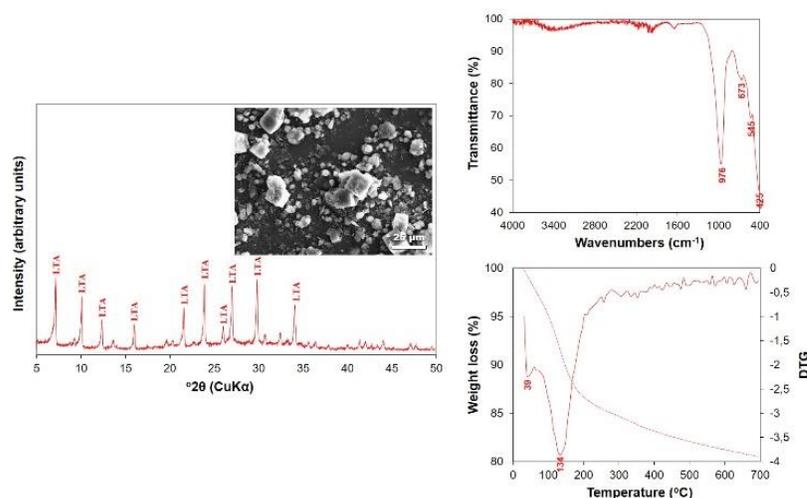
Source: Adapted and modified after Baerlocher et al. [50].

Fuente: Adaptado y modificado después de Baerlocher et al. [50].

3.1 Characterization of sorbents

As shown in Figure 3, zeolite LTA has several common peaks of moderate intensity located at 7.14° , 10.10° , 12.38° , 16.20° , 21.58° , 23.92° , 27.00° , 29.82° and 34.08° 2θ on its XRPD pattern in agreement with Ríos, et al. [46]. The SEM micrograph shows the typical cubic morphology of the zeolite LTA, which is similar to that reported in previous studies [46,46,55]. It locally displays fluorite-type interpenetration twinning, which indicates that it is a thermodynamically metastable phase that was successively replaced by more stable phases, such as sodalite and cancrinite [43,47,56]. According to the FT-IR spectrum, characteristic vibration bands of the zeolite LTA at 976 cm^{-1} due to the internal vibration of (Si,Al)-O asymmetric stretching, 673 cm^{-1} due to the internal vibration of (Si,Al)-O symmetric stretching, 545 cm^{-1} due to the external vibration of D4Rs, and 425 cm^{-1} due to the internal linkage vibrations of the TO4 (T=Si or Al) tetrahedra [47,57] were observed. The band related to OH (not shown in the spectrum) also appeared at about 1635 cm^{-1} [58]. The TGA/DTG curves of the zeolite LTA show up to two dehydration steps; the position of the DTG peaks and the number of dehydration steps can be attributed to the different compensating cation-water binding energies as well as to the different energy associated with the diffusion of the desorbed water through the porous structure of the zeolite LTA [59]. The peak observed at 39°C corresponds to surface water in the zeolite LTA and the peak observed at 134°C indicates zeolitic water.

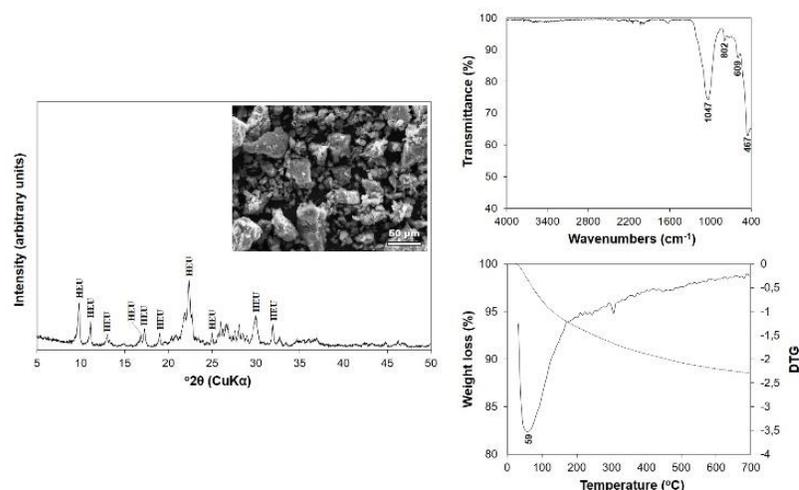
Figure 3. XRPD pattern, SEM image, FT-IR spectrum and TGA/DTG curves of the zeolite LTA.
Figura 3. Patrón XRPD, imagen SEM, espectro FT-IR y curvas TGA / DTG de la zeolita LTA.



