

REMOVAL OF Cr(III) FROM AQUEOUS SOLUTIONS USING ZEOLITE NaY PREPARED FROM RICE HUSK ASH

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Abstract

The efficiency of the synthesized zeolite NaY from rice husk ash (RHA) in the removal of Cr(III) from aqueous solution was studied. Zeolite NaY was synthesized from RHA via seeding technique and the identification of its structure was done by X-ray diffraction (XRD) technique and the elemental analysis was carried out by X-ray fluorescence (XRF). The physicochemical properties which were related to the use of the zeolite NaY as a sorbent was also investigated. The synthesized zeolite NaY has higher cation exchange capacity (CEC) than the commercial zeolite NaY due to the higher amount of sodium content in the synthesized as well as the lower ratio of silica to alumina. The synthesized zeolite NaY together with the commercial one as comparison was used in the sorption of the Cr(III) in aqueous solution by batch sorption experiments. The kinetic study showed that the Cr(III) uptake by both zeolites were based on the pseudo second order model. Synthesized zeolite NaY exhibited greater sorption capacities than the commercial zeolite NaY since the former has higher surface area and cation exchange capacity (CEC) and lower ratio of silica to alumina which have a tendency to provide more exchange sites.

Abstrak

Keberkesanan zeolit NaY yang disintesis daripada abu sekam padi (RHA) untuk menyingkirkan kromium(III) dalam larutan akueus telah dikaji. Zeolit NaY disintesis daripada RHA melalui kaedah pembenihan dan strukturnya dianalisis melalui teknik pembelauan sinar-X (XRD) dan analisis unsur dijalankan melalui teknik sinar-X berpendarflour (XRF). Sifat-sifat fisiko-kimia yang berkaitan dengan penggunaan zeolit NaY sebagai penjerap juga dikaji. Zeolit NaY yang disintesis mempunyai kapasiti penukaran kation (CEC) yang lebih tinggi daripada zeolit NaY komersil disebabkan oleh kandungan natrium yang lebih tinggi kuantitinya dan nisbah silika terhadap alumina yang lebih rendah. Zeolit NaY yang telah disintesis dan zeolit NaY komersil yang dijadikan sebagai perbandingan digunakan untuk menjerap kromium(III) dalam larutan akueus melalui eksperimen secara berkelompok. Kajian kinetik pengambilan kromium(III) oleh kedua-dua zeolit adalah berdasarkan kepada model pseudo-tertib kedua. Zeolit NaY yang disintesis menunjukkan kapasiti penjerapan adalah lebih tinggi berbanding zeolit NaY komersil kerana zeolit NaY yang disintesis mempunyai luas permukaan dan kapasiti penukaran kation (CEC) yang lebih tinggi dan nisbah silika terhadap alumina yang lebih rendah yang menyebabkan ia berkecenderungan untuk mempunyai lebih banyak tapak penukaran.

Introduction

Chromium is one of the transition metals that can exist in oxidation states +2, +3, +4, +5 and +6. The most common, stable and abundant forms are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The Cr(VI) species is more toxic and carcinogenic than Cr(III), however, it is possible that Cr(III) may be oxidized to Cr(VI) in the appropriate condition, hence the toxicity of Cr(VI) takes place. Usually, Cr(III) is readily oxidized to the hexavalent state at high pH [1].

Chromium is an ubiquitous element, not only because of its occurrence in nature, but also due to the many anthropogenic sources resulting from its widespread industrial applications [2]. Chromium and its compounds are used in organic chemical synthesis, leather treatment, photomechanical processing and industrial treatment, including treatment of cooling tower water [3]. As chromium is very widely used, there are many sources of leaching the chromium into the natural water system and it should be removed practically. Recently, a wide range of sorbent is available for the removal of Cr(III) from water including the biosorbents such as brown seaweed biomass [4] and *saccharomyces cerevisiae* [5]. Besides that, the ion exchanger resin in the cation form [6], zeolite [7, 8], bentonite [9] and activated carbon [10] have been used to remove Cr(III) from water.

Zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration [11]. Zeolite NaY is the synthesized zeolite Y of which the sodium cations neutralize the framework structure of aluminosilicate and this material is in the same group with zeolite X. Both zeolites exhibit a structure similar to naturally occurring faujasite types. The synthesis of zeolite NaY requires a source of silica as the main raw material, hence, the rice husk ash which is believed to have high content of amorphous silica was used [12]. In addition, the rice husk is produced in abundance in Malaysia as agro-waste and which needs to reprocess to value added product thus to solve the environmental problem.

The preliminary objective and scope of this study is to synthesis zeolite NaY by using rice husk ash as a source of silica via seeding technique, subsequently characterized it by X-ray diffraction (XRD) technique, X-ray fluorescence (XRF) and the physicochemical properties which are related to the use of zeolite NaY as a sorbent. All of the characterizations were compared to the commercial zeolite NaY. The second objective is to investigate the kinetics parameters and the efficiency of the removal of Cr(III) from aqueous solution by the synthesized zeolite NaY and compared it to the commercial zeolite NaY.

Experimental

Preparation of rice husk ash as a source of silica

The raw material, rice husk was obtained from Bernas (Beras Nasional), Selangor. Rice husk ash (RHA) that was used as a source of silica in the synthesis of zeolite NaY was prepared through physical combustion of the dried rice husk at constant temperature of 600 °C and constant pressure for an hour. Rice husk ash was characterized for its phase using X-ray diffraction (XRD) technique and the elemental analysis by X-ray fluorescence (XRF) and can be readily used as a source of silica in the synthesis of zeolite NaY.

Synthesis of Zeolite NaY

The starting materials employed in the synthesis of zeolite NaY were sodium aluminate supplied by Riedel De Haen, sodium hydroxide pellets from Merck and silica from RHA. The procedure for the synthesis of zeolite NaY was done according to Ginter, D. M. [13] but with different compositions and types of raw materials. Zeolite NaY was synthesis by seeding technique in which the preparation involved three major steps namely the preparation of seed gel, followed by feedstock gel and finally the overall gel.

Batch composition for seed gel is 10.67 Na₂O : Al₂O₃ : 10SiO₂ : 180 H₂O and it contributed 5% from the overall gel composition. Firstly, to prepare the aluminate solution, the prepared NaOH solution was added to the sodium aluminate, followed by stirring and heating gentle until the mixture became an apparent solution. For the preparation of silicate solution, RHA was mixed with the prepared NaOH solution and subsequently stirred and heated in the water bath at boiling water temperature. The aluminate and silicate solution were then mixed in the PTFE beaker and stirred for half an hour to achieve homogenization. Finally, the mixture was transferred to the Teflon bottle and capped for the ageing process to take place by leaving it at room temperature for 24 hours. The preparation of feedstock gel which comprises 95% of the whole gel having the batch composition of 4.30 Na₂O : Al₂O₃ : 10 SiO₂ : 180 H₂O. The procedure for the preparation of feedstock gel was similar to the preparation of seed gel but with different amount of raw materials. Lastly, the overall gel was prepared by mixing the feedstock gel and seed gel. The mixture was then stirred for homogenization and left for ageing for 24 hours. After that, the mixture was heated in an oven at 100 °C for 22 hours. Subsequently, the solid product was separated by filtration, washed and dried for overnight. The solid dried product was sieved to obtain the desired size of zeolite particles and ready to be characterized and use for the removal of Cr(III) from aqueous solutions.

