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SYNTHESIS AND CHARACTERISATION OF CERIUM-EXCHANGED ZEOLITES AND ITS APPLICATION IN THE REMOVAL OF ARSENIC FROM WASTEWATER SAMPLES

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By

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Chairman : Professor Md Jelas Haron, PhD

Faculty : Science

Zolite P was synthesized from silica of rice husk ash (SRHA) via alkaline hydrothermal technique with sodium aluminate and sodium hydroxide. The zeolite produced was characterized by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) and, the morphology was analysed by Scanning Electron Microscopy (SEM), and the elemental analysis was carried out by Energy Dispersive X-ray (EDX) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The synthesized zeolite P was exchanged with cerium (III) and cerium (IV) ions. The ability of Ce(III) exchanged zeolite P (Ce3ZP) and Ce(IV) exchanged zeolite P (Ce4ZP) to sorb and remove arsenic (V) from aqueous solution was investigated. Parameters investigated for arsenic removal include pH, initial As(V) concentration, temperature and effect of foreign ions on the sorption. The sorbent was tested for removal of arsenic from industrial wastewater samples of wood treatment industry which utilized the largest amount of arsenic compound.

The XRD pattern shows that the zeolite produced was zeolite P which has GIS frame work topology of type NaP1. The XRD intensity of zeolite P increases for increased ratio of SRHA:Al during preparation, indicating the progress in crystallization of the product. SEM-EDX analysis shows that the zeolite P produced contains Si/Al ratio of 2:1 with the formula of $Na_6Al_6Si_{12}O_{36}.8H_2O$. The formation of zeolite was also confirm by FTIR absorption at 1040 cm^{-1} and 432 cm^{-1}, the regions commonly observed in aluminosilicate due to Si-O and Al-O stretching and bending modes. Exchange capacity of Ce(III) and Ce(IV) in the zeolite increased with increased in temperature with highest loading obtained 75.4 and 170.0 mg/g, respectively. The existence of cerium in the zeolite was confirmed by EDX spectrum. The resulting cerium exchanged zeolites were used for As(V) sorption experiments.

Sorption of As(V) by both modified zeolite occurred over a wide pH range, which was pH 1 – 11 for Ce4ZP and pH 3-10 for Ce3ZP with maximum sorption at about pH 4. The sorption capacities increased with increasing initial As(V) concentrations and followed the Langmuir model with maximum sorption capacities of 22.0 mg g^{-1} at 25°C and increased to 34.0 mg g^{-1} at 90°C. This is higher than the values for Ce3ZP which was 8.72 mg g^{-1} at 25°C and increased to 23.42 mg g^{-1} at 90°C, indicating that the As(V) sorption process is endothermic. The endothermic nature of sorption process was confirmed by the positive value of sorption enthalpy change, $\Delta H°$. The free energy change, $\Delta G°$ for the sorption was negative showing that the sorption process is spontaneous. The increase in ΔS^0 upon As(V) sorption could be partly due to the release

of coordinated water molecules from Ce(IV) ion in the zeolite. Kinetic study showed that the As(V) sorption by Ce4ZP follows a second order kinetic model.

The unmodified Zeolite P did not significantly remove As(V). This result infers that the active sorption site for As in the Zeolite was the cerium metal ion. In the acidic to natural pH range, sorption of arsenate ion was also followed by increase in pH of the solution from its initial value. The mechanism of sorption process could be a ligand exchange reaction with hydroxide ion on the surface of cerium ion and the formation of surface complexes between oxygen on the arsenate with the cerium metal ion on the zeolite.

The selectivity study showed that the sorption of As(V) was affected by the presence of phosphate but not affected with bromide, chloride, nitrate, sulphate, carbonate and chromium. The Ce exchanged zeolite was found effective for the removal of arsenic in wastewater samples from wood treatment industries.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS DAN PENCIRIAN CERIUM TERTUKAR ZEOLITE DAN APLIKASI DALAM PENYINGKIRAN ARSENIK DARI SAMPEL AIR SISA INDUSTRI

