Application of Illite- and Kaolinite-Rich Clays in the Synthesis of Zeolites for Wastewater Treatment

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1. Introduction

Water is the source of life and is the basic condition of human survival. However, the severe water contamination and insufficient water source are nowadays two thorny problems. Industrial effluents are contaminated with highly toxic, non-biodegradable and cancerogenic heavy metals, which are generated by industries such as electroplating, mineral processing, galvanization plants, paints formulation, porcelain enameling, nonferrous metal and vegetable fat producing industries (Meena et al., 2005). Due to the discharge of large amounts of metal-contaminated wastewater, the electroplating industry is one of the most hazardous among the chemical-intensive industries (Pereira et al., 2010). If not carefully managed, however, wastewater may produce both short- and long-term effects on human health and the ecological system. In many developing countries there are deadly consequences associated with exposure to contaminated water, as many developing countries have increasing population densities, increasingly scarce water resources, and no water treatment utilities. Therefore, there are huge challenges all over the world regarding the handling of waste water for a sustainable future.

The processes of dissolution, transport and immobilization of heavy metal ions are very important in environmental science and technology. Many industrial processes involve solubilisation of heavy metal ions to aqueous solutions which then are released into the environment via wastewater; as heavy metal ions persist in the environment, an effective protection strategy requires the ions to be sequestered from the wastewater (Nestle, 2002). Several treatment technologies for wastewater treatment, including chemical precipitation, electrodeposition, ion exchange, membrane separation and adsorption, have been developed (Diz & Novak, 1998; Webster et al., 1998; Feng et al., 2000; Mohan & Chander, 2006; Chartrand & Bunce, 2003; Santos et al., 2004; Gibert et al., 2005; Johnson & Hallberg, 2005; Watten et al., 2005; Wei et al., 2005; Kalin et al., 2006; Ríos et al., 2008), although adsorption has been the preferred method for heavy metal removal, because it is considered to be a particularly effective technique if it takes in consideration the use of suitable, cheap, and environmentally friendly sorbent materials. Heavy metal removal from electroplating wastewater have been investigated by several researchers (Algara et al., 2005; Sousa et al., 2009). 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 counter ion (metal ion), ion hydration, varying metal solubilities, presence of competing and complexing ions, all affect the amount of metal ion to be adsorbed (Ikhsan et al., 1999) and therefore the sorbent selectivity.

One of the biggest advantages of clays that have to be used as raw materials in the synthesis of zeolites is their relatively low cost, which allows applications to be industrially feasible. Clays, such as clay minerals such as kaolinite (Breck, 1974; Barrer, 1982; Boukadir et al., 2002; Ríos, 2008; Ríos et al., 2009, 2011), halloysite (Klimkiewicz & Drag 2004; Zhao et al., 2010), illite (Mezni et al., 2011), montmorillonite (Song & Guo, 1997; Ruiz et al., 1997; Cañizares et al., 2000; Boukadir et al., 2002), vermiculite (Johnson & Worrall, 2007), serpentine (Saada et al., 2009) and interstratified illite-smectite (Baccouche et al., 1998), have been used as the Al and Si sources for the synthesis of several types of zeolites.

Due to their exceptional properties, zeolites have been widely used as catalysts, adsorbents and ion exchangers (Breck, 1974). Numerous types of adsorbents such as organic and inorganic materials have been tested for their ability to remove heavy metals. Water researchers are seeking cheaper raw materials low-cost sorbents such as clay-based zeolites with application in the uptake of heavy metals from polluted effluents. Such adsorbents would be a viable replacement or supplement to chemicals, although they should be readily available, economically feasible, and should be regenerated with ease. The potential use of clay-based zeolites in the treatment of wastewater has been evaluated by a number of research groups (Bhattacharyya & Gupta, 2008; Jamil et al., 2010; Ibrahim, 2010).