Characterization of zeolite NaY

The synthesized zeolite NaY together with the commercial zeolite NaY was characterized by various characterization techniques. The commercial zeolite NaY was purchased from Zeolyst International (CBV 100). The identification of zeolite NaY structure was determined using X-ray diffraction (XRD) method (Bruker AXS GmbH, German). The X-ray fluorescence (XRF) (Phillips PW 1480 Spectrometer) technique was used to determine the elements present in the zeolites quantitatively. The specific surface area was determined using the instrument QuantaChrome Autosorb-IC. The determination of the unit cell of zeolites was carried out according to the standard test method for the determination of the unit cell dimension of a Faujasite-type zeolite (D 3942-03) provided by the international standard test method (ASTM). The procedure for the determination of total cation exchange capacity (CEC) was based on Chapman, 1965 [14]. The summary of the procedure requires the

zeolite samples to be mixed with an excess of sodium acetate solution, and subsequently washed with isopropyl alcohol and finally, an ammonium acetate solution was then added which replace the adsorbed sodium with ammonium. The concentration of displaced sodium was then determined by flame atomic absorption spectroscopy (FAAS) (GBC, model Avanta, Australia).

Kinetic study

The kinetic study which was based on the effect of stirring time for the Cr(III) removal was carried out via the batch method and with different contact times. The stock solution of 250 and 500 mg/L of Cr(III) was prepared by dissolving an appropriate amount of Cr(NO₃)₃.9H₂O (Merck) in 250 mL distilled deionized water. A constant amount of zeolite samples (0.1000 g) was mixed with 25 mL Cr(III) solution in a 50 mL centrifuge tube. The suspension was shaken for varying periods of time starting from 10 minutes to 48 hours using an orbital shaker with constant agitation rate. The solid phase was then separated by filtration through a Whatman filter paper. The concentrations of chromium in the supernatant solution after adsorption were determined with flame atomic absorption spectrophotometer (FAAS) (GBC, Model Avanta, Australia).

Results and Discussions

Characterization of Rice Husk Ash (RHA)

The XRD pattern of RHA is shown in Figure 1. This diffractogram reveals that the silica present in RHA was completely amorphous to XRD as indicated by the featureless pattern and the absence of significant peaks and the appearance of diffuse maximum at 2θ = 23° typical for amorphous silica [15].

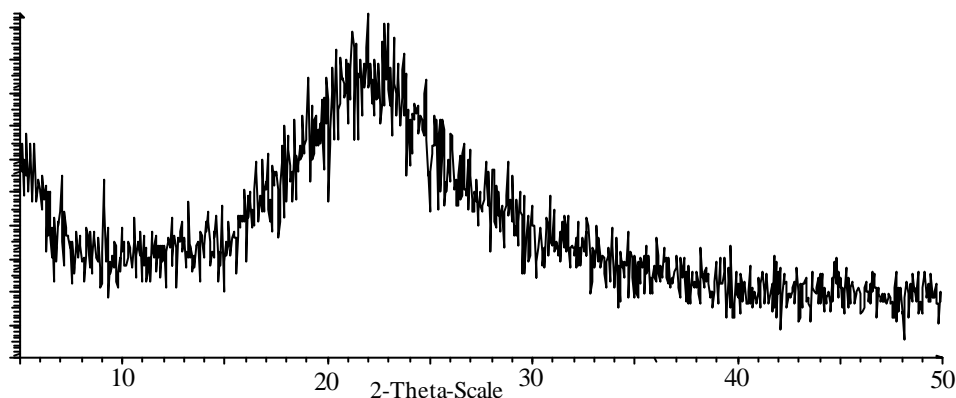


Figure 1. X-ray diffractogram of RHA

The composition of major elements present in the RHA as analyzed by X-ray fluorescence (XRF) technique can be seen in Table 1. The silica content in RHA is somewhat higher because most of the impurities were eliminated during combustion at 600 °C. Since the RHA contains high amorphous silica, thus it can be used as a source of silica for the synthesis of zeolite NaY.