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November 2008

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Zeolite P telah disintesis dari silika abu sekam padi SRHA melalui teknik hidroterma dengan sodium aluminat dan sodium hidroksida. Zeolite yang terhasil telah dicirikan dengan spektroskopi belauan sinar-x (XRD) dan spektroskopi infra merah transformasi Fourier (FTIR), analisis morfologi menggunakan mikroskopi elektron pengimbasan (SEM) dan, analisis unsur menggunakan kaedah penyerakan tenaga sinar-x (EDX) dan spektrometri pemancaran atom plasma berganding aruh (ICP-AES). Zeolite P yang disintesis diubahsuai melalui penukaran ion dengan cerium (III) dan cerium (IV). Kebolehan zeolite P tertukar ion Ce(III) (Ce3ZP) dan zeolite P tertukar ion Ce(IV) (Ce4ZP) untuk mengerap dan menyingkirkan arsenik (V) dari larutan akueus telah dikaji. Parameter yang mempengaruhi erapan arsenik yang dikaji termasuklah pH, kepekatan awal As(V), suhu dan kesan ion asing. Pengerap juga diuji keberkesanannya bagi menyingkirkan arsenik dari sampel air buangan industri perawatan kayu yang mana merupakan industri paling banyak menggunakan sebatian arsenik.

Pola belauan sinar-x menunjukkan zeolite membentuk zeolite terhasil adalah zeolite P yang mempunyai rangka topologi GIS jenis NaP1. Keamatan puncak sinar-x mengingkat dengan peningkatan nisbah mol SRHA:Al semasa penyedian menunjukan peningkatan pembentukan kristal dalam bahan yang terhasil. Analisis SEM-EDX menunjukkan zeolite P yang terhasil mengandungi nisbah Si/Al 2:1 dengan formula $Na_6Al_6Si_{12}O_{36}.8H_2O$. Pembentukkan zeolite juga disahkan oleh serapan FTIR pada 1040 cm^{-1} dan 432 cm^{-1}, merupakan kawasan serapan yang biasa diberikan oleh aluminosilikat yang merupakan mod regangan dan mod bengkokan Si-O dan Al-O. Muatan pertukaran ion Ce(III) dan Ce(IV) kedalam zeolite mengikat dengan peningkatan suhu dan muatan pertukaran tertinggi diperolehi masing-masing adalah 75.4 dan 170.0 mg/g pada suhu 90˚C. Kehadiran cerium didalam zeolite disahkan oleh spektrum EDX. Zeolite tertukar cerium yang terhasil digunakan dalam kajian erapan As(V).

Erapan As(V) oleh kedua-dua zeolite terubahsuai berlaku pada julat pH yang besar, iaitu pada pH 1-11 bagi Ce4ZP dan pH 3-10 bagi Ce3ZP dengna muatan erapan maksima berlaku pada pH 4. Muatan erapan meningkat dengan kepekatan awal As(V) dan mematuhi model isoterma Langmuir dengan muatan erapan maksima 22.0 mg g^{-1} pada 25°C dan meningkat kepada 34.0 mg g^{-1} pada 90°C untuk Ce4ZP. Nilai muatan ini adalah lebih tinggi berbanding Ce3ZP iaitu 8.7 mg g^{-1} pada 25°C dan meningkat kepada 23.4 mg g^{-1} pada 90°C yang menunjukkan proses erapan adalah spontan. Peningkatan perubahan entropi $\Delta S°$ selepas erapan As(V) pula mungkin disebabkan sebahagiannya oleh pelepasan molekul air terkoordinat daripada ion Ce(IV) pada zeolite. Kajian kinetic pula menunjukkan erapan As(V) oleh Ce4ZP mematuhi model kinetik order kedua.

Zeolite P tidak terubahsuai didapati tidak dapat menyingkirkan As(V) secara berkesan. Keputusan ini menunjukkan cerium merupakan tapak aktif untuk erapan As(V) pada zeolite terubahsuai. Pada keadaan pH berasid hingga natural, erapan As(V) juga diikut oleh peningkatan nilai pH berbanding pH larutan asal. Mekanisma erapan mungkin merupakan proses pertukaran ligan dengan ion hidroksida pada ion cerium dan pembentukan kompleks permukaan antara atom oksigen pada ion arsenat dengan ion hidroksida pada logam cerium dalam zeolite.

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I certify that a Thesis Examination Committee has met on 3 November 2008 to conduct the final examination of Farha binti Ab Rahim on her thesis entitled **“Synthesis and Characterisation of Cerium-Exchanged Zeolite and its Application in the Removal of Arsenic from Wastewater Samples”** in accordance with the Universities and University Collages Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the (Master of Science).