The aims of this study are to combine two areas of expertise, water science and clay minerals and zeolites chemistry as well as to address the problem of environmental pollution by removal of heavy metal contaminants.

2. Experimental procedure and materials

2.1 Materials

The natural clays used as starting materials in zeolite synthesis corresponds to illite-rich clay from the Barroblanco mine, situated in the municipality of Oiba (Santander), and kaolinite-rich clay cropping out around the Sochagota Lake, Paipa (Boyacá). The raw materials were prepared prior to the synthesis process by drying during 24 h, and pulverized with an agate Mortar grinder RETSCH RM 100. Finally, the samples were sieved and particles of 63 μm selected for zeolite synthesis. Activating was done using the following chemical reagents: sodium hydroxide, NaOH, as pellets (99%, Aldrich) and distilled water. To determine the removal efficiency of Cr^{+3} and Ni^{+2} of the as-synthesized zeolite, a wastewater sample was collected from an electroplating industry located at Bucaramanga (Santander).

2.2 Hydrothermal transformation of clays into zeolites

The synthesis of faujasite-type zeolite from clays was conducted under hydrothermal conditions. An alkaline fusion step was introduced prior to hydrothermal treatment, because it plays an important role in enhancing the hydrothermal conditions for zeolite synthesis. On the other hand, this approach was adopted in this study because larger amounts of aluminosilicates can be dissolved employing this method. Raw and calcined at 900 °C materials were dry mixed with NaOH pellets (starting material/alkaline activator = 1/1.2 in weight) for 30 min and the resultant mixture was fused at 600 °C for 1 h. The alkaline fused product was ground in a mortar and then 4.40 g of this was dissolved in 21.50

ml of distilled water (ratio = 1/4.9) under stirring conditions for 30 min and then the reaction gel was aged for 24 h to form the amorphous precursors. The amount of reagents used for the preparation of the hydrogels was based on previous experimental work developed by Ríos and co-workers (Ríos, 2008; Ríos et al., 2009). Crystallization was carried out by hydrothermal synthesis under static conditions in PTFE vessels of 65 ml at 80°C for different reaction times (6, 24 and 96 h). At the end of the process the solid is separated by filtration, washed thoroughly several times with distilled water until the filtrate pH reduced to less than 10. The precipitated solid dried at 100° C overnight. The dried samples were weighed and kept in plastic bags for characterization.

2.3 Characterization of the raw materials and as-synthesized zeolites

Powder X-ray diffraction patterns of the raw materials and as-synthesized products were recorded with a Philips PW1710 diffractometer operating in Bragg–Brentano geometry with Cu-K α radiation (40 kV and 40 mA) and secondary monochromation. Data collection was carried out in the 2 θ range 3–50°, with a step size of 0.02°. Phase identification was performed by searching the ICDD powder diffraction file database, with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds.

2.4 Sorption tests and water analyses

Clay-based faujasite was studied in laboratory batch experiments to determine its sorption of Cr⁺³ and Ni⁺², which was carried out at room temperature to investigate the efficiency of the as-synthesized zeolite as sorbent material for removing heavy metals from aqueous solution. A weighted amount of sorbent (0.25 and 0.5 g) was introduced in 180 g amber glass bottles, and then a volume of 50 ml of electroplating industry wastewater was added. Later, the sorbent:aqueous solution mixtures were continuously shaken for 24 h, and the temporal evolution of the solution pH and electrical conductivity was monitored. At several scheduled reaction times the bottles were removed from the shaker and the adsorbents were separated by filtration, while the filtrates were stored in a refrigerator for chemical analyses. All measurements were done according to the “Standard Methods for the Examination of Water and Wastewater” (APHA, AWWA, WEF, 2005). The pH and electrical conductivity of the original and treated aqueous solutions were measured using a pH Meter Lab 870 (Schott Instruments) and a 712 conductometer (Metrohm AG), respectively. The metal concentrations were determined using a Perkin-Elmer 372 atomic absorption spectrophotometer. The efficiency of treatment of the electroplating effluent using faujasite was then determined by the following equation:

$$\text{Metal Removal Efficiency} = (C_1 - C_2) / C_1 \times 100,$$

Where C_1 = initial metal concentration and C_2 = metal concentration after treatment.

