Fuel 215 (2018) 499–505

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

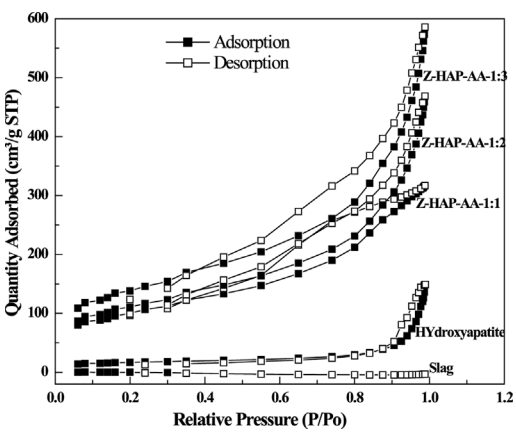
Full Length Article

Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption

W.A. Khanday[a,b], B.H. Hameed[a,*]

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[b] Department of Chemistry, Govt. Degree College, Anantnag 192102, Jammu & Kashmir, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Adsorption
Hydroxyapatite
Oil palm ash
Steel slag
Tetracycline
Zeolite

ABSTRACT

Mesoporous zeolite-hydroxyapatite-activated palm ash (Z-HAP-AA) composites were synthesized through hydrothermal method using different ratios of oil palm ash and electric arc furnace (EAF) steel slag under alkaline conditions. Structural properties of the synthesized materials were studied by various characterization techniques. Ca/P = 1.667 and SiO_2/Al_2O_3 = 3, characteristic to hydroxyapatite and zeolite-X respectively were obtained. Increase in activated oil palm ash ratio during synthesis resulted in increased surface area of Z-HAP-AA composite due to increase in carbon component. Among various synthesized composites Z-HAP-AA-1:3 was selected as best adsorbent for tetracycline. Adsorption performance of Z-HAP-AA-1:3 was examined for tetracycline removal in batch process with respect to initial tetracycline concentration (50–400 mg/L), temperature (30–50 °C) and pH (3 − 1 3). Best representation of data was obtained by the Freundlich model. Maximum monolayer adsorption capacity of Z-HAP-AA for tetracycline at 30 °C, 40 °C and 50 °C was 186.09 mg/g, 212.56 mg/g, and 244.63 mg/g respectively.

1. Introduction

Environmental related problems, such as safety, industrial and domestic waste disposal, and recycling of natural resources, have gained increased global interests. Currently, conversion of domestic and agricultural wastes into special materials with valuable importance has

* Corresponding author.
E-mail address: chbassim@usm.my (B.H. Hameed).

https://doi.org/10.1016/j.fuel.2017.11.068
Received 1 April 2017; Received in revised form 22 October 2017; Accepted 19 November 2017

been the focus of studies, instead of using conventional methods of disposal. Zeolites have been synthesized using industrial waste materials to minimize wastes and generate low cost and commercially valuable materials; waste materials include slags and clays [1,2], ashes [3,4], and naturally occurring rocks [5], which contain abundant Si and Al.

Silicon-rich materials can be easily converted into zeolites; however, if the material also contains CaO exceeding 15 wt%, then it cannot be converted into zeolite because silicate reacts with calcium to form calcium silicate [6]. Although steel slag composed of Al_2O_3, SiO_2, CaO, MgO, and other oxides [7] is a good source of Al and Si, the use of this material for zeolite synthesis remains limited because of its high Ca content. In this regard, researchers employed pretreatment methods, such as acid leaching of Fe and Ca, to synthesize zeolites from steel slag [8]. However, this methodology results in large loss of Ca and is not favorable in terms of utilization of resources. To address this limitation, Kuwahara et al. [9] attempted to convert steel slag into zeolites without removal of Ca by converting water-granulated slag into hydroxyapatite-zeolite composite material. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is alkaline in nature and used in adsorption and catalysis; however, its applications remain limited because of its low surface area which can be enhanced by adding other carbon sources.

Oil palm ash is another waste material produced by palm oil mills through burning oil palm shells and fiber to fuel the boiler during steam generation. Malaysia, as the world's largest palm oil supplier, operates more than 200 palm oil mills and disposes tons of ash annually without any commercial gain [10]; hence, recycling these wastes into useful materials remains a challenge for researchers. Previous study [11] reported that oil palm ash contains 40% SiO_2 and 6% Al_2O_3, which are essential constituents for zeolite formation, as well as 5.5% unburned carbon, which can be activated. Various ashes have been transformed to zeolites to be utilized as cheap adsorbents for the removal of pollutants from environment [12–15].

Tetracycline is a pharmaceutical considered to be safe and effective medicine among antibiotics and for this reason has been in clinical use for infection treatment continuously from last six decades [16]. Post infection treatment they get discharged into environment because of incomplete metabolism and result in toxicity by triggering antibiotic resistant bacterial growth [17]. Thus removal of tetracycline has attracted many eyebrows as it is counted as one among the newly emerging pollutants. Recently many techniques have been developed to remove such pollutants from wastewater [18–22].