Table 1: Chemical composition of rice husk ash from the XRF technique

Oxide	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I
%	91.65	0.03	0.27	0.27	0.07	0.58	0.58	0.74	0.74	0.19	4.88

Characterization of zeolite NaY

The zeolite NaY with high purity was successfully synthesized from RHA by seeding and ageing techniques without the marked presence of impurities, i.e. zeolite P and A. Figure 2 shows the XRD pattern of the zeolite NaY that was synthesized via these techniques. The diffractogram exhibits many significant peaks from 2θ=5° to 50° indicating that the samples are in the crystalline form. Furthermore, when this pattern was matched up with the peaks corresponding to the zeolite NaY structure as shown in Figure 2, it shows that the product formed from the synthesized zeolite NaY from RHA was high purity zeolite NaY because all of the peaks were well matched with the peaks of zeolite NaY structure. In addition, the diffractogram also demonstrates that no other significant peaks corresponding to other phases emerged which confirmed the absence of impurities and other phases in the synthesized zeolite NaY.

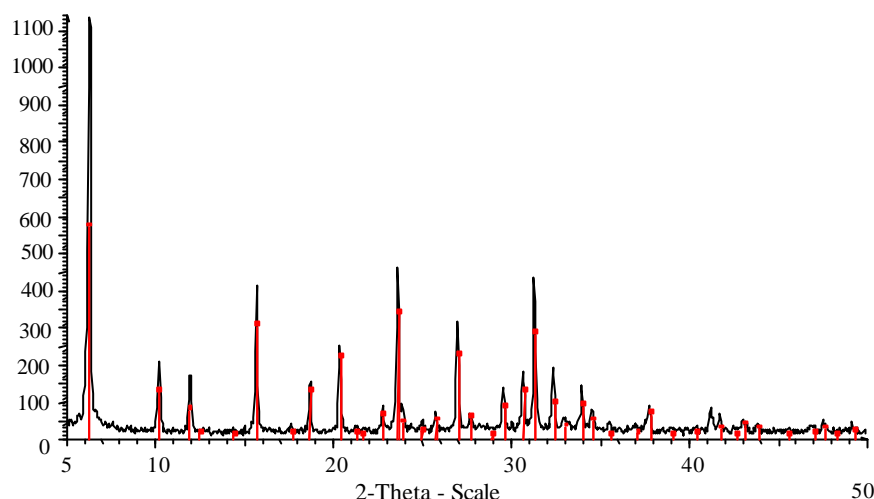


Figure 2.XRD pattern of synthesized zeolite NaY match up with the sodium aluminum silicate hydrate NaY pattern existed in Powder Diffraction Files (PDF).

The quantitative determinations of elements contained in the zeolite samples were carried out using the wavelength dispersive Xray fluorescence (XRF) technique. Table 2 gives the percent amount of major elements in the synthesized and commercial zeolite NaY from the XRF technique.

Table 2. Percentage amount of major elements contained in zeolite samples

Elements	Synthesized Zeolite NaY	Commercial Zeolite NaY
SiO ₂	43.74	47.63
TiO ₂	0.04	0.09
Fe ₂ O ₃	0.17	<0.01
Al ₂ O ₃	18.35	15.66
MnO	0.04	<0.01
CaO	0.45	0.19
MgO	<0.01	0.02
Na ₂ O	12.4	8.47
K ₂ O	0.37	0.03
P ₂ O ₅	0.12	0.06
L.O.I.	24.32	27.85

The information regarding the physicochemical properties of the synthesized and commercial zeolite NaY is very important and essential since the zeolites were utilized as sorbent for Cr(III) from aqueous solution. Table 3 gives a list of the physicochemical properties and respective values for the synthesized and commercial zeolite NaY.

