



Facile synthesis of new amino-functionalized agrogenic hybrid composite clay adsorbents for phosphate capture and recovery from water



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ABSTRACT

New hybrid clay materials with good affinity for phosphate ions were developed from a combination of biomass-*Carica papaya* seeds (PS) and *Musa paradisiaca* (Plantain peels-PP), ZnCl₂ and Kaolinite clay to produce iPS-HYCA and iPP-HYCA composite adsorbents respectively. Functionalization of these adsorbents with an organosilane produced NPS-HYCA and NPP-HYCA composite adsorbents. The pH_{pzc} for the adsorbents were 7.83, 6.91, 7.66 and 6.55 for iPS-HYCA, NPS-HYCA, iPP-HYCA and NPP-HYCA respectively. Using the Brouer-Sotolongo isotherm model which best predict the adsorption capacity of composites for phosphate, iPP-HYCA, iPS-HYCA, NPP-HYCA, and NPS-HYCA composite adsorbents respectively. When compared with some commercial resins, the amino-functionalized adsorbents had better adsorption capacities. Furthermore, amino-functionalized adsorbents showed improved adsorption capacity and rate of phosphate uptake (as much as 40-fold), as well as retain 94% (for NPS-HYCA) and 84.1% (for NPP-HYCA) efficiency for phosphate adsorption after 5 adsorption-desorption cycles (96 h of adsorption time with 100 mg/L of phosphate ions) as against 37.5% (for iPS-HYCA) and 35% (for iPP-HYCA) under similar conditions. In 25 min desorption of phosphate ion attained equilibrium. These new amino-functionalized hybrid clay composite adsorbents, which were prepared by a simple means that is sustainable, have potentials for the efficient capture of phosphate ions from aqueous solution. They are quickly recovered from aqueous solution, non-biodegradable (unlike many biosorbent) with potentials to replace expensive adsorbents in the future. They have the further advantage of being useful in the recovery of phosphate for use in agriculture which could positively impact the global food security programme.

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1. Introduction

The occurrence of some anions at desirable quantity is crucial to the environment, but the presence of these anions in the environment and the ingestion by humans at high concentrations could, however, be detrimental to both the environment and human health. For instance, anions such as phosphates and nitrates

are essential nutrients for all life forms. They are crucial nutrients in the aqua system to maintain a reasonable level of productivity in lakes, rivers, and estuaries. However, high concentrations of phosphates and nitrates have been linked to eutrophication of water bodies and blue baby disease in infants (Oliveira et al., 2012; Bekele et al., 2014). There are point and non-point sources of phosphates in water which include discharge from industries and effluent from municipal sewage treatment plants and factories for the former and agricultural activities like runoff from farmlands treated with phosphate fertilizers, atmospheric deposition, and stormwater runoff for the later.

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Excess concentration of phosphates in surface water can lead to excessive algal growth followed by decomposition, depletion in dissolved oxygen, eutrophication and a reduction in water quality. Consumption of high concentrations of phosphate has been implicated in kidney damage and osteoporosis (Oliveira et al., 2012). It has been shown that continuous discharge of phosphate into a water body increases the level of toxins in such water body (Zhang et al., 2011).

In this regard, different approaches and technologies have been employed for removal of phosphates in water. These include biological treatment, chemical precipitation, and adsorption (Lin and Juang, 2002; Shen and Wang, 1994; Unuabonah et al., 2013). Biological treatment and chemical precipitation technologies are, however, not very efficient because of associated problems, such as; limited versatility, operational difficulties, the high cost of operation among others. Adsorption technique has been found to be more economical and efficient (Ugurlu and Salman, 1998) as it can also serve the purpose of nutrient recovery (Oladoja et al., 2015) especially in the face of depleting world supply of phosphate resources.

It is, therefore, important to look for cheap, versatile and efficient treatment technology which is applicable even in rural settings to remove anions from contaminated water. In this regard, the potentials of different adsorbents for the capture of phosphates in water have been investigated. Such adsorbents include fly ash, red mud, snail shell, hydrocalumite, (Huang et al., 2008; Oladoja et al., 2014; Ugurlu and Salman, 1998; Xie et al., 2015). However, these adsorbents were of low efficiency, adsorption capacity and rate of uptake of phosphate because of the non-functionalization of their surfaces.