Source: Authors.
Fuente: Autores.

As shown in Figure 4, the XRPD pattern of the zeolite HEU is quite similar to that reported for this framework type [50]. The SEM micrograph shows a tabular morphology of the zeolite HEU, with crystals having monoclinic symmetry and some of them with tabular and blocky morphology as reported in previous studies from [60]. The characteristic peaks of the zeolite HEU correspond to vibration bands at 1047 (asymmetric T-O stretching vibrations), 802 (symmetric T-O stretching vibrations), 609 (4- or 6-membered double rings) and 467 (bending vibrations of T-O) cm^{-1} . Vibration bands at 3436 (hydroxyl groups Si-OH-Al) and 1980 and 1616 (deformation vibration of the adsorbed water) cm^{-1} are not shown in the FT-IR spectrum. However, FT-IR vibration bands are in agreement with Mansouri et al. [61]. The TGA/DTG curves obtained for the zeolite HEU showed major and rapid mass loss between 25 and 200°C , with slower and less significant mass loss at higher temperatures. The peak observed at 59°C corresponds to surface water in the zeolite HEU.

Figure 4. XRD pattern, SEM image, FT-IR spectrum and TGA/DTG curves of the zeolite HEU.
Figura 4. Patrón XRPD, imagen SEM, espectro FT-IR y curvas TGA / DTG de la zeolita HEU.



Source: Authors.
Fuente: Autores.

3.2 Sorption of heavy metals and ammonium from synthetic polluted solutions

The sorption process considered here refers to a sorbent (zeolites LTA and HEU) and a polluted aqueous media containing dissolved metal ions and ammonium to be sorbed. There is a strong affinity of the sorbent for the metal ions, which are attracted into the sorbent and bound there by different mechanisms. The objective of this laboratory investigation was to evaluate the heavy metal and ammonium removal during the treatment of an artificially polluted solution in order to compare the capacity and selectivity of zeolites LTA and HEU during the treatment process and to confirm that they have an advantage over other ion exchangers taking into account their much lower cost and ion selectivity. Table 1 summarizes the values of pH, EC and concentration of heavy metals and ammonium of an untreated artificially polluted solution and those of the leachates obtained by using a sorbent:solution mixture of 0.25 g/20 ml during 300 min.

Table 1. pH, EC and concentration of heavy metals and ammonium.

Tabla 1. pH, CE y concentración de metales pesados y amonio.

Contact time (min)	pH	EC (μS m ⁻¹)	T (°C)	Heavy metal concentration (ppm)					Ammonium (mg l ⁻¹)
				Cu	Pb	Zn	Cr	Ni	
SPS	4.94	266	22.6	12.59	30.26	12.23	7.43	11.09	7.8
<i>Batch reaction of zeolite LTA</i>									
5	8.81	289	21.5	0.02	0.05	0.03	0.04	0.05	0.9
10	9.25	301	21.7	0.02	0.05	0.02	0.04	0.05	0.8
30	9.35	305	21.8	0.02	0.06	0.03	0.04	0.06	1.2
45	9.44	323	21.8	0.02	0.07	0.02	0.04	0.05	1.1
60	9.33	321	21.7	0.02	0.06	0.03	0.04	0.05	1.0
120	9.49	360	21.8	0.02	0.05	0.03	0.04	0.05	0.9
180	9.42	402	22.2	0.02	0.04	0.02	0.03	0.04	1.0
240	9.28	402	22.3	0.00	0.01	0.01	0.03	0.03	0.8
300	9.06	414	22.9	0.00	0.01	0.01	0.02	0.03	0.9
<i>Batch reaction of zeolite HEU</i>									
5	5.82	282	21.6	6.1	2.27	9.00	1.02	8.61	3.9
10	5.89	277	21.6	6.72	1.59	8.87	1.19	8.37	2.8
30	5.91	280	21.7	6.69	0.81	8.61	1.17	8.23	3.2
45	5.9	284	21.5	6.43	0.33	8.35	0.99	8.33	2.3
60	5.97	281	21.8	5.81	0.21	7.67	0.82	7.88	4.4
120	6.26	289	22.0	4.31	0.04	7.11	0.50	7.84	2.0
180	6.05	293	22.2	4.38	0.01	6.77	0.54	8.01	1.7
240	6.12	297	22.4	4.69	0.03	6.97	0.6	8.21	1.8
300	5.98	288	22.9	3.92	0.01	6.38	0.34	8.02	1.7

