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Removal of Fe(III), Mn(II) and Zn(II) from palm oil mill effluent (POME) by natural zeolite

M.A. Shavandi [a], Z. Haddadian [a], M.H.S. Ismail [a,b,*], N. Abdullah [a], Z.Z. Abidin [a,b]

[a] Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[b] Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

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ABSTRACT

The adsorption capacity of natural zeolite for the removal of heavy metal ions, zinc Zn(II), manganese Mn(II) and iron Fe(III), found in palm oil mill effluent was investigated in this study. The effects of contact time, agitation speed, pH, and sorbent dosage on the sorption of heavy metals were evaluated. The desorption potential of zeolite was also investigated. The sorption was fast with equilibrium reached within 180 min. The metal sorption increased with pH, and adsorption capacities ranged between 0.015 and 1.157 mg/g of zeolite. Equilibrium data followed the Langmuir isotherm model while the kinetic data were well described by the pseudo-second-order model. Maximum desorption was attained by HCl with 69.638, 58.575 and 61.516% of the initial adsorbed amount for Fe, Zn and Mn, respectively. More than 50% of Zn(II) and Mn(II) and about 60% of Fe(III) could be removed in the experiments.

1. Introduction

The input of metals on ecosystems has an adverse effect on human health and the environment. Metals can bioaccumulate in living organisms and the soil organic layer, contaminate the ground and surface water and even cause air pollution [1–4]. Malaysia is the largest producer of palm oil in the world and consequently, generates an extraordinary volume of wastewater, known as palm oil mill effluent (POME) [5]. POME contains different metals at critical levels such as iron(Fe), zinc(Zn) and manganese(Mn). In 2008, the production of palm oil in Malaysia, was individually recorded at 16.3 million tones and approximately 2.5–3.5 t of POME were generated for each ton of crude palm oil produced [6]. The discharge of this huge volume of metal ion polluted effluent into the waterways may cause serious problems for public health hazard and food chain. Thereupon, the proper treatment of this effluent is crucial for a viable industry. Various techniques such as chemical precipitation, electroflotation, ion-exchange, membrane separation, reverse osmosis, electro dialysis and solvent extraction have been investigated for the treatment of effluents containing heavy metals, but these methods are mainly expensive or incomplete [7,8].

Adsorption is another approach that is mainly recommended for the removal of low concentrations of metal ions in wastewater, particularly when natural, low-cost materials are abundantly available in the form of industrial or agricultural wastes that may have potential as a cost effective sorbents [9]. Citrus peel [10], egg shell [11], coconut shell carbon [2], fly ash [12], clay [13] and natural zeolite [14] are examples.

Zeolites are safe, naturally occurring crystalline aluminosilicates that have a three-dimensional structure, Which comprise assemblies of SiO_4 and AlO_4 tetrahedra joined together in different regular arrangements through the sharing of oxygen atoms and form a honeycomb structure containing pores [15]. The participation of Al^{3+} and Si^{4+} ions into the framework, introduce negative charges which must be balanced by exchangeable cations. Natural zeolite is a promising adsorbent media that has a potential application as a metal ion adsorbent and has gained interest among researchers, particularly due to its ion exchange, molecular sieve properties and also its relatively high surface area [12,16]. Zeolites have wide application as gas and odor filter, as a part of animal feed, and as ammonia removers from different wastewaters [17–21]. The metallic ions sorbent behavior of natural zeolites has been also studied by several researches, and it has been recognized as a promising sorbent for heavy metals [3,14,17,22–29].

Despite various researches that shown the feasibility of its application for removal of heavy metals from aqueous solution under various experimental conditions, limited studies have been carried out on the metal removal ability of natural zeolite from real industrial wastewater [3,16]. Furthermore, to our knowledge, no

* Corresponding author at: Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia. Tel.: +60 3 8946 4397; fax: +60 3 8656 7120.
E-mail address: mshalim@eng.upm.edu.my (M.H.S. Ismail).

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Table 1
Mineralogical, chemical composition, physico-chemical properties and cation exchange capacity of zeolite samples.