The study is aimed at recycling of two wastes EAF steel slag and oil palm ash into porous and good surface area zeolite/hydroxyapatite-activated palm ash (Z-HAP-AA) composite to be used as an effective adsorbent for the removal of tetracycline in batch process. The fabricated composite exhibits the advantages of its individual components, namely, zeolite, hydroxyapatite, and activated carbon; hence, the composite can be used as a good adsorbent for the removal of various pollutants from the environment.

2. Experimental

2.1. Materials

Oil palm ash was obtained from a local palm oil mill in Penang, Malaysia and used without purification. EAF steel slag generated during EAF processing of raw steel was supplied after ball milling by a local industry in Penang, Malaysia. The milled EAF slag was meshed to a size of 45 μm prior to use. Analytical grade tetracycline (> 98% purity) was obtained from local pharmaceutical company. Phosphoric acid (> 99% purity), NaOH (> 99% purity), $NaAlO_2$ (> 99% purity), and all other chemicals of high-quality analytical grade were supplied by Sigma Aldrich (Malaysia) and used as received.

2.2. Synthesis of Z-HAP-AA

A three-step procedure was used to synthesize Z-HAP-AA from oil palm ash and EAF steel slag. In the first step, 10 g of oil palm ash was impregnated with NaOH (purity 99% from Sigma Aldrich) at a ratio of 1: 3 by mass and activated by heating in a horizontal tubular stainless steel reactor at 800 °C for 90 min in N_2 atmosphere (99.995%; flow rate, 100 cm^3/min). NaOH was used because it can activate carbon and facilitate the hydrothermal synthesis of zeolites.

In the second step, 5.0 g of meshed EAF steel slag was mixed with the activated ash at different ratios (steel slag/activated oil palm ash ratios of 1:1, 1:2, and 1:3). The mixture was added with a fixed volume (19.9 mL for 1:1, 22.4 mL for 2:2 and 25.1 mL for 1:3) of aqueous solution of 1.0 M H_3PO_4 and continuously stirred at 60 °C until dissolution. Prolonged agitation was prevented to inhibit the formation of gel-like hydrous calcium phosphate at lower solid/liquid ratios (EAF steel slag/H_3PO_4) [9].The fixed volume of 1.0 M H_3PO_4 was used as per calculation to maintain the fixed Ca/P molar ratio of 1.667, which is the stoichiometric composition of hydroxyapatite.

In the third step, a specific amount of $NaAlO_2$ was added to each mixture based on calculations to balance the SiO_2/Al_2O_3 ratio at around 3. Each mixture was then slowly added with 30 mL of aqueous solution of 3 M NaOH under continuous stirring and then aged overnight. These mixtures were incubated in a Teflon-lined autoclave and heated for 48 h at 100 °C. After hydrothermal treatment, different Z-HAP-AA composites were obtained (subsequently named as Z-HAP-AA-1:1, Z-HAP-AA-1:2, and Z-HAP-AA-1:3 depending on the EAF steel slag/oil palm ash ratio considered). The composites were filtered, washed with deionized water to adjust the pH to 7, and then dried in an oven at 60 °C overnight.

Fresh hydroxyapatite powder was prepared for comparison with Z-HAP-AA composites. The powder was synthesized from H_3PO_4 and Ca $(OH)_2$ through a reported conventional precipitation method while keeping the Ca/P ratio equal to 1.667 [23].

2.3. Characterization of Z-HAP-AA composite

Powder X-ray diffraction patterns of raw steel slag, hydroxyapatite, and various Z-HAP-AA composites were recorded within 2θ of 5°–50° with 2°/min scanning rate by using SIEMENS XRD D5000 equipped with Kα Cu radiation (λ = 1.54056 Å) at 30 mA and 40 kV.

The surface physical properties of these materials were analyzed by Autosorb I (Quantachrome Corporation, USA) using N_2 as adsorbate at −196 °C. Barrett–Joyner–Halenda (BJH) method was employed to determine pore size distribution and average pore width.

The surface functional groups of raw steel slag, hydroxyapatite, and various Z-HAP-AA composites were characterized using Perkin–Elmer Spectrum GX Infrared Spectrometer with wave number ranging from 400 cm^{-1} to 4000 cm^{-1}. The resolution was set as 4 cm^{-1}, and potassium bromide disc method was used for investigation.

Field-emission scanning electron microscope (FESEM LEO SUPRA 35VP) equipped with EDAX system was used for scanning electron microscopy (SEM) analysis to study the surface morphology and textural structure of raw steel slag, hydroxyapatite, and various Z-HAP-AA composites. The same instrument was used for energy dispersion spectroscopy (EDS) for elemental analysis of these materials.

2.4. Adsorption studies

200 mL of tetracycline solutions with varying initial concentrations (50–400 mg/L) were taken in stoppered Erlenmeyer flasks (250 mL) to which 0.2 g of Z-HAP-AA-1:3 were added and continuously agitated at 120 rpm in isothermal water bath shaker for 30 h at 30 °C to perform batch adsorption experiments. At various time intervals the tetracycline final concentration was determined until the attainment of equilibrium. For temperature studies these solutions were continuously agitated at