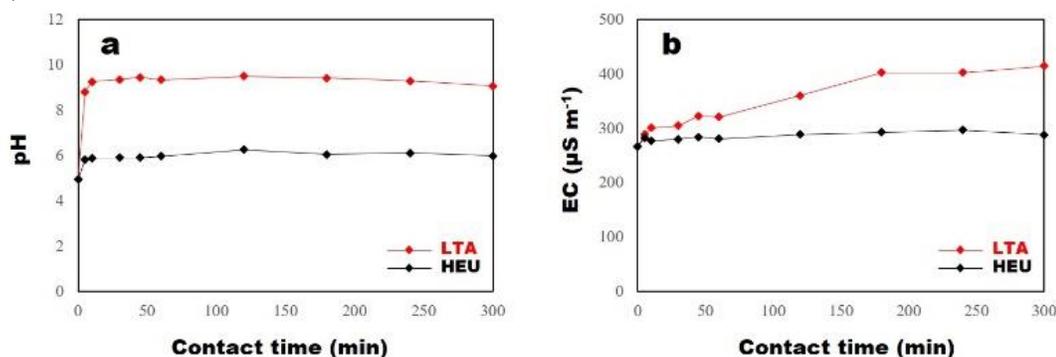
Source: Authors.
Fuente: Autores.

Kinetics of the neutralization reaction

Neutralization is generally the first step in wastewater treatment. Therefore, the kinetics of the neutralization reaction was investigated by monitoring the pH and EC (Figure 5) of sorbent:synthetic polluted solution mixtures (0.25 g/20 ml) over a period of 300 min. A very rapid increase of the initial pH (4.94) of the contaminated solution occurred on contact with zeolite LTA (8.81) and zeolite HEU (5.82) within the first 5 min of contact time as shown in Figure 5a, which can be attributed to an ion exchange process, which incorporates protons into the zeolite within the first minutes of the process, and the hydrolysis of species present in zeolites [62]. The increase of the pH in the acidic pH-range could mainly be attributed to the binding of the protons to the Lewis basic sites of zeolites, and to a lesser extent to the H^+ absorption through ion exchange reactions [62-64]. The reaction rates decrease as equilibrium is approached. pH can increase as a consequence of the progressive dissolution of the sorbent during the shaking process, and it can decrease due to the release of relict organic matter. Breakthrough to alkaline pH was obtained at 5 min of contact time with zeolite LTA, whereas zeolite HEU failed to neutralize the contaminated solution, although both zeolites produced similar pH trends. The reaction rates decrease as equilibrium is approached. pH was stabilized after 30 min of treatment of the contaminated solution using zeolites LTA and HEU as sorbents. Final pH values (9.06 for zeolite LTA, and 5.98 for zeolite HEU) are similar to those obtained after batch experiments by Ríos [43], which have been attributed to hydrolysis of zeolites as well as cationic exchange [65]. pH increase is almost unavoidable in a zeolite - heavy metal system [66-67]. EC (Figure 5b) ranges from 289 to 414 $\mu S\ cm^{-1}$ (zeolite LTA) and from 282 to 288 (zeolite HEU) $\mu S\ cm^{-1}$. A slight increase in EC was observed during the first 5 min for all batch experiments, indicating that very soluble material dissolved very quickly resulting in a rapid and irregular increase in EC during the initial contact sorbent: synthetic polluted solution. After 30 min of reaction, EC values maintained fairly stable for the rest of the time intervals when zeolite HEU was used, whereas zeolite LTA promoted a regularly and systematically progressive increase in EC. After an initial very rapid increase in EC, the release of solutes to the solution slows down during further reaction [68]. However, this study should be complimented to determine whether the decrease in metal concentration is due to cation exchange or to solid precipitation. Adsorption is thus ascribed to be a surface effect rather than involving incorporation into the channels of the zeolite structure [69].