3. From clays to zeolites

Both clays and zeolites are aluminosilicates, which differ, however, in their crystalline structure. Clays have a layered crystalline structure and are subject to shrinking and swelling as water is absorbed and removed between the layers. Zeolites have a rigid, 3-dimensional crystalline structure consisting of a network of interconnected tunnels and cages. Water moves freely in and out of these pores but the zeolite framework remains rigid. Clays are characterized by two-dimensional sheets of corner sharing SiO₄ and AlO₄ tetrahedra. In these tetrahedral sheets, each tetrahedron shares 3 of its vertex oxygen atoms

with other tetrahedra forming a hexagonal array in two-dimensions. The fourth vertex is not shared with another tetrahedron and all of the tetrahedra point in the same direction. The tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as Al^{+3} or Mg^{+2} , coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the center of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure. Clays can be categorized depending on the way that tetrahedral and octahedral sheets are packaged into layers, and they are commonly referred to as 1:1 and 2:1 clays with t-o and t-o-t layers, respectively. A 1:1 clay would consist of one tetrahedral sheet and one octahedral sheet (e.g., kaolinite, Figure 1a). A 2:1 clay consists of an octahedral sheet sandwiched between two tetrahedral sheets (e.g., illite, Figure 1b), which occurs due to two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet. The crystal structure is formed from a stack of layers interspaced with the interlayers (spaces between the t-o or t-o-t layer packages). In the kaolinite structure, the layer will be electrically neutral (uncharged) and the t-o layers are bonded together only by weak intermolecular forces (van der Waals' bonds). In the illite structure the layer will have a net negative charge and K^+ ions will be attached themselves to clay surfaces in the so-called interlayer sites. In each case the interlayers can also contain H_2O molecules.

Fig. 1. Diagrammatic sketch of the structure of kaolinite and illite.

Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals with open 3D framework structures built of $[\text{SiO}_4]^{-4}$ and $[\text{AlO}_4]^{-5}$ tetrahedra linked to each other by sharing all the oxygen atoms to form cages connected by pore openings of defined size, developing a rich variety of beautiful zeolite structures (Breck, 1974; Barrer, 1982; Szostak, 1989), such as the low-silica zeolites Na-X (FAU, faujasite), with a molar ratio of Si/Al of 1:1. A polymerization (Figure 2) should be the process that forms the faujasite-type zeolite precursors, which contains tetrahedra of Si or Al randomly distributed along polymeric chains that are cross-linked so as to provide cavities sufficiently large to accommodate the charge balancing alkali ions. The faujasite-type zeolite is based on the primary building units (TO_4) where the central tetrahedrally bonded (T) atom is usually either Si^{4+} or Al^{3+} , surrounded by four O^{2-} . The primary TO_4 units can be linked to create secondary building units. In the faujasite-type zeolite, a combination of 4- and 6-rings promoted the formation of the β -cage. The secondary building units consist of n-ring structures, with each corner in the secondary building units representing the center of a tetrahedron. Secondary building units can be linked to form cages or channels within the faujasite structure. The aluminosilicate cages and the 6-rings connect to form a three

dimensional net type structure. The framework of faujasite, consists of sodalite (SOD) cages composed of six 4-rings and eight 6-rings. Therefore, the framework of faujasite consists of β -cages (SOD) and α -cages (supercages); β -cages are linked together by double six-membered rings (D6R) and form the supercages of faujasite, which has a diameter of 13.0 Å, is surrounded by 10 β -cages and is interconnected to four other supercages by tetrahedrally disposed 12-membered-ring windows.