Composition (wt%)	Mineralogy composition (%)	Physico-chemical properties	Cation exchange capacity (cmol(+)/kg)
SiO_2	Clinoptilolite	Appearance	105
71.23	84	gray green	
Al_2O_3	Illite	Odor	
12.9	4	–	
CaO	Plagioclase	Bulk density	
4.8	3–4	1600–1800 kg/m^3	
K_2O	Cristobalite	Density	
3.1	8	2200–2440 kg/m^3	
Fe_2O_3	Quartz	Porosity	
1.6	Traces	24–32%	
MgO		Absorbability	
0.9		34–36%	
Na_2O		Specific surface	
1.1		30–60 m^2/g	
TiO_2			
0.3			

literature published on the removal of metallic ions from POME by natural zeolite.

In this study, the applicability of natural zeolite as an adsorbent material for the removal of iron, manganese and zinc ions from real POME was explored under batch conditions, and the sorption kinetics and other related parameters are examined as well.

2. Materials and methods

2.1. Preparation and characterization of sorbent and sorbate

Natural zeolite (clinoptilolite) samples were used in this study supplied from Slovakia. Prior to the experiment, the zeolite was crushed and passed through a No. 20 sieves, then it was washed with distilled water and dried in an oven at 120 ± 5 °C for 18 h. The mineralogical analysis was carried out by X-ray diffraction (XRD), and the result showed that the sample mainly consisted of clinoptilolite (84%) along with cristobalite (8%), Plagioclase (4%), lillit (4%) and a trace amount of quartz.

The chemical composition of the natural zeolite was determined by X-Ray Fluorescence (XRF), and the cation exchange capacity (CEC) of the zeolite samples was evaluated by the ammonium acetate saturation method as described by Kitsopoulos [30]. The surface area of the natural zeolite is determined by the Brunauer Emmet Teller (BET) method using a Quantachrome Autosorb1 surface analyzer. The values of other physiochemical properties were obtained from the provider (AVAS spol. s r.o) of natural zeolite. The results are summarized in Table 1.

Samples of POME were collected from the first aerobic pond of a palm oil factory in Kuala Selangor, Malaysia. The concentration of Zn, Fe and Mn in the samples was 2.785, 179.105 and 14.447 mg/L, respectively. The characteristics of the sample are summarized in Table 2.

Table 2
Characteristics of POME before treatment by zeolite.

Characteristics (mg/L)	Values
Oil and grease	16,000
COD	3057.651
BOD	344
TSS	338
NTU	633
Fe	179.105
Zn	2.785
Mn	14.447
pH	6.75

2.2. Batch sorption studies

Batch sorption experiments were carried out in 500 ml beakers containing 250 ml of POME, and the suspensions subjected to mix in a conventional jar test apparatus at room temperature in order to identify the effect of process parameters such as the dosage of natural zeolite (1.25, 2.5, 5, 10, 15, 20, 25 and 30 mg/250 ml), period of shaking (10, 20, 30, 40, 50, 60, 120, 180 and 240 min), variable mixing speed (90, 120, 180 and 200 rpm), and pH value (3–9). The final concentration of metals was determined with atomic absorption spectrophotometer (Termo Scientific iCE3300) using standard recommended methods for examining water and wastewater [30]. The presented data are mean values of all assays carried out in triplicate. The percentage of metal removal and the amount of metal ions adsorbed by the zeolite were calculated by the following equations:

$$\%\,\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of metal ions in solution respectively; q_e is the amount of metal ions adsorbed at equilibrium, V is the solution volume, and m is the mass of zeolite.

2.3. Point of zero charge

The point of zero charge is the pH value at which the number of cations and anions present on the surface are equal, so that the surface has no electrical charge. The point of zero charge (pH_{zpc}) for the natural zeolite sample was identified using the potentiometric titration method [12]. Some 45 ml of 0.1 N KNO_3 was added to a series of 100 ml capped bottles. The range of initial pH values of KNO_3 were adjusted from 2 to 10 by adding 0.1 N KOH and HNO_3. The total volume of the KNO_3 solution was exactly adjusted to 50 ml by adding further 0.1 N KNO_3. After that 1.0 g of accurately weighed sorbent was added to all bottles and capped securely. The suspensions were then agitated in a shaker for 24 h. The pH values of the suspension were then recorded and from this data the ΔpH curve versus pH_i was plotted to find the point where the plot crosses the line equal to zero [31]. From this, the pH_{zpc} was calculated to be 3.46 as shown in Fig. 1.