Figure 5. pH (a) and EC (b) variation as a function of time during the adsorption batch experiments with starting pH of 4.94 and EC of 266 $\mu S\ m^{-1}$, sorbent dose of 0.25 g, and SPS volume of 20 ml. SPS, synthetic polluted solution.

Figura 5. Variación de pH (a) y CE (b) en función del tiempo durante los experimentos por lotes de adsorción con pH inicial de 4,94 y CE de 266 $\mu S\ m^{-1}$, dosis de sorbente de 0,25 g, y volumen de SCS de 20 ml. SCS, solución contaminada sintéticamente.



Source: Authors.

Fuente: Autores.

Heavy metal removal

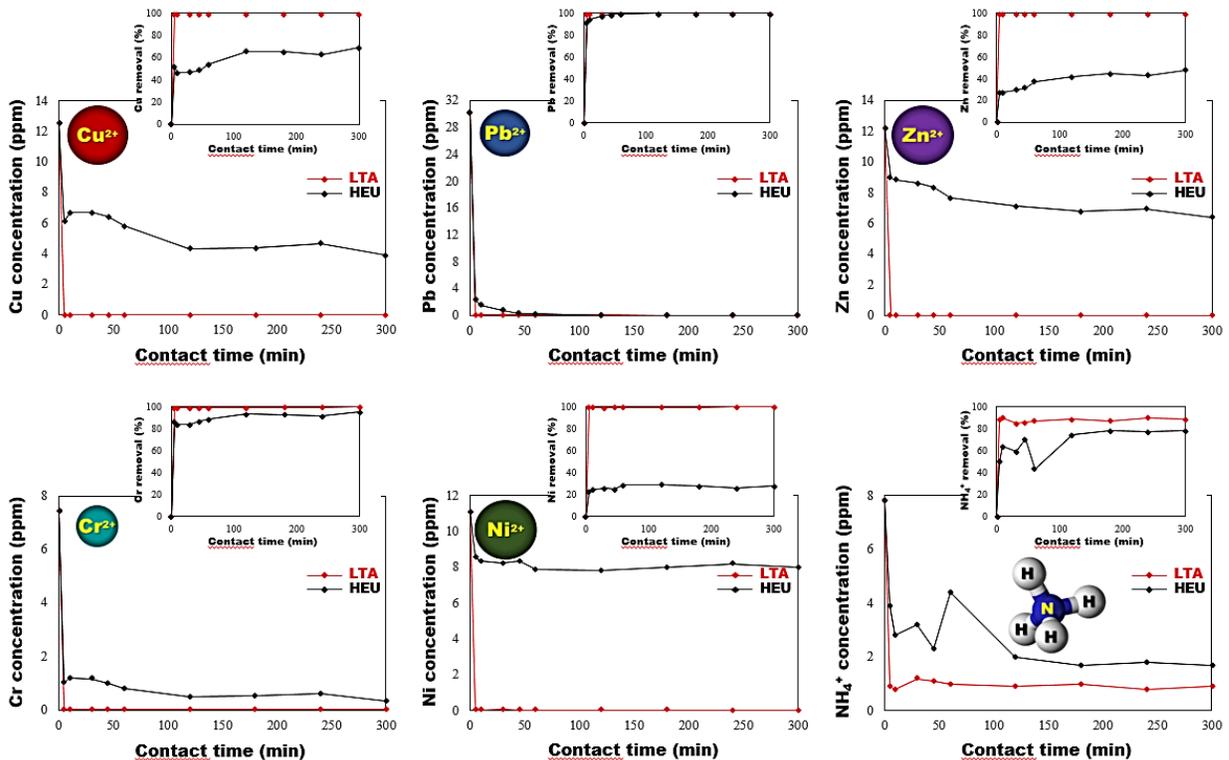
Zeolite LTA produced similar trends of Zn and Ni (Figure 6) with an abrupt decrease after the first 5 min of contact time, followed by a slight increase until 2 h, reaching very stable behavior after this time. On the other hand, using zeolite HEU, a sudden decrease in Zn and Ni after the first 5 min of contact time was followed by a progressive decrease, although showing the highest residual concentrations of these metal ions, which reveals the poor efficiency of HEU to remove Zn and Ni. Cu concentration is characterized by a steep decrease after the first 5 min of contact time, using all sorbents, reaching very stable behavior after 1 h, although with zeolite HEU showing a poor efficiency to remove Cu and slight fluctuations in concentration. Cu probably was almost totally removed after longer reaction times using zeolite LTA but not when zeolite HEU was used. In the case of Cr, an abrupt decrease was obtained after the first 5 min of contact time, followed by a progressive slight decrease until 1 h, when it tended to stabilize. However, during this period zeolite HEU produced slight fluctuations in concentration. The removal efficiency for Cr is in the following order zeolite LTA > zeolite HEU. Pb showed a steep decrease after the first 5 min of contact time using both sorbents, followed by slight fluctuations in concentration for the remaining time intervals, with zeolite LTA and zeolite HEU showing the higher and lower efficiency, respectively, to remove Pb. In general, zeolite LTA produced high metal removal efficiencies compared with zeolite HEU. Metal ion removal behaved distinctly when zeolite HEU was used, although Pb showed a different removal pattern, taking into account that this sorbent showed the best efficiency of Pb removal, with the lowest residual concentrations; zeolite HEU exhibited a slightly higher affinity for Pb respect to Cr, Cu, Zn and Ni. The following