



Column, kinetic and isotherm studies of PAH (phenanthrene) and dye (acid red) on kaolin modified with 1-hexyl, 3-decahexyl imidazolium ionic liquid



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ABSTRACT

Adsorption studies were carried out to determine the efficiency of kaolin modified with a novel long chain ionic liquid (IL) 1-hexyl, 3-decahexyl imidazolium. Synthesis of IL was carried out and characterised with NMR and fourier transform infrared (FT-IR) spectroscopy. Kaolin was modified with IL to form hydrophobic kaolin (modified-kaolin) by adding IL in excess of the cation exchange capacity of kaolin. Modified-kaolin was characterised using FT-IR, x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). Modified-kaolin was used in column and batch adsorption studies for phenanthrene and acid red dye. Modified-kaolin was an efficient material for the removal of phenanthrene and acid red dye. For column studies, the adsorption capacity, depth of exchange zone, time required for the pollutant to move through the exchange zone which is the height of the adsorbent in the column and adsorption rates were investigated using the Adams-Bohart, Yoon-Nelson model flow and Thomas sorption model. Column adsorption capacity at the same flow rate (5.0 mL min^{-1}) and different concentrations ($50, 100$ and 200 mg L^{-1}) for phenanthrene were $222.9, 611.8$ and 1093.5 mg g^{-1} , while that of acid red dye were $877.0, 1337.4$ and 1350.7 mg g^{-1} , respectively. Thomas and Yoon–Nelson models best explained the column studies. Data from both batch studies fitted well to pseudo-second order. The Langmuir isotherm had the best fit with an adsorption capacity of 842.7 mg g^{-1} for dye and the Freundlich isotherm best described phenanthrene with an adsorption capacity of 188.9 mg g^{-1} .

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1. Introduction

Water pollution with organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and dyes are a worldwide concern. PAHs are considered possible human carcinogens by the US EPA. Much attention has been drawn to their distribution in the environment and potential risks to human health [1]. Phenanthrene (PHN), which is a PAH is an abundant component of crude oil and can enter natural water through oil spillage or leakage, industrial effluents, urban run-off, and municipal effluents [2]. Dyes get into wastewater from various industries such as dyestuff, textile, leather, paper and plastics. Dyes are difficult to remove, they resist aerobic breakdown, and are stable with oxidizing agents. Moreover, the wastes generated from dyes are not just

considered toxic, but they are also potentially carcinogenic [3]. Therefore, removal of these organic pollutants from effluents becomes environmentally important.

A number of methods have been used for the removal of PAHs and dyes from wastewater including chlorination, oxidation, and ultrasonic irradiation. Photo degradation, coagulation, precipitation, biodegradation, membrane separation and adsorption have also been utilized [3,4]. Adsorption is commonly applied in the removal of organic compounds and dyes from wastewater due to its high removal efficiency [5]. Activated carbon is the most commonly used adsorbent, but it comes with limitations in application which includes its inefficiency in removing oil, grease, natural organic matter, and other large organic molecules [6]. Organoclays are however capable of removing oil and grease at 5–7 times the rate of activated carbon or at 50% of its dry weight [7]. The affinity of clay for hydrophobic organic compounds is generally considered less significant due to its hydrophilic surface [8]. However, clays can be activated for hydrophobic sorption via

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simple ion exchange reactions using organic cations [9,10] thus converting it to organoclay. The adsorption of organic molecules (ionic and non-ionic) on organoclays has been extensively studied [9,11]. Also, previous studies showed that organoclays are good adsorbents for the removal of organic pollutants [12–16]. The adsorption mechanism and capacity depend on the molecular structure, amount of exchanged organic cations or ammonium cation, chemical properties of the organic compounds, and the CEC of the clay mineral [12,13,15,17–19]. Long hydrocarbon chains that are greater than 12 carbon atoms have proven to be very good modifiers of clay for the purpose of adsorbing ionic and non-ionic compounds [19–21]. The alkyl chains create an organic partition medium that can adsorb organic pollutants through hydrophobic interaction [22]. In the work of Upson et al., and other researchers, hexadecyltrimethylammonium was used for the adsorption of organic pollutants [15,18,23]. A similar result was reported for the adsorption of xylene onto smectite modified with tetramethylammonium [24]. Huang et al. [25] reported that kaolin and montmorillonite modified with aromatic organic constituents have higher adsorption capacities of naphthalene and phenanthrene than those modified with aliphatic organic compounds. Organo-montmorillonite has also been used for the adsorption of dye [26,27].

Ionic liquids have been used to modify adsorbents for the adsorption of organic pollutants. Recently, Lawal and Moodley [28] adsorbed amaranth dye using montmorillonite modified with 1-methyl, 3-decahexyl imidazolium. The adsorption of reactive red-120 and 4-(2-pyridylazo) resorcinol from aqueous solution by ionic liquid modified Fe_3O_4 magnetic nanoparticles was reported by Absalan and coworkers [29]. Also, the adsorption of folic acid, riboflavin, and ascorbic acid has been reported using ionic liquid modified Fe_3O_4 magnetic nanoparticles [30]. There is presently limited information on the adsorption of organics using IL modified materials and to the best of our knowledge there are no reports on IL modified kaolin for the adsorption of either polycyclic aromatic hydrocarbons (phenanthrene) or dye (acid red). This lack of research on IL modified kaolin for the adsorption of phenanthrene or acid red dyes has prompted our investigation into the adsorption behavior of these two organic pollutants on IL modified kaolin.