Fig. 2. Framework structure of zeolite Na-X (FAU), showing their characteristic cages and channels.

4. Results

4.1 Characterization of the raw clays

As shown in the XRD pattern of Fig. 3a, illite is the predominant mineral phase in the starting material and is identified by a series of basal reflections at 10.1 Å, 4.98–5.01 Å, 3.33 Å, and 2.89–2.92 Å. Similar results have been reported by Mezni et al. (2011). As shown in the XRD pattern of Fig. 3b, kaolinite is the predominant mineral phase, which can be identified by its distinctive reflections at 12.34° and 24.64° 2 θ as reported by Zhao et al. (2004). In both clays quartz was identified by its distinctive reflections at 4.26 Å and 3.35 Å. The 3.35 Å peak of quartz was more intense than the other peaks.

Fig. 3. X-ray diffraction patterns of the raw clays and as-synthesized faujasites.

4.2 Characterization of the clay-based faujasites

As shown in Figure 3, an almost complete transformation of the starting clay-rich materials into faujasite-type zeolite of high purity occurred. However, relictic quartz of the starting materials still remain in the synthesis products. Newly formed compounds dissolved in water more readily than the mineral phases in the starting materials, which have a low velocity of dissolution with the occurrence of some of them as relict phases in the synthesis products. The activation of the starting materials produced a rapid dissolution of the alkaline-fused products only after 6 h of reaction, and the complete disappearance of characteristic peaks of illite and kaolinite, accompanied by the gradual decrease in peak intensity of quartz that persisted in the products obtained. Moreover, the occurrence of faujasite was recorded after 24 h, showing an increase in the intensity of characteristic peaks between 24 and 96 h. Both samples produced a similar zeolite phase (faujasite), except for the fact that kaolinite-based faujasite showed less intense peaks than illite-based faujasite. Therefore, we decide to use the illite-based faujasite in the sorption tests.

5. Effectiveness of illite-based zeolites as sorbent material in heavy metal uptake

5.1 Kinetics of the neutralization reaction

The kinetics of the neutralization reaction was investigated by monitoring the pH and electrical conductivity of faujasite /aqueous solution mixtures (0.25 g/50 ml and 0.50 g/50 ml) over a period of 24 h. The effect of contact time on pH and EC during the sorption experiments for Cr^{+3} and Ni^{+2} is shown in Figure 4. Results reveal that the adsorption process of these heavy metals by faujasite was highly pH-dependent and increased with increasing pH conditions. pH increased rapidly within the first 5 min of contact between the solution and the sorbent (illite-based faujasite), and then it thereafter become stable (Figures 4a and 4b). According to Genç-Fuhrman et al. (2007), pH increases mainly due to dissolution of the sorbent in the process of shaking. Final pH values of 7.58-7.69 for Cr^{+3} and 8.42-8.53 for Ni^{+2} were observed in the batches. This significantly increased pH value during the experiments can be explained by the simultaneous uptake of hydrogen ions by faujasite, the hydrolysis of faujasite and the cationic exchange. Similar results are reported elsewhere with a remark that the pH increase is almost unavoidable in a removal of heavy metals by zeolite, taking into account its alkaline nature. On the other hand, results reveal that there is an increase in pH with sorbent dosage. A similar behavior was observed for EC as shown in Figures 4c and 4d.

5.2 Uptake of Cr^{+3} and Ni^{+2}

Removal of heavy metal ions such as Cr^{+3} and Ni^{+2} from electroplating wastewater has been investigated in order to determine the effectiveness of illite-based faujasite as sorbent material in the immobilization of Cr^{+3} and Ni^{+2} , exploiting the sorption capacity of this zeotype in order to evaluate its potential for the reduction of metal mobility and availability and its possible application for the remediation of wastewater.