heavy metal and ammonium removal ranges were obtained for the zeolites LTA and HEU, respectively: Cu (100-69%); Pb (100% in both zeolites); Zn (100-48%); Cr (100-95%); Ni (100-29%); NH_4^+ (90-78%). Metal ions were rapidly removed by zeolites LTA and HEU after 30 min with 99-100% and 22-92% of removal achieved for zeolites LTA and HEU, respectively, after the first 5 min of contact time. However, zeolite HEU produced lower heavy metal removal (28-69%) for Cu, Zn and Ni, 95% for Cr and 100% for Pb. Therefore, the competition for sorbent adsorption sites in the presence of Pb produced a decrease in the uptake of the other metal ions. No significant adsorption was observed after 1 h. On the other hand, the low efficiency of zeolite HEU used in this study on the removal of heavy metals can be explained by the presence of impurities, the coarser particle size, the difference between the relative cationic radius of metal and the porous diameter of the zeolite. In general, as solution pH abruptly increases after the first 5 min of contact time, the heavy metal removal also increases due to the low competition between H^+ ions with heavy metal cations for the same exchange sites [70]. The abrupt decrease in heavy metal concentration after the first 5 min of contact time can be explained as a consequence of a very fast diffusion of the metal species from the aqueous solution to an ion exchange site of the sorbents. However, some metals may be removed to a greater extent than others with more favourable equilibrium partitioning if the latter diffuse slower [40]. The removal of all metal ions occurred very quickly (after the first 5 min of contact time) at the initial stage of sorption and no appreciable increase was observed beyond this time which proves the saturation of the active sites in the sorbents. It was also observed that under the experimental conditions, the removal of heavy metals by zeolite HEU is much slower and the sorption of these metal ions after 1 h is of little significance. For zeolite HEU, the results demonstrate that around 90% of the metal ions are removed in the first 5 min. On the other hand, the retention efficiency of the metal ions is in the order $\text{Pb} > \text{Cr} > \text{Cu} > \text{Zn} > \text{Ni}$, which is in agreement with the results obtained by Zamzow et al. [71]. According to Shaheen et al. [72], Pb, due to its chemical properties, can be sorbed stronger than other heavy metals, thus representing a lesser threat to wastewaters.