In this work, cationic IL (1-hexyl, 3-decahexyl imidazolium) was synthesised and used in modifying kaolin. The modified kaolin was then used to adsorb phenanthrene and acid red dye (ARD) using column and batch studies.

2. Experimental

2.1. Materials

Kaolin (CAS Number 1318-74-7) used in the study with chemical formula of $\text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ and DMSO (CAS Number 67-68-5) was purchased from Sigma Aldrich. 1-bromodecahexane (CAS Number 1318-93-0), imidazole (CAS Number 288-32-4), 1-bromohexane (CAS Number 111-25-1), benzyl bromide (CAS Number 602-057-002), acid red dye and phenanthrene were purchased from Merck. Double distilled water was used for all sample preparation.

2.2. Analytical technique

^1H and ^{13}C NMR spectra of the derivatives were recorded on an AVANCE DPX-400 (400 MHz) spectrophotometer (Bruker, U.S.A.) with tetramethylsilane (TMS) as the internal standard. FT-IR spectra of kaolin and kaolin modified with 1-hexyl, 3-decahexyl imidazolium (modified-kaolin) were recorded on a Tensor 27 FT-IR spectrometer (Bruker Optics, Inc.). Thermal gravimetric analysis and differential thermal analysis (TGA-DTA/DSC) (SDT Q 600 V 20.9 Build 20 instrument) was used to measure changes in chemical and physical properties of the material. This was measured as a function of increasing temperature from ambient to 1000°C (with a constant heating rate of 5°C min^{-1}) under nitrogen atmosphere with a flow rate of 50 mL min^{-1} . The surface morphology of the material was examined by scanning electron microscopy (SEM) using the Leo 435 VP model. Chemical composition analysis of kaolin was determined using a Leo 1450 Scanning Electron Microscope equipped with energy dispersive x-ray analyser (EDX). The interlayer spacing of kaolin and K-IL was measured by x-ray powder diffraction (XRD, Shimadzu XRD-6000, Japan, Cu $\text{K}\alpha$ radiation, 40 kV, 40 mA, Japan), and data were collected for 2θ ranging from 1.3° to 10° with a scan speed of 1 min^{-1} .

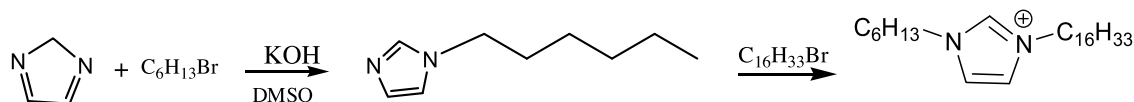
The point of zero charge (pH_{pzc}) of modified-kaolin was determined using the Faria, et al. [31] method. pH_{pzc} is the pH point where $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$. Briefly, 50 mL of 0.01 M NaCl solution was added to a series of conical flasks, and the pH was adjusted to 2–12 using 0.1 M HCl or 0.1 M NaOH when applicable. Samples of modified-kaolin (0.15 g) was added to the flasks, which were then sealed and shaken for 48 h at 25°C . The pH values of individual samples were measured and recorded.

2.3. Synthesis of ionic liquid (IL) 1-hexyl, 3-decahexyl imidazolium

1-Hexyl, 3-decahexyl imidazolium (IL) is a salt consisting of imidazolium (a five membered ring compound with two nitrogen atoms with one of them a quaternary ammonium) at the center with a hexyl group and decahexyl alkyl (16 carbon) chain attached to the ammonium and the quaternary ammonium in the ring, respectively. The preparation was in two stages, formation of the 1-hexyl imidazole and formation of the salt.

The formation of the 1-hexyl imidazole was prepared by modification of the method used by Starikova et al. [32]. Briefly, KOH (0.84 g, 0.015 mmol) was added to the solution of imidazole (0.01 mol) in DMSO (30 mL) and stirred at room temperature for 2 h. Freshly distilled alkyl halide (0.01 mol) was added drop wise to the mixture under vigorous stirring and thereafter cooled in a water bath. After 5 h the mixture was diluted with distilled water and extracted with dichloromethane ($10 \times 10\text{ mL}$), the organic layers were washed with distilled water to pH 7, and dried over MgSO_4 . After removal of chloroform the residue was distilled under vacuum. Column chromatography was used for product purification. Before formation of the salt, the product was characterised by ^1H and ^{13}C NMR to ascertain its purity. (Spectral data can be found in the supporting information (SI)).

Formation of the salt was achieved using the Dzyuba method [33]. An oil bath with a stirred flask containing equimolar amounts of 1-hexyl imidazole and the primary alkyl bromide (bromodecahexane) was heated at 140°C for 10–15 min and thereafter cooled. The solution was heated again in the oil-bath at 140°C for



Scheme 1. Synthesis of 1-hexyl, 3-decahexyl imidazolium.

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