Table 3. Physicochemical properties of the synthesized and commercial zeolite NaY

Physicochemical properties	Synthesized Zeolite NaY	Commercial Zeolite NaY
Unit cell, <i>a_o</i> (?)	24.76	24.70
^a SiO ₂ /Al ₂ O ₃	3.871	4.553
^b SiO ₂ /Al ₂ O ₃	2.384	3.042
Surface area (m ² /g)	506.6	484.9
Cation exchange capacity , CEC (meq/g)	3.150	2.545

Notes: a: from unit cell, b: from elemental analysis

The synthesized zeolite NaY has higher CEC than the commercial zeolite NaY due to the lower ratio of SiO₂/Al₂O₃ since each AlO₄ tetrahedra in the zeolite framework provides a single cation exchange sites.

Removal of Cr(III) Study

In order to accomplish the kinetic study, experiments on the effect of contact time on the Cr(III) removal by the synthesized and commercial zeolite NaY were carried out with two different initial concentrations of Cr(III) which are 250 mg/L and 500 mg/L ranging from 10 minutes to 48 hours. The initial concentration, C_o (mg/L) and metal concentrations at preset time intervals, C_t (mg/L) were determined and the Cr(III) uptake, q (mg Cr(III) sorbed/g zeolite) was calculated from the equation as follows:

$$q = \frac{(C_o - C_t)v}{1000w} \tag{1}$$

where v is the volume of the solution (mL) and w is the mass of the sorbent (g). The uptake values of Cr(III) from the solution as a function of contact time are presented in Figures 3 and 4 for synthesized and commercial zeolite Y, respectively.

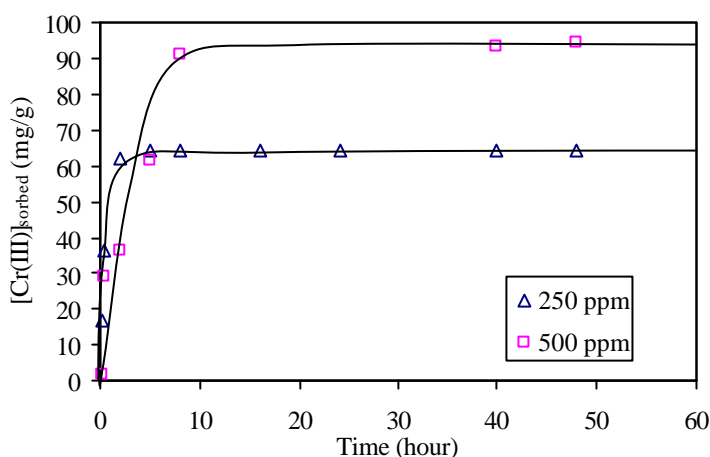


Figure 3. Sorption kinetics graph for synthesized zeolite NaY from two different initial concentrations of Cr(III). (Conditions: 0.1 g sorbents, 25 mL Cr(III) solution)

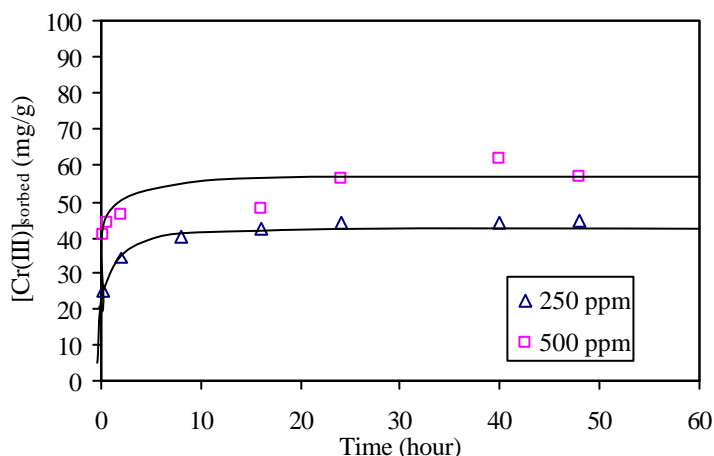


Figure 4. Sorption kinetics graph for commercial zeolite NaY with two different initial concentrations. (Condition: 0.1 g sorbents, 25 mL Cr(III) solution)