In spite of the several factors that can affect the heavy metal removal of zeolites, the particle size is very important because it strongly control the rate and sorption capacity [41], taking into account that smaller particles can adsorb significantly more metal ions and have larger surface area and shorter pores than larger particles. The uptake of heavy metals increases when pH increases from 4.94. Given the behaviour of the zeolitic materials tested for heavy metal retention, they could be considered as low-cost sorbents for

wastewater treatment, although the use of natural zeolites (e.g., zeolite HEU), which have relatively low ion exchange capacity would require their modification by physical or chemical methods to improve their ion exchange capacity. However, the interpretation given above on the uptake of heavy metals by the sorbents by ion exchange may not represent the most important process to be considered. Therefore, it is necessary to highlight at this point that the pH of the artificial polluted solution has a strong influence on the heavy metal removal, as a consequence of surface charge of the adsorbent (Figure 6). The uptake of heavy metal ions removed from solution increases abruptly from pH 4.94 to pH 8.81 (zeolite LTA) and 5.82 (zeolite HEU) after the first 5 min of contact time, with a complete removal of heavy metals, except in the case of zeolite HEU (lowest efficiency of uptake of heavy metals), and for the rest of the time intervals (with pH remaining almost constant), there was not a gradual increase on metals uptake due to the complete removal. In general, the amount of heavy metal ions removed from solution increased as the pH increased. Therefore, the change of pH in solution with the addition of the sorbents has a strong influence in the uptake of metal ions as a consequence of the immediate increase in alkalinity, causing (almost certainly) the precipitation of hydroxyl-metal complexes onto the surface of the sorbents.

Figure 6. Heavy metal and ammonium concentration and removal as a function of time during the adsorption batch experiments with starting pH of 4.94 and EC of $266 \mu\text{S m}^{-1}$, sorbent dose of 0.25 g, and SPS volume of 20 ml. SPS, synthetic polluted solution.

Figura 6. Concentración y eliminación de metales pesados y amonio en función del tiempo durante los experimentos de adsorción por lotes con un pH inicial de 4,94 y una CE de $266 \mu\text{S m}^{-1}$, una dosis de sorbente de 0,25 g, y un volumen de SPS de 20 ml. SCS, solución contaminada sintéticamente.



Source: authors.

Fuente: Autores.

Ammonium removal

The removal of the ammonium from aqueous solution using zeolites LTA and HEU is due to the ion exchange reaction between NH_4^+ (solution) and Na^+ (zeotypes), although the presence of other cations (K^+ , Ca^{2+} or Mg^{2+}) in the solution decreased the uptake of ammonium due to cation competition [73]. Figure 6 shows the ammonium trends are characterized by strong fluctuations after 1 h. An abrupt decrease in NH_4^+ concentration from 7.8 to 0.9 (zeolite LTA) and 3.9 (zeolite HEU) mg l^{-1} was observed within the first 10 min, which can be explained by an increase in concentration of other exchangeable metal cations (Na^+ , K^+ , Ca^{2+} or Mg^{2+}) with a simultaneous strong absorption of NH_4^+ by the sorbent. From 10-30 min a sudden increase in NH_4^+ concentration occurred as a consequence of ion exchange, mainly with Na^+ and K^+ . Finally, a progressive decrease in concentration with reaction time is related to NH_4^+ adsorption to the sorbent surface. A different NH_4^+ uptake was found between the tested zeolites at shorter reaction times (< 2 h), with the following order of removal efficiency for NH_4^+ : zeolite LTA $>$ zeolite HEU. At longer reaction times (> 2 h), no difference in the pattern of NH_4^+ uptake was observed with the following order of removal efficiency for NH_4^+ : zeolite LTA $>$ zeolite HEU, although a complete removal of ammonium after 300 min was not obtained using these sorbents, with zeolite LTA producing the smallest residual concentrations. The selectivity order of ammonium ion over other cations would depend on the ion exchange capacity of the zeolitic material. There are several factors that influence the sorption capacity of the ion exchangers used in this study, such as total capacity, concentration and type of ions to be sorbed, site accessibility, pH variation, temperature and agitation rate [74]. On the other hand, Hendricks [75] described additional aspects playing very important roles in the reaction between specific sorbents and the aqueous medium, which include competing ions and interactions between sorbent and metal ions. In addition to the exchangeable metal contaminants to be removed, there are other species which interfere with the ion exchange process by competing for available exchange sites on the ion exchanger. This may adversely affect the process and therefore it is beneficial to investigate the effect of competing ions on the metal loading onto a given ion exchanger. It is also important to understand the dynamics involved in the reaction in the sorbent-solution interface, which should consider reactions such as ion exchange, surface hydrolysis, hydration, competing exchange reactions between metal ions in solution and free hydronium ions (H^+).