The kinetics of adsorption process on porous materials such as zeolites is controlled by three consecutive steps (Mohan et al., 2001; Baniamerian et al., 2009): transport of the adsorbate from the bulk solution to the film surrounding the adsorbent, diffusion from the film to the proper surface of adsorbent, and diffusion from the surface to the internal sites followed by adsorption immobilization on the active sites.

Fig. 4. Variation of pH and electrical conductivity as a function of time during the sorption tests for Cr^{3+} (a-c) and Ni^{2+} (b-d). Starting pH and EC of 3.20 and 43.24 $\mu\text{S}/\text{cm}$ for Cr^{3+} and 6.75 and 142.80 $\mu\text{S}/\text{cm}$ for Ni^{2+} .

Our study of adsorption kinetics of Cr^{3+} and Ni^{2+} ions was performed on faujasite-type zeolite at room temperature over 24 hours. Metal uptake trends as a function of contact time after batch reaction are illustrated in Figure 5. Results indicate that faujasite produced a steep decrease in Cr^{3+} concentration within the first 5 min, reaching very low residual concentrations. However, after 45 min plateau values were reached for the rest of the time intervals, indicating a complete removal. Cr^{3+} shows an abrupt decrease in concentration from 0 to 45 min and tends to stabilize at values between 0.922 and 1.695 mg/L (0.25g of faujasite) and between 0.946 and 1.513 mg/L (0.5g of faujasite). The Cr^{3+} exchange character is irreversible. Ni^{2+} showed an inconsistent variation of concentration between 0 and 360 min, which is revealed by the fluctuations observed during the batch experiments, and tends to stabilize at values between 35,614 and 38,763 mg/L (0.25g of faujasite) and between 47,963 and 50,184 mg/L (0.5g of faujasite). Therefore, a lower sorption of Ni^{2+} was observed which can be attributed to the higher selectivity to Cr^{3+} by illite-based faujasite. In general, the adsorption capacity increase as pH approaches neutral.

Several studies (e.g., Kannan & Rajakumar, 2003) report the apparent increase of the percentage of removal of heavy metals with increase in the dose of sorbent due to the active sites/surface area for the adsorption of metal ions, whereas, at lower sorbent dosage the number of metal ions was relatively higher, compared to availability of adsorption sites/surface area. However, results from this study reveal that there is not a strong difference in percentage of metal ion removal with sorbent dosage. Therefore, it is clear that it is very important to investigate in future studies the optimum dosage of faujasite-type zeolite tested as sorbent material.

Fig. 5. Variation of concentration of Cr^{3+} and Ni^{2+} as a function of time during the sorption batch experiments. Starting concentration 117,300 mg/L for Cr^{3+} and 132,300 mg/L for Ni^{2+} .

According to Jenne (1998), heavy metal cations can be immobilized by zeolites by two mechanisms: ion exchange and chemisorption. Ion exchange involves substitution of ions present in zeolite crystalline lattice by metal ions from the solution (Inglezakis et al., 2002). The type of cation (the position of the cation in the selectivity series) as well as the cation concentration in the solution will determine the ion-exchange efficiency (Mozgawa & Bajda, 2005). Chemisorption results in the formation of stable inner-sphere complexes (Godelitsas, 1999). This is due to the fact that functional groups (mainly OH^-) form strong chemical bonds with metal ions outside the hydration envelope (Jenne, 1998).

As reported in previous studies (e.g. Mozgawa & Bajda, 2005), after zeolite reaches the saturation level of a metal ion sorbed, further pH lowering causes the increase in the zeolite crystalline lattice positive charge, which reduces the zeolite ability of metal cations chemisorption. The proportion of chemisorption and ion-exchange processes depends on pH changes and inherent properties of the metal.

