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Scavenging of aqueous toxic organic and inorganic cations using novel facile magneto-carbon black-clay composite adsorbent

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ABSTRACT

New magneto-carbon black-clay composite adsorbents derived from feldspar clay, acorn (*Quercus robur*) fruit pericarp have been developed for efficient removal of both organic (methylene blue- MB) and inorganic (Cd(II)) pollutants from aqueous solutions. The facile composite adsorbents prepared in a one-pot process using two varying mass ratios of clay to carbon black of 0.5:1 (BMF-0.5) and 1:1 (BMF-1) exhibited higher cation exchange capacity (CEC) than any of the starting adsorbents. The rates of removal of MB were faster than for Cd(II) ions in both composites, and consequently, faster equilibrium (30 and 120 min, respectively). The pseudo-second order kinetic model described the adsorption data better suggesting that the removal mechanism involved electrostatic interactions. Surface adsorption (≥56%) accounted for the bulk of cations removal on the BMF-0.5 composite, while adsorption on pores or within various partitions was dominant (≥54%) on the BMF-1 adsorbent for both cations. The equilibrium data for both cations adsorption onto BMF-0.5 and BMF-1 fit the Langmuir-type adsorption isotherm implying that adsorption of both cations occurred on adsorption sites having equal affinity for these cations and with the formation of only monolayer cations on adsorbent surfaces at equilibrium. Cd(II) was more adsorbed than MB on the adsorbents while increase in temperature enhanced adsorption to an extent: 298 > 288>308 K. The adsorption capacities of BMF-0.5 and BMF-1 for both cations were approximately 14 and 16 mg/g, respectively. Pre- and post-adsorptive IR spectra study suggested that the positions of active interactions between the cations and the adsorbents involved surface functional groups such as the −OH, $-COO^-$, and −C−N groups. The composite adsorbents could be reused more than three times without significantly losing the cation adsorption efficiency. Thus, magneto-carbon black-clay composite is a promising adsorbent for removal of organic and inorganic pollutants from water.

1. Introduction

It is estimated that more than one out of six persons lack access to safe drinking water (Okoli et al., 2016; Olu-Owolabi et al., 2017), and with the current increase in world population, the situation may worsen. This is the result of numerous recent anthropogenic activities such as agriculture, manufacture, and diverse services (Adesina et al., 2017; Mokwenye et al., 2016; Olu-Owolabi et al., 2016b) which release vast amounts of pollutants into various receiving water bodies. Commonly encountered pollutants include the toxic metals [such as Cd(II) and Pb(II)] and various organics [such as dyes, pesticides, and polycyclic aromatic hydrocarbons]. With the aforementioned, the need for efficient, easy-to-use, cheap, and accessible water treatment techniques cannot be overstated.

Sorption-based water treatment techniques have proven to be significant in this regard due to several associated techno-economic and environmental advantages, including adsorbent availability, environmental friendliness, and low cost of materials and processing (Aksu, 2005; Diagboya and Dikio, 2018; Olu-Owolabi et al., 2012; Pacheco et al., 2011). However, most adsorbents, especially the low-cost, suffer one or more drawbacks during applications, such as instability, non-durability, low mechanical strength, low cation exchange capacity, bleeding, non-reusability, low pore size and surface area, etc. Synergistic combination of low-cost adsorbents is a recent breakthrough in adsorption science which is quite exciting (Olu-Owolabi et al., 2017, 2016a, 2018; Unuabonah et al., 2013, 2017). This is because it has enabled well-supplied low-cost materials which suffer a few drawbacks in sorption applications to overcome these drawbacks, and become useful through synergistic combination of their functional properties in new composites. Such

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combinations have resulted in improved adsorbent properties such as better stability and durability, high cation exchange capacity, high pore size, re-usability, reduced bleeding, enhanced mechanical strength, or even higher surface area. These have consequently resulted in higher sorption efficiency.

Though these new composites have shown promising results, they, like several other adsorbents in literature (Asuquo and Martin, 2016; Danmaliki and Saleh, 2016, 2017; Diagboya and Dikio, 2018; Diagboya et al., 2014a; Han et al., 2010; Igberase et al., 2017a, 2017b; Okoli et al., 2015; Wang et al., 2015; Xu et al., 2011; Zhou et al., 2015), present a major challenge in the separation of pollutant-loaded-adsorbents from water after the adsorption process. This is encountered during the batch adsorption process which employs the cumbersome filtration or centrifugation techniques. Both techniques are not cost-effective and difficult to handle when dealing with a large volume of wastewater. Thus, there is need for less cumbersome, more cost-effective, and easy-to-handle batch process.

Magnetization of low-cost composite adsorbents represents a potentially less cumbersome, cost-effective, and easy method of removing pollutant-loaded-adsorbents from treated water. This involves magnetizing the low-cost composite adsorbents during the preparation and the magnetized low-cost composite adsorbent is then used for the batch adsorption. At the end of the treatment process, the adsorbent can be easily removed from water by subjecting it to the influence of a strong magnetic field. Such technique has been employed for separating magnetized individual adsorbents from solution (Anbia et al., 2015; Diagboya et al., 2015; Kang et al., 2011; Li et al., 2011; Nassar, 2010; Oliveira et al., 2003; Wang et al., 2015).