As shown in Figures 3 and 4, the Cr(III) removal increases with time and attains equilibrium in 8 hours for both zeolites. This trend emphasizes that sorption times have important effects on the removal efficiency, which increases significantly with increasing zeolites contact time with the Cr(III) solution. This is a consequence of the molecular sieve property of the zeolites where the larger size Cr(III) species needed more time to exchange with sodium cation that is neutralized in the pore of the zeolite framework. At a low concentration (250 mg/L), the duration for the uptake of Cr(III) by the synthesized zeolite NaY to reach the equilibrium state was faster

than the commercial one. In addition, the Cr(III) uptake versus time curves for this initial concentration are single, smooth and continuously leading to saturation, suggesting the possible monolayer coverage of Cr(III) on the surface of the sorbent [16].

In order to compare the efficiency of Cr(III) uptake by both zeolites from different initial concentrations of Cr(III), the percentage of the removal of Cr(III) from the solution as a function of shaking time were performed. The definition of percent removal is as follows:

$$\%removal = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

A plot of the percentage of the Cr(III) removal against contact time is shown in Figures 5 and 6 for Cr(III) initial concentration of 250 mg/L and 500 mg/L, respectively. These figures indicate that the synthesized zeolite NaY is more efficient in removing the Cr(III) species from the aqueous solution than the commercial one. The synthesized zeolite NaY completely removed Cr(III) from the 250 mg/L solution after 8 hours of shaking period while the commercial zeolite NaY removed only 65% of Cr(III) having the same concentration of 250 mg/L. Both zeolites removed only half the Cr(III) species from the initial concentration of 500 mg/L.

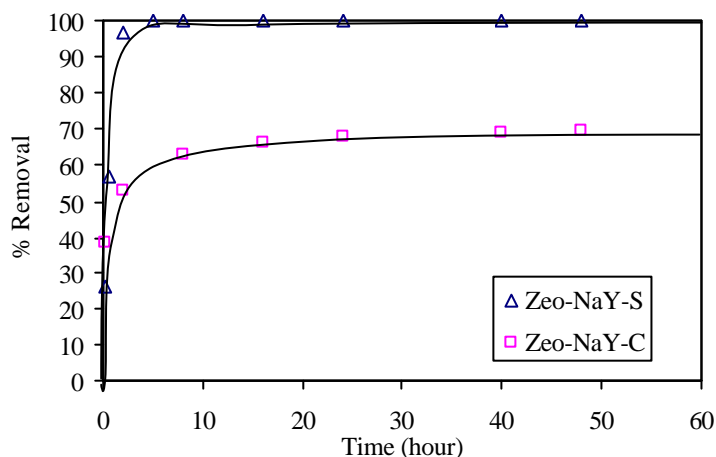


Figure 5. Percentage of the Cr(III) removal by synthesized (Zeo-NaY-S) and commercial zeolite NaY (Zeo-NaY-C) with $[Cr(III)]_{initial} = 250$ mg/L. (Condition: 0.1 g sorbent, 25 mL Cr(III) solution)

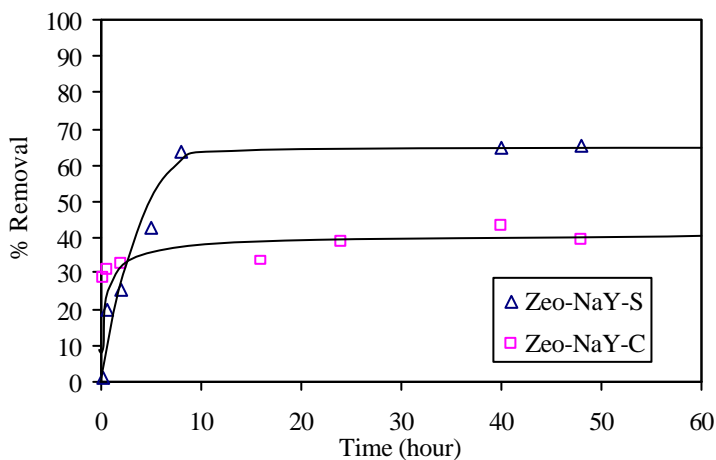


Figure 6. Percentage of the Cr(III) removal by synthesized (Zeo-NaY-S) and commercial zeolite NaY (Zeo-NaY-C) with $[Cr(III)]_{initial} = 500$ mg/L. (Condition: 0.1 g sorbent, 25 mL Cr(III) solution)