The retention efficiency (for the metals considered) depended, not only on the ionic exchange capacity of the as-synthesized zeolite, but also on the decrease of the acidity induced by the zeolitic product. The retention efficiency of faujasite produced the following ranges: Cr^{3+} (90.53-99.21%, 0.25 g of zeolite, and 88.31-99.19%, 0.5 g of zeolite), and Ni^{2+} (44.74-77.73%, 0.25 g of zeolite, and 62.07-78.30%, 0.5 g of zeolite). Sorption tests reveal that both metal ions were rapidly removed by faujasite within 45 min (Cr^{3+}) and 360 min (Ni^{2+}) with 88.31-90.53% and 63.24-73.54% of the metal removal achieved in the first 5 min for Cr^{3+} and Ni^{2+} , respectively. According to Mozgawa & Bajda (2005), the contribution of chemisorption and ion-exchange processes to the metal immobilization on zeolite depends on the metal type and the reaction

time. In the case of Cr^{+3} and Ni^{+2} , after the first minutes of reaction, it is probably that the chemisorption process becomes more dominant than the ion-exchange process, similar to data reported by Mozgawa & Bajda (2005). Faujasite-type zeolite produced lower Ni^{+2} removal (88.31-99.21%) compared with that for Cr^{+3} (44.74-78.30%). However, the competition for sorbent adsorption sites in the presence of Cr^{+3} produced a decrease in the uptake of Ni^{+2} . No significant adsorption was observed after 45 min (Cr^{+3}) and 360 min (Ni^{+2}) of contact time. According to Peric et al. (2004), the immobilization of heavy metals from aqueous media is a complex process, which consists of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface. On the other hand, the addition of an alkaline material such as faujasite to the electroplating wastewater increased the pH. (7.58-7.69 for Cr^{+3} and 8.42-8.53 for Ni^{+3}) and these metal ions could be hydrolyzed and precipitated as suggested by Evangelou and Zhang (1995). However, the efficiency of the tested sorbent with respect to metal retention and/or metal concentration control during its application for the treatment of metal-bearing aqueous media is governed by parameters like contact time, pH, temperature and sorbent nature as demonstrated in previous studies (Helquet et al., 2000). On the other hand, mechanisms of interactions, such as precipitation and adsorption, between Cr^{+3} and Ni^{+3} and illite-based faujasite are strongly influenced by pH.

6. Conclusions

Natural clays were successfully transformed into highly crystalline faujasite-type zeolite by fusion with NaOH powder followed by hydrothermal treatment. The adsorption studies showed rapid uptake in general for the first 45 min (Cr^{+3}) and 360 min (Ni^{+2}) with 88.31-90.53% and 63.24-73.54% of the metal removal achieved in the first 5 min for Cr^{+3} and Ni^{+2} , respectively. After this initial rapid period, the rate of adsorption decreases. The as-synthesized faujasite proved to have great potential in the immobilization of Cr^{3+} and Ni^{2+} from electroplating wastewater. Results of this work can be also used as a reference for future in depth studies considering alternative technologies applied to remediation of electroplating industry wastewater.

7. Acknowledgments

This research forms part of the background experience of the authors in the field of clay and zeolite technology and has benefited from research facilities provided by the Universidad Industrial de Santander, and the Instituto Zuliano de Investigaciones Tecnológicas. We thank to Miguel Ramos for assistance with XRD data acquisition.

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Earth and Environmental Sciences

Edited by Dr. Imran Ahmad Dar

ISBN 978-953-307-468-9

Hard cover, 630 pages

Publisher InTech

Published online 07, December, 2011

Published in print edition December, 2011

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How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Carlos Alberto Ríos Reyes and Luz Yolanda Vargas Fiallo (2011). Application of Illite- and Kaolinite-Rich Clays in the Synthesis of Zeolites for Wastewater Treatment, Earth and Environmental Sciences, Dr. Imran Ahmad Dar (Ed.), ISBN: 978-953-307-468-9, InTech, Available from: <http://www.intechopen.com/books/earth-and-environmental-sciences/application-of-illite-and-kaolinite-rich-clays-in-the-synthesis-of-zeolites-for-wastewater-treatment>

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