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Preparation of immobilized activated carbon-polyvinyl alcohol composite for the adsorptive removal of 2,4-dichlorophenoxyacetic acid

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ABSTRACT

Polymer-based activated carbon-polyvinyl alcohol (AC-PVA) composite was successfully fabricated and immobilized on a glass plate where it is has not been reported elsewhere due to the PVA solubility in aqueous solution. The formulation was mixed with glutaraldehyde (GLA) as cross-linker to avoid PVA from dissolved in water, ammonium peroxodisulfate (APS) and silica (Si) as additives to improve the adhesiveness. The immobilized AP12 sample which containing 4 g AC, 32 mL PVA, 20 mL GLA, 0.56 g APS and 0.2 g Si is the optimum AC-PVA formulation with the high relative strange and adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D). The immobilized AP12 presents a BET surface area of 202 m^2/g, a micropore volume of 20.8 cm^2/g and an average pore size of 4.4 nm. The SEM and FTIR analyses indicated the interaction or cross-linking within the AC and PVA composite in the presence of the GLA explaining the high adhesiveness of immobilized AP12 and can be reused up to 4 times with excellent of 2,4-D removal. The adsorption kinetic and isotherm fitted with pseudo-second-order kinetic and Langmuir isotherm models with maximum adsorption capacities, q_{max}, calculated from the isotherm was 55.9 mg/g.

1. Introduction

Intensive agricultural activities have led to the extensive usage of a large amount of herbicide in fields worldwide. Among the numerous herbicides applied, 2,4-dichlorophenoxy acetic acid (2,4-D) has been widely use for the broad-leaved weeds controlling [1,2]. However, the extensive usage of 2,4-D has led to the released of this persistent contaminant in the surface and groundwater which poses a potential risk to human health [3,4].

Numerous methods for the removal of 2,4-D herbicide in water have been applied, including catalytic process [5], advanced oxidation process [6], and adsorption technique [7]. Adsorption onto solid adsorbents has been widely applied to remove herbicide from water due to the ease of operation and effectiveness of application [8]. Activated carbon (AC) has been extensively applied as an adsorbent to treat contaminated water due to its interesting structure and chemical properties [9]. Its high surface area and effectiveness in eliminating liquid-phase contaminants have made AC as one of the most powerful adsorbents in wastewater treatment [10,11].

AC-based adsorption either in a powder or granular form as well as micro to nano-scale is commonly applied for the wastewater treatment [12–14]. Stability and reproducibility are important properties of the adsorbents in practical perspectives. Therefore, it is a challenge to develop a sustainable, low-cost, and eco-friendly adsorbent. Recently, there have been great interest in developing membrane form or composite-based adsorbents which has an excellent adsorption performance and regeneration properties. For instance, several membrane or composite-based AC have been reported. This includes magnetic carbon composite [15], graphene/AC composite for dyes and heavy metal removal [13,16–18], graphitic carbon nitride nanosheets embedded in polyvinyl alcohol (PVA) nanocomposite membrane [19], polyacrylonitrile (PAN) nanofibrous membranes with poly(vinyl pyrrolidone) (PVP) as blend solution for heavy metal removal [20], and polyvinylpyrrolidone (PVP)-coated magnetite nanoparticles over granular activated carbon [21]. Despite the intensive application of composite-based AC, immobilizing the AC composite on the glass plate with

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PVA polymer-based have not been extensively reported before due to the solubility of this material in water. Moreover, some studies have reported PVA has a significant behavior in enhancing the degradation rate of the organic pollutants due to the presence of C=C bonding in PVA molecular structure and the effect of photoetching of the binders prior the photocatalytic degradation [22,23].

This present study focuses on the development of a simple and environmentally-friendly method of polymer-based AC composite which offers the simplicity of design and preparation. The immobilized AC composite on a glass plate was prepared for the first time using PVA as polymer adhesive and GLA as the cross-linker agent. Other additives, such as ammonium peroxodisulphate (APS) and silica (Si) were also used in the preparation of the immobilized AC composite as a catalyst and functionalized filler. Glass plate was used as the support for the immobilization of the AC composite. The immobilized AC-PVA composite was characterized using scanning electron microscope energy dispersive X-ray spectroscopy (SEM-EDX), Brunauer-Emmett-Teller (BET), and Fourier transform infrared spectroscopy (FTIR) analyses. The adsorption performance of the immobilized AC-PVA composite was also optimized using 2,4-D as the model herbicide pollutant.

2. Materials and method

2.1. Chemicals

2,4-Dichlorophenoxyacetic acid (2,4-D), ammonium peroxodisulfate (APS, $(NH_4)_2S_2O_8$, 98%), silica fumed and commercial AC (Activated charcoal Norit @ type Norit W35, CAS No. 7440-44-0, peat based, BET surface area: 712 m^2/g, pore diameter: 4.01 nm, pore volume: 0.73 m^2/g, bulk density: 250–550 kg/m^3) were obtained from Sigma-Aldrich, Germany, Glacial acetic acid (CH_3COOH, 98%), glutaraldehyde (GLA, $CH_2(CH_2CHO)_2$, 25%), hydrochloric acid (HCl, 37%) and polyvinyl alcohol (PVA, 88% hydrolyzed) was purchased from Systerm (Malaysia), Merck (Germany), QRec™ (Malaysia) and Fluka (UK), respectively.