Experiments were also established in order to understand the kinetics of Cr(III) removal by both zeolites from two different initial concentrations. The kinetics of sorption describing the solute uptake rate which in turn governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption. Mathematical models that are used most frequently to describe kinetics of sorption in a free suspension in a well agitated batch system are pseudo first and pseudo second order equations [17]. The kinetics of Cr(III) uptake by both zeolites followed the pseudo second order kinetic model since the plotting of the graphs fitted well with this model.

The pseudo second order model is based on the assumption that the sorption follows a second order mechanism and this model is represented by the following expression:

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (3)$$

where $k_{2,ads}$ is the rate constant of second order (g/mg/h) and q_e is the amount of sorbed Cr(III) ions on the sorbent at equilibrium (mg/g). A plot of t/q against time will yield straight lines hence the rate constant and the amount of sorbed Cr(III) cations on the sorbents at equilibrium can be determined. The values of these parameters together with the correlation coefficients for the adsorption of Cr(III) on synthesized and commercial zeolite NaY are listed in Table 4.

Table 4: Values of pseudo second order model parameters for the adsorption of Cr(III) by synthesized and commercial zeolite NaY

Zeolite	[Cr(III)] _{initials} (mg/L)	slope	Y-intercept	r ²	k _{2,ads} (g/mg/h)	q _e (mg/g)
Synthesized	250	0.0154	0.003	0.9999	0.0791	64.9350
	500	0.0102	0.0211	0.9976	0.00493	98.0392
Commercial	250	0.0222	0.0110	0.9997	0.0448	45.0450
	500	0.0167	0.0223	0.9912	0.0125	59.8802

The results from Table 4 prove that the uptake of Cr(III) by the zeolite NaY fitted well with the pseudo second order model since the correlation coefficient (r^2) was higher than 0.99. The sorption capacity of Cr(III) by both zeolites increased with increasing Cr(III) concentrations. The uptake of Cr(III) by synthesized zeolite NaY at equilibrium is higher than the commercial ones for both initial concentrations possibly due to the higher cation exchange capacity (CEC) and surface area of the synthesized zeolite NaY compared to the commercial one.

Conclusions

Rice husk ash (RHA) which contains high quantity of amorphous silica (more than 90%) was prepared by the combustion of dried rice husk at 600 °C for an hour. The amorphous form of RHA was indicated from the XRD diffractogram while the silica content was determined by the XRF technique. The RHA was also reactive towards the synthesis of the zeolite; hence it was used as the source of silica for the synthesis of the zeolite NaY. The high purity of the zeolite NaY has been successfully synthesized from RHA by seeding and ageing techniques. Physicochemical properties that had been studied for the synthesized zeolite NaY from RHA and the commercial zeolite NaY were unit cell, silica per alumina ratio, surface area and cation exchange capacity (CEC). These physicochemical properties were related to the application of the zeolite as a sorbent for Cr(III) in water. It was found that the synthesized zeolite NaY have higher CEC than the commercial ones due to the lower silica/alumina ratio and higher surface area for the synthesized zeolite NaY which tends to give more exchange sites. The kinetic of Cr(III) uptake by both zeolites was based on the pseudo second order kinetic model with the amount of sorbed Cr(III) ions on the synthesized zeolite NaY at equilibrium much higher than the commercial one. The synthesized zeolite NaY sorbed more Cr(III) from aqueous solutions than the commercial one due to the physicochemical properties of the synthesized zeolite NaY which governs the sorbent efficiency. It can be concluded that the zeolite NaY prepared from the rice husk ash is suitable to be used as a sorbent for Cr(III) in water.

