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Adsorption behavior of cadmium ions onto phosphoric acid-impregnated microwave-induced mesoporous activated carbon

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ABSTRACT

This study investigated the potential of mesoporous activated carbon derived from oil palm shell using phosphoric acid (H_3PO_4) impregnation followed by microwave-induced irradiation, for adsorption of cadmium from aqueous solution. This study investigated the effects of H_3PO_4 impregnation ratio (1:1, 1:2 and 1:3 w/w) and microwave irradiation time (5 and 8 min) on the characteristics of the synthesized activated carbon, encompassing the textural, morphological, proximate and chemical properties. Batch adsorption studies were conducted for the activated carbon to determine the effects of contact time, initial cadmium concentration (20–200 mg/L) and solution pH (2–10) on the cadmium ions uptake at 30 °C. The synthesis process resulted in the development of pores, with average diameter of 2.22 nm, on the surface of the oil palm shell, which contributed to the relatively large BET surface area and total pore volume of 854.42 m^2/g and 0.74 cm^3/g, respectively. Batch adsorption studies showed that the adsorption of cadmium increased with increasing concentration and was more favourable at acidic pH, achieving up to 99% removal. The adsorption of cadmium on the activated carbon was of chemisorption and governed by external mass transport. The maximum monolayer adsorption capacity of 227.27 mg/g showed the potential of the proposed synthesis method for deriving mesoporous oil palm shell-based activated carbon for removing cadmium from aqueous solutions. The saving in terms of the reduction of activation time and energy usage shall make the production of activated carbon from agricultural biomass to be more environmental friendly and sustainable for wastewater treatment.

1. Introduction

Contamination of aqueous medium by non-biodegradable heavy metals in industrial wastewater effluent is among the key environmental problems mainly due to the toxicity and accumulation of the metal ions in the food chain [1]. Despite the application of technologies to control the industrial wastewater effluent quality, the concentration of toxic metals such as cadmium in the vicinity of premises typically exceeds the regulated limit. Industries which produce wastewater containing cadmium include metal smelting, electroplating, cadmium-nickel batteries, phosphate, refining process, fertilizers, mining, pigments, stabilizers, alloy industries and sewage sludge [2,3]. The presence of cadmium in the ground has adverse impact to the vegetation growth as it can affect the action of enzymes and impedes respiration, photosynthesis and transpiration [4]. If contaminated groundwater is consumed, cadmium can cause adverse impact on human health such as renal damage, emphysema, hypertension, testicular atrophy and the 'Itai-itai' disease [2–4]. Therefore, cadmium is the target pollutant in this study.

As a single step in a wastewater treatment system, adsorption is considered to be an effective separation process for water decontamination applications [5,6]. Activated carbon has been extensively used as adsorbent for the advanced treatment of wastewater especially for the removal of organic and inorganic pollutants from aqueous media [7]. The sludge-free treatment involves simple operation and maintenance, and proven effective for adsorbing a plethora of adsorbates [8–12]. Activated carbon has also been used as adsorbent in permeable reactive barrier to inhibit the migration of contaminants in groundwater [13]. Nevertheless, the wide use of activated carbon is limited by the costly production and adverse environmental pollution due to the inten-

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sive energy requirement and carbon emission through the thermal treatment. There has been extensive effort to promote the usage of activated carbon by using agricultural waste to reduce raw material cost, and chemical treatment to reduce the activation requirement in terms of energy and time. In addition, the recycling of agricultural waste into value product can help to reduce the use of costly non-renewable material such as petroleum coke and bituminous coal [14] and amount of wastes to be landfilled, which prolong the lifespan of landfill. Various agricultural biomass such as rice waste, wheat waste, coconut waste and fruit peels have been shown to be feasible for biosorption of heavy metal ions from wastewater [15]. From studies reported to date, oil palm shell is still among the outstanding precursor for producing good quality granular activated carbon due to its relatively greater carbon content and mechanical stability as it does not dissolve or disintegrate easily in water. There is a great potential for synthesizing activated carbon from oil palm shell commercially, with its substantial production by the oil palm industry in Malaysia in which oil palm shell constitutes about 20% of crude palm oil produced [16]. The current utilisation of oil palm fibers and shells for boiler fuel in the mill is 60%, whereas the rest is either incinerated or returned to the plantation as organic fertilizers through natural decomposition [17–19]. Therefore, oil palm shell is used as the precursor for synthesizing the activated carbon in this study.