2.2. Preparation of immobilized AC-PVA composite

AC-PVA composite was prepared by introducing 4 g of AC powder in 32 mL of 8 wt/v% PVA solution. 20 mL of 0.05 M GLA, 0.56 g APS solution and 0.2 g of silica was added into the AC-PVA composite to produce cross-linked composite. Then, 25 mL of 0.2 M HCl was added into the suspension for dispersion process. The AC-PVA composite formulation was then homogenized by grinding in a ball mill grinder (Pascall Engineering Grinder, UK) for 3 h at 80 rpm. The homogenized AC-PVA composite formulation was casted evenly on the surface of the glass plates using the drop casting method. The evenness of the immobilized samples was standardized by using the same dropping area, volume of formulation (~0.3 g) and casting technique. The immobilized samples were finally dried completely at room temperature (27 °C) before used. The immobilized AC-PVA samples with different compositions were prepared by using the same procedure.

2.3. Characterizations

The surface morphology was observed using a scanning electron microscope energy dispersive X-ray spectroscopy (SEM-EDX) (Model Leo Supra 50 VP, Germany). The surface area and pore size distribution of AC-PVA composite were evaluated using a Brunauer-Emmett-Teller (BET) surface analyzer (Micromeritics, Model ASAP 2010, USA) under N_2 gas at −196 °C. On the other hand, Fourier transform infrared (FTIR) spectra were recorded within 4000 -650 cm^{-1} on a FTIR spectrometer (Model 2000, Perkin-Elmer, USA).

The optimum ratio of AC, PVA, GLA, Si, and APS in the AC-PVA composite was selected via its relative strength using the sonication method. The immobilized AC-PVA composite at different AC, PVA, GLA, Si, and APS ratios were immersed in a beaker filled with distilled water. The beaker was placed in an ultrasonic cleaner (Tru-Sweep by Crest Ultrasonics, USA) and sonicated for 30 s. The remaining composite that still adhered onto the glass plate was dried in an oven at 100 °C for 10 min and weighed. The relative strength is based on the percentage of the composite remained on the surface of the glass plate. It is calculated using the following equation:

$$\text{Relative Strength}(\%) = \left(\frac{W_t}{W_i}\right)100 \quad (1)$$

where W_t is the remaining weight of the composite after 30 s and W_i is the initial weight of the composite deposited on the glass plate.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted in a 5 cm × 8 cm × 1 cm custom-made glass cell. The prepared AC-PVA composite was immersed into the glass cell containing 20 mL of 2,4-D solution at various concentrations. The solution was aerated with air at 100 mL min^{-1} for proper mixing and improve mass transport of the pollutant towards the immobilized adsorbent. The adsorption process was optimized by varying the adsorbent dosage (0.87–3.7 mg cm^{-2}), solution pH (2–8), contact time (0–2 h) and initial dye concentration (20–100 mg L^{-1}). The concentrations of 2,4-D were monitored at different time interval by using a high-performance liquid chromatography (HPLC) (Model LC-10AT, Shimadzu Corp, Japan with a UV/Vis detector). Chromatographic separation was accomplished on a Supelcosil C18 reverse phase column (Supelcosil, Germany, 25 cm × 4.6 mm, 5 µm) at 25 °C and monitored at 230 nm. The mobile phase used was a mixture of 50% ultra-pure water, 50% acetonitrile and 0.2% acetic acid pumped at a flow rate of 1 mL min^{-1}. The percentage of 2,4-D removed (R, %) and the amounts of 2,4-D adsorbed at equilibrium (q_e, mg/g) were calculated as follows:

$$\%R = \left(\frac{C_o - C_e}{C_o}\right)100 \quad (2)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

where C_o is the initial concentration of 2,4-D (mg L^{-1}), C_e is the concentration of 2,4-D at the equilibrium (mg L^{-1}); V is the volume of 2,4-D solution (L); and m is the mass of AC-PVA composite (g).

2.5. Modelling

2.5.1. Adsorption kinetics

The equation for the kinetic models are expressed as follows [24–26]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of 2,4-D adsorbed by the immobilized AP12 composite at equilibrium and time t, respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant, and k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant.

The best-fitted model was assessed using the coefficient of determination (R^2), normalized standard deviation (NSD) and average relative error (ARE). The equations of the functions are given as follows:

$$R^2 = 1 - \frac{\sum_{n=1}^{n}(q_{t.meas} - q_{t.cal})^2}{\sum_{n=1}^{n}(q_{t.cal} - \overline{q_{t.cal}})^2} \quad (6)$$