The role of competing cations on the performance of zeolites in wastewater treatment is still little known [66,76-78]. The effect of competing cations on the uptake of heavy metals has been evaluated by Wingenfelder et al. [77], with uptake of some heavy metals only slightly influenced, whereas in others it decreased strongly with increasing Ca concentrations, which is comparable with the results of Kesraoui-Ouki and Kavannah [66], which can be explained by different selectivity and affinity of zeolites for different cations. Experimental data reveal that heavy metals and ammonium removal will depend on the sorbent material and pH, and according to Teutli-Sequeira et al. [78], the presence of Na^+ , Ca^{2+} , Mg^{2+} or NH_4^+ interferes in the sorption of heavy metals by the zeolitic material, and it depends on the chemical nature of the interfering ions as well as on their initial concentration in the contaminated solutions. Table 2 summarizes the results obtained after batch reaction using zeolites LTA and HEU as sorbents.

Table 2. Efficiency and affinity of zeolites towards heavy metals and ammonium, and neutralization.

Tabla 2. Eficiencia y afinidad de las zeolitas hacia metales pesados y amonio, y neutralización.

Sorbent	Efficiency and affinity for heavy metals					Efficiency and affinity for ammonium	Neutralization
	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cr^{2+}	Ni^{2+}	NH_4^+	
Zeolite LTA	High	High	High	High	High	Moderately high	Produced a neutral to basic solution
Zeolite HEU	Moderately low	High	Low	Relatively high	Low	Relatively low, with some inconsistencies due to dissolution processes	Did not neutralized the solution

Source: Authors.

Fuente: Autores.

4. CONCLUSIONS

The removal of heavy metals (Cu, Zn, Cr, Ni and Pb) and ammonium (NH_4^+) from artificial polluted solutions using low-cost adsorbents, such as zeolites LTA and HEU was explored. The adsorption process by zeolites takes place mainly by ion exchange. There are two competing processes involved, release of alkalinity from zeolites and removal of acidity from contaminated solutions. Our experimental data reveal that heavy metals and ammonium removal will depend on the sorbent material and pH. The presence of Na^+ , Ca^{2+} , Mg^{2+} or NH_4^+ play a very important role in the sorption capacity of zeolites. However, to improve removal efficiencies and adsorption capacities of the raw materials used in this study, chemical modifications of these adsorbents should be done. The widespread uses of low-cost adsorbents for wastewater treatment applications are strongly recommended due to their availability, technical feasibility, engineering applicability and cost effectiveness. Results obtained, particularly for short contact times, suggest that the use of zeolites LTA and HEU for adsorption processes might become interesting in other different industrial applications. The heavy metal selectivity of these zeolites was determined as $\text{Cu} > \text{Zn} > \text{Cr} > \text{Ni} > \text{Pb}$, and it also showed a high affinity for ammonium. In general, zeolites LTA and HEU contain considerable amounts of minor phases that partly dissolve during the batch reaction, which may explain the sudden increase or decrease in metal concentration and, therefore, the release rate of these elements is controlled by sorbent dissolution. However, zeolite LTA showed the best efficiency in the removal of heavy metals and ammonium compared with zeolite HEU and, therefore, is a potential adsorbent for the treatment of wastewater. These results could assist in waste management scenarios. However, it will be necessary to design and execute more detailed experiments to explore further applications of adsorbents for wastewater cleaning. In spite of the results obtained in this sorption study, the geochemical modelling can be a very useful tool to assist in the interpretation of the aqueous geochemical data, particularly with respect to speciation of metal ions in an aqueous solution, which significantly affects their interaction with the adsorbent. Several metal ions can be mainly present in solution as mononuclear hydrolysis products, although their species distributions are related to many factors, such as pH, ionic strength, anions and metal ion concentration.

ACKNOWLEDGMENTS

This research was supported by the Programme Alban, 'the European Union Programme of High Level Scholarships for Latin America' (Scholarship No. E05D060429CO), and the Universidad Industrial de Santander (remunerated commission) for funding C.A. Ríos, and has benefited from research facilities provided by the School of Applied Sciences at the University of Wolverhampton. We thank to Dr. David Townrow and Mrs. Barbara Hodson for assistance with analytical data acquisition.

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