Besides the source of precursor, the production cost of activated carbon is affected by the activation process, i.e. physical and chemical activation. Chemical activation is preferred as it enables the reduction of thermal energy requirement and activation duration compared to that of physical activation [20]. In addition, chemical activation typically produces carbon with larger pore structure than that using physical activation; enabling the adsorption of larger molecules [21]. Phosphoric acid (H_3PO_4) is a widely used activating agent for synthesis of activated carbon due to several attributes such as non-polluting characteristics, easily extracted using water and ability to produce porous structures which is favourable for adsorption [21]. Budinova et al., [20] reported that the properties of activated carbon are influenced by the H_3PO_4 concentration, impregnation ratio and gases used for activation. Budinova et al. [20] suggested the optimum impregnation ratio (weight of biomass:weight of H_3PO_4) of 1:1.5 using concentration of 20 and 50 wt% while Yagmur et al. [21] reported greater surface area and porous structure at impregnation ratio of 1:3 using concentration of 85 wt%. This study attempts to use impregnation ratio of 1:1, 1:2 and 1:3, similar to that of Yagmur et al. [21].

Microwave-induced pyrolysis and activation of biomass is an alternative technology that has received increasing attention in recent years, as this technique has been reported to improve the pyrolysis and activation process in terms of energy input, cost and processing time [22]. In conventional heating process, heat transfer occurs by conduction; however in microwave irradiation method, the carbon bed receives the energy at molecular level and converts it into heat by dipole rotation and friction within the matrix [23]. Recently many studies have been reported on the thermochemical conversion of oil palm shell using microwave pyrolysis in which the thermophysical properties have been the focus of these studies [24–28]. Limited works have been conducted on the derivation of oil palm shell-based activated carbon using synthesis technique which combined chemical activation via phosphoric acid (H_3PO_4) impregnation followed by thermal treatment using microwave-induced irradiation. Kundu et al. [29] applied this method to synthesize activated carbon which was shown to be promising for adsorption of methylene blue. Therefore, this research focus on evaluating the feasibility of producing mesoporous activated carbon from oil palm shell using H_3PO_4 impregnation followed by microwave-induced irradiation, especially for adsorption of cadmium from aqueous solutions. The prepared activated carbon was characterized by textural, morphological, proximate and surface chemistry analyses. The isotherms, kinetics and mechanism for the adsorption of cadmium ions onto the activated carbon were then investigated through the evaluation of the equilibrium and kinetic data of the adsorption process.

2. Materials and methods

2.1. Preparation of activated carbon

The oil palm shell used as the precursor for preparation of activated carbon was collected from a palm oil mill at Kota Samarahan, Sarawak. The precursor was first washed with deionized water to remove dirt on the surface and soaked in *n*-hexane to remove oil residue and other impurities. The sample was dried at 100 °C in an oven overnight, then ground and sieved to 2 mm particle size. The pre-treated precursor was subjected to chemical treatment using H_3PO_4 with different impregnation ratio (1:1, 1:2 and 1:3 w/w). The mixture was dehydrated at 100 °C in an oven for 24 h. The chemical treated sample was then subjected to thermal treatment by using a 2450 MHz microwave oven (model NN-CS599S, Panasonic, Japan) with microwave irradiation power of 700 W. The irradiation time studied was ranged from 5 to 8 min. The activated carbon produced was repeatedly washed with hot deionized water followed by cold deionized water until the washing solution reached a constant pH value of 6–7. The activated carbon was finally dried in an oven at 100 °C for 12 h to remove the moisture, then cooled in desiccators to room temperature and kept in air-tight container for further characterization and analysis.

2.2. Characterization of activated carbon

The lignocellulosic content of oil palm shell was reported to be 31% cellulose, 20% hemicellulose and 49% lignin [30]. Textural characterization of the precursor, H_3PO_4 treated sample and prepared activated carbon was carried out by N_2 adsorption at 77 K using a gas sorption analyzer (model Autosorb iQ, Quantachrome Instrument, USA), in order to determine the Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution of the activated carbon. Scanning electron microscope (SEM) (model JSM-6390, JEOL, USA) was used to study the surface morphology of the precursor, H_3PO_4 treated sample and activated carbon. Thermogravimetric analyzer (TGA) (model DTG-60H, Shimadzu, Japan) was used to perform the proximate analysis at a heating rate of 25 °C/min. The surface chemistry of the precursor, H_3PO_4 treated sample and activated carbon was analyzed using Fourier transform infrared spectrophotometer (FTIR) (model IRAffinity-1, Shimadzu, Japan) with the wave number ranging from 600 to 4000 cm^{-1}. The pH value of the activated carbon was determined by gently boiling 100 mL of distilled water in an Erlenmeyer flask containing 0.1 g of activated carbon for 5 min. The solution was diluted to 200 mL and cooled to room temperature before measuring the pH value using an electronic pH meter (model AB15, Fisher Scientific, USA).

2.3. Batch equilibrium studies

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$) supplied by Sigma-Aldrich was used as the adsorbate in this study. Stock cadmium solution was prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ in 1000 mL of deionized water [31]. Working standards were prepared by progressive dilution of the stock cadmium solution using deionized water. 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were used to adjust the pH of the solution. A set of preliminary study was carried out to identify the best activated carbon that would be used in the batch equilibrium studies.

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