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References

- [1] Katz, S. A. and Salem, H. (1993). The toxicology of chromium with respect to its chemical speciation: a review. *J. Appl. Toxicol.* 13(3): 217-224.
- [2] Martinez-Bravo, Y., Roig-Navarro, A. F., Lopez, F. J. and Hernandez, F. (2001) Multielemental determination of Arsenic, selenium and chromium (VI) species in water by high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *J. Chromatogr., A.* 926: 265-274.
- [3] Katz, S. A. and Salem, H. (1994). *The biological and environmental chemistry of chromium*. New Jersey, USA: VCH Publishers, Inc.
- [4] Yun, Y. S., Park, D., Park, J. M. and Volesky, B. (2001). Biosorption of trivalent chromium on the brown seaweed biomass. *Environ. Sci. Technol.* 35: 4353-4358.
- [5] Ferraz, A. I., Tavares, T. and Teixeira, J. A. (2004). Cr(III) removal and recovery from *Saccharomyces cerevisiae*. *Chem. Eng. J.* 105: 11-20.
- [6] Rengaraj, S., Joo, C. K., Kim, Y. and Yi, J. (2003). Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. *J. Hazard. Mater.* B102: 257-275.
- [7] Barros, M. A. S. D., Silva, E. A., Arroyo, P. A., Tavares, C. R. G., Schneider, R. M., Suszek, M. and Aousa-Aguiar, E. F. (2004). Removal of Cr(III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX. *Chem. Eng. Sci.* 59: 5959-5966.
- [8] Bosco, S. M., Jimenez, R. S. and Carvalho, W. A. (2005). Removal of toxic metals from wastewater by brazilian natural scolecite. *J. Colloid Interface Sci.* 281: 424-431.
- [9] Chakir, A., Bessiere, J., Kacemi, K. and Marouf, B. (2002). A comparative study of the removal of trivalent chromium from aqueous solutions by bentonite and expanded perlite. *J. Hazard. Mater.* B95: 29-46.
- [10] Cordero, T., Rodriguez-Mirasol, J., Tancredi, N., Piriz, J., Vivo, G. and Rodriguez, J. J. (2002). Influence of surface composition and pore structure on Cr(III) adsorption onto activated carbons. *Ind. Eng. Chem. Res.* 41: 6042-6048.
- [11] Breck, D. W. and Flanigen, E. M. (1964) *Synthesis and properties of Union Carbide zeolites L, X and Y*. USA: Union Carbide Corporation.
- [12] Yalcin, N. and Serinc, V. (2001). Studies on silica obtained from rice husk. *Ceram. Int.* 27: 219-224.
- [13] Robson, H. (2001). *Verified synthesis of zeolitic materials*. Amsterdam: Elsevier Science.
- [14] Wilson, M. J. (1994). *Clay mineralogy: Spectroscopic and chemical determinative method*. Great Britain: Chapman & Hall.
- [15] Halimatun Hamdan, Mohd Nazlan Mohd Muhid, Salasiah Endud, Endang Listiorini and zainab Ramli. (1997). ²⁹Si MAS NMR, XRD and FESEM studies of rice husk silica for the synthesis of zeolites. *J. Non-Cryst. Solids.* 211: 126-131.
- [16] Namasivayam, C. and Ranganathan, K. (1995). Removal of Cd(II) from wastewater by adsorption on "waste" Fe(III)/Cr(III) hydroxide. *Water Res.* 29: 1737-1744
- [17] Aksu, Z. (2000). Equilibrium and kinetic modelling of cadmium(II) sorption by *C. vulgaris* in a batch system: effect of temperature. *Separation Purif. Technol.* 21: 285-294.