In order to improve the efficiency and rate of phosphate uptake of these adsorbents used in environmental pollution control, several investigations have been dedicated to the surface functionalization of different mesoporous materials using aminoalkoxy silanes (Calvo et al., 2009; Hamoudi et al., 2010; Huang et al., 2008; Najafi et al., 2012; Puglisi et al., 2009; Xie et al., 2015). Furthermore, the uptake of several heavy metals such as mercury, lead, cobalt, copper and zinc cations (Lee et al., 2016; Najafi et al., 2012; Nakanishi et al., 2014; Xin et al., 2012), and even organic molecules (Ghorbani et al., 2016; Tu et al., 2015; Zhang et al., 2015) with amino-functionalized mesoporous materials have been well documented. The uptake of anions such as chromate, arsenate and selenate, nitrate and phosphate with protonated amino-functionalized mesoporous silicas has also been studied (Chen et al., 2015; Ebrahimi-Gatkash et al., 2015; Elwakeel et al., 2016; Morales et al., 2016). Even though there have been reports on the use of phosphate-modified clay adsorbents for removal of heavy metal ions (Adebowale et al., 2008; Olu-Owolabi and Unuabonah, 2011; Unuabonah et al., 2010), there is however, no report on the removal and recovery of phosphate from aqueous solution using amino-functionalized agrogenic based hybrid clay composite adsorbents.

In this present study, new amino-functionalized Zn-doped agrogenic-clay (Zn-HYCA) composite adsorbents were prepared from Kaolinite, *Carica papaya* seed and Plantain Peels (*Musa paradisiacal*), characterised and applied for phosphate ion removal in water. Microwave-assisted technique was used prior to amino-functionalization. It has been suggested that microwave irradiation provide efficient pre-treatment of biomass for adsorption (Simha et al., 2017). Amino-functionalization, aside from improving the adsorption capacity of the adsorbents for the adsorption of phosphate ions, enhanced the rate of uptake of phosphate and helped retain more of the adsorbents' capacity even after 5 adsorption-desorption cycles. The technique employed in the preparation of these adsorbents is simple and could be upscaled for

large-scale treatment of water.

2. Materials and methods

2.1. Materials

Raw kaolinite clay was obtained from Redemption City, Ogun State, Nigeria and the *Carica papaya* seeds and plantain peels were collected from different locations in Nigeria. Zinc chloride, [3-(2-aminoethylamino) propyl] trimethoxysilane (AEPTS, $C_8H_{22}N_2O_2Si$, ≥ 80.0 wt%) were Sigma-Aldrich Chemie products; Toluene, Isopropanol, Potassium dihydrogen phosphate, Ammonium metavanadate, Ammonium molybdate hexahydrate, the Hydrochloric acid used were of analytical grade.

2.2. Methods

2.2.1. Preparation of hybrid clay adsorbents with microwave assisted method

Raw kaolinite clay was processed for the removal of stones and other heavy particles present in the sample. The clay material was purified according to the method described by Adebowale et al. (2005) via several washes and filtration processes with a 100 mesh size sieve after treatment with 30% H_2O_2 . The biomasses (*Carica papaya*, and Plantain peels) were pretreated by sun drying until constant weight was obtained and subsequently pulverised. They were collected and stored in separate airtight containers.

Kaolinite, crushed *Carica papaya* seeds or plantain peels, and $ZnCl_2$ were weighed in the ratio (1:1:2) and thoroughly mixed in a beaker with 50 mL deionized water. The mixture was allowed to stand for 24 h with intermittent stirring and was subsequently dried in an oven. The impregnated mixture was transferred into a microwave transparent reactor, purged with nitrogen gas for about 5 min and calcined for 15 min at 450 W in a microwave oven (Kenwood model K30GSS13). The product was allowed to cool in a desiccator, washed with dilute HCl and washed several times with deionized water until a clear solution was observed. These materials were dried in an oven at 105 °C, cooled in the desiccator, packed in sample bottles and labelled as iPS-HYCA and iPP-HYCA composite adsorbents (where PS and PP represent *Carica papaya* seeds and Plantain Peels respectively).

2.2.2. Functionalization of adsorbents

The hybrid clay composite adsorbents iPS-HYCA and iPP-HYCA prepared were functionalized using the method described by Li et al. (2008). The materials were dried at 105 °C in an oven to remove adsorbed water molecules on the surface of the materials, and 10 g of the materials was stirred vigorously in toluene containing [3-(2-aminoethylamino) propyl] trimethoxysilane (AEPTS, $C_8H_{22}N_2O_2Si$, ≥ 80.0 wt%). The reactant mixture was refluxed at 100 °C for 6 h. The product was filtered and washed with 50 mL isopropanol, then dried at 50 °C. The amino groups on the surface of the materials were then activated via interaction with 0.1 M HCl for 6 h. This step is aimed at converting surface amino groups to ammonium moieties. The materials were washed to a neutral pH and dried to constant weight at 50 °C. The materials were packed and labelled as NPS-HYCA and NPP-HYCA composite adsorbents.

2.3. Physicochemical characterization

The crystallinity and mineralogical assemblage of the adsorbents were determined via X-ray diffraction (XRD). The X-ray diffraction patterns were recorded on a Siemens D-5000 X-ray Diffraction equipment from 3.0 to 70° 2θ at $0.02^\circ s^{-1}$. The surface morphology and elemental composition were determined by

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