With the aforementioned in mind, the objective of this study was to develop an efficient magnetic composite adsorbent from feldspar clay and a common nuisance ornamental biomass – acorn (*Quercus robur*) fruit pericarp; both materials are readily available at low-cost. The magnetic composite adsorbent will then be utilized for the removal of two model organic (methylene blue) and inorganic (Cd(II)) cationic pollutants, and the experimental data described using kinetic and adsorption isotherm models.

2. Materials and methods

2.1. Materials, clay and biomass pretreatments

Analytical grade chemical reagents were used for this study. The clay was obtained from the clay reserve of Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria. Feldspar clay (FLC) was treated to remove organic matter and oven dried. After cooling, the clay was ground, sieved through a 230 μm mesh size sieve and stored in an air-tight container prior to the study (see details in SM 1.0). Details of the treatment process are described elsewhere (Olu-Owolabi et al., 2017).

The Acorn (*Quercus robur*) fruit pericarp was obtained from ornamental gardens around Vaal University of Technology. The fruits were cleaned, pericarp separated from the cotyledons and dried to constant weight, before pulverizing to fineness and sieving through a 230 μm mesh size sieve (see details in SM 1.0). The pulverized pericarp biomass was stored in air-tight container prior to the study.

2.2. Preparation of the iron oxide magnetic nanoparticles, biochar, and composites

The Fe_3O_4 magnetic nanoparticles (MNP) was prepared from a 400 mL solution of $FeCl_3$ (7.8 g, 28 mmol) and $FeSO_4$ (3.9 g, 14 mmol) at room temperature using the chemical co-precipitation method (Oliveira et al., 2003). The solution was continuously stirred with an overhead stirrer while 1.0 M NaOH solution was added drop-wise to precipitate the MNP. The MNP was magnetically separated, washed with water and then ethanol before drying. The mass of MNP after drying was noted.

The pulverized pericarp (PER) was separately charred in a crucible at 250 °C for 4 h to obtain the pericarp biochar (PBC). The biomass was first dried at 110 °C for 1 h before increasing the temperature at a rate of 5 °C/min until 250 °C which was maintained for 4 h. The PBC was then cooled, ground, sieved through a 230 μm mesh size sieve. This was followed by washing until the filtrate was colourless indicating no leaching of residual Fe or carbon. The PBC was again dried at 105 °C for 2 h, cooled, weighed noted, and stored.

The Biochar–MNP–FLC combo (BMF) was prepared by calcining the treated FLC, PER, and MNP. The MNP was prepared by chemical co-precipitation in the presence of the FLC and pulverized pericarp, and subsequently calcining at 250 °C. Typically, the FLC and pulverized pericarp were suspended in a 400 mL solution of $FeCl_3$ (7.8 g) and $FeSO_4$ (3.9 g) and stirred thoroughly to allow for wetness. A solution of 1.0 M NaOH solution was added drop-wise to raise suspension pH to 10 and precipitate the MNP on the FLC and PER surfaces. The solution was further stirred for 30 min before separation by centrifugation at 2500 rpm for 4 min. followed by filling of the residue into a crucible for the calcining process. The crucible was heated at 110 °C for 1 h before raising the temperature at a rate of 5 °C/min until 250 °C which stood for 4 h. The amount of FLC, PER, and MNP were adjusted in order to obtain final weight ratios for FLC-MNP-PBC of 1:1:1 (BMF-1) or 0.5:1:0.5 (BMF-0.5) (Fig. 1*a*). Higher ratios were formulated but lacked appreciable magnetic power. After the calcining process, the BMF combos were cooled and washed with water until the filtrate was colourless indicating no leaching of organic matter or iron. The BMF were subsequently dried at 105 °C for 2 h and stored.

The FLC, MNP, PBC, BMF-0.5, and BMF-1 samples were characterized by determining their pH in water, pH at point zero charge (pH_{PZC}) by using the solid addition method, Cation Exchange Capacity (CEC) using the sodium saturation method, infra-red spectra using Fourier transform infrared (FTIR) spectrometer (Perkin Elmer Instruments, USA), and *X*-ray diffractograms using X-ray diffractometer (XRD-7000, Shimadzu, Japan).

2.3. Adsorption experiments

Analytical grade methylene blue –MB and Cadmium chloride salt (Aldrich) were used for stock solutions (500 mg/L) preparations in this study. Adsorption studies were performed at varying times (1–240 min; concentration of 100 mg/L for MB and $CdCl_2$), pH (3–11; 100 mg/L for MB and $CdCl_2$ at 120 and 180 min, respectively), concentration (15–150 mg/L; 150 and 180 min for MB and $CdCl_2$, respectively) and temperature (15, 25, and 35 °C; same conditions as concentration). The reusability of the adsorbents was examined. All working solutions were prepared in 0.005 M of $CaCl_2$ background electrolyte and each experiment carried out in replicate. Typically, the adsorption experiments were carried out by adding 20 mL solution of specified concentration of any of the cations above into vials containing 100 mg of the adsorbent. The adsorbent and cation mixtures were then equilibrated at 150 rpm at pH 6.7 ± 0.5 and 16 °C (except otherwise stated) on an orbital shaker. When necessary pH of working solutions were adjusted by adding drops of either 0.1 M HCl or NaOH. After each experiment, appropriate vials were withdrawn, centrifuged at 4000 rpm for 10 min and the supernatant used to determine the amount of cation left in solution.

The reusability study was carried out using 0.1 g of the cation-