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of **Master of Science**. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

FARHA AB RAHIM

Date:4 May 2009

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LIST OF ABBREVIATIONS

α	:	Limiting amount of metal ion that can be taken per mass of adsorbent
ppm	:	part per million
RHA	:	Rice husk ash
XRD	:	X-ray diffraction
FTIR	:	Fourier transform infrared
SEM-EDX	:	Scanning Electron Microscopy and Energy Dispersive X-ray Analyses
CeIVZP	:	Cerium (IV) loaded with Zeolite P
CeIIIZP	:	Cerium (III) loaded with Zeolite P
CeIIIZY	:	Cerium (III) loaded with Zeolite Y
n	:	Parameter of Freundlich equation

CHAPTER 1

INTRODUCTION

Arsenic is harmful to man and living organisms and suspected carcinogenic [Cantor 1997]. However, due to its unique properties arsenic compounds are still widely used in many applications. They are used for the productions of wood preservative, lead shot, storage batteries, semiconductors, pesticides and fertilizers [Brooks 2007]. In addition to natural weathering of arsenic rocks and minerals, arsenic also enters the environment through other anthropogenic activities such as petroleum refineries, fossil fuel power plants and smelting of non-ferrous ores such as copper, lead, zinc, gold and uranium [Korte and Fernando, 1991]. Most international drinking water standards for arsenic were lowered to 0.01 mgl^{-1} as regulated by Word Health Organization [Johannesson 2002] where else many international standards for industrial waste effluent were set to 0.05 mgl^{-1} [Huang et al., 2007, Direct Art Company 2007]. Due to this scenario, development of new methods and sorbents for arsenic removal from water has been the subject of intense research lately.

Conventional precipitation methods for arsenic removals using iron and aluminum salts have not been successful to meet drinking and effluent standards for As due to limitation of solubility of the resultant products. Another problem is the production of a large volume of a bulky toxic waste sludge which is difficult to dry and usually face disposal problem. One of possible methods to improve this problem is using an adsorbent including ion exchange materials [Leist et al., 2000, Vagliasindi and Benjamin, 1998].

The arsenic sorbed can be eluted and recovered in a smaller volume and the sorbent can be reused. Among others, the removal of As(V) by adsorption methods have been studied using spodic [Lindberg 1997], aquifer material [Carrillo and Drever, 1998], oxides of antimony and manganese [Galer et al., 1997], iron hydroxide [Raven et al., 1998] and iron coated catalyst [Huang 1997].

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations normally of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium, as well as water molecules in their structural frameworks. Structurally, they are complex, porous, crystalline inorganic polymers, enclosing interconnected cavities in which the metal ions and water molecules are contained. They are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen ions [Bhatia 1990]. Zeolites may be represented by an empirical formula of $M_{2/n}Al_2O_3xSiO_2.yH_2O$. In this oxide formula, M is metal cation, x is generally equal to 2 or greater, y represents the water contained in the voids of the zeolite and n is the valence of metal cation which neutralize the permanent negative charge on the aluminosilicate framework, which was created by the replacement of Si^{4+} with Al^{3+} [Breck 1974]. The charge balancing counter ions, M can be easily exchanged with other metal cation, which produce the cationic exchange properties of zeolite [Bordiga et al., 1995].

Since zeolites have a permanent negative charge on their surface, they have no affinity for anions. However recent studies have shown that modification of zeolites with certain surfactants or metal cations yield sorbents with a strong affinity for many anions [Li et al., 1998]. In order to sorb anions such as arsenate, the modified surface must either possess positively charged exchange sites, or there should be replacement of weakly held counter ions of the surfactant by more strongly held counter ions. Cationic-surfactant-modified zeolites were shown to remove arsenate from aqueous solutions. Since As(V) presence in water as arsenate anion in wide pH range, the removal of As(V) by zeolites could be enhanced after loading it with various metal cations such as Al [Xu et al., 2000], Fe [González, 2001], Pb [Gonzalez et al., 2001, Miranda and Olguin, 2007] and La [Miranda and Olguin, 2007, Haron et al., 2007].

It is known that a stable and insoluble cerium arsenate can be produced by reacting solution of cerium salt with arsenic acid [Alberti et al., 1969, Janardanan et al., 1998]. Cerium hydroxide has been known to adsorbed arsenic As(V) quantitatively from aqueous solution [Plotnikov and Usatova, 1964]. Recently hydrous cerium oxide was also shown to poses an anion exchange with high capacity for As(V) [Zhang et al., 2005] and other anions [Misak and Mikhail, 1981, Tokunaga et al., 1995]. Further more cerium doped iron oxide was reported to adsorb As(V) at higher capacity compared to alumina [Zhang et al, 2003]. Our previous study also showed that Ce(III) loaded-chelating exchanger could sorb As(V) effectively from aqueous solution [Haron et al., 1997].

In this research, we prepared cerium exchanged-zeolite P (CeZP) and investigated its ability to sorb As(V) from aqueous solution. The sorbent was tested for removal of