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Phosphate removal from aqueous solutions using kaolinite obtained from Linthipe, Malawi

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ABSTRACT

Earlier work on stream water and effluent from wastewater treatment plants in Blantyre, Malawi, has revealed high phosphate levels ranging from 0.63 to 5.50 mg/L. These phosphate levels would stimulate excessive growth of plants and toxic cyanobacteria in stagnant receiving water bodies hence posing a threat to aquatic life and water quality. Phosphate removal by kaolinite obtained from Linthipe, Malawi, was investigated as a function of pH, contact time, clay dosage, competing ions and initial phosphate concentration by means of jar tests. Phosphate uptake was pH dependent with adsorption mechanisms on kaolinite and iron oxide surfaces dominant generally below pH 7 and precipitation by calcium ions dominant above pH 7. Maximum phosphate removal occurred at high pH values of 11.22 (97.1%) and 10.96 (100%) for raw and treated kaolinite, respectively. Acid treated kaolinite indicated higher phosphate removal efficiency than the raw one at the normal working pH of 9.0 ± 0.2. This was attributed to release of extra calcium ions from $CaCO_3$ present in the kaolinite samples during acid treatment. At the maximum dosage of 80 g/L, percent phosphate removal was 69.7 ± 0.100% and 98.5 ± 0.0577% for raw and treated kaolinite, respectively. This indicates requirement for high dosages to effect phosphate removal from the aqueous solutions. Studies on the effects of competing ions indicate that phosphate uptake decreased in the presence of CO_3^{2-}, was little affected by SO_4^{2-}, and increased in the presence of Ca^{2+}, and Mg^{2+} ions. Furthermore, phosphate uptake approached equilibrium slowly at 20 °C and was faster at 40 °C.

1. Introduction

Phosphorus is one of the primary nutrients that cause detrimental eutrophication in aquatic environments. A continuing elevated level of phosphorus in stagnant water systems stimulates growth of aquatic plants and toxic cyanobacteria. The common forms of phosphorus in wastewater are polyphosphates (polymers of phosphoric acid), organically bound phosphates, and the most abundant orthophosphates (Hammer and Hammer Jr., 2001). Large quantities of phosphates are used in many industrial applications with fertilizers being the most important. Other applications include domestic use of detergents containing phosphate formulations as well as excessive fertilizer application to agricultural lands. Phosphorus content of effluents or streams that discharge directly into lakes and dams is regulated by national and international water standard authorities with maximum limits ranging from 0.1 to 2.0 mg/L as P, and many established at 1.0 mg/L (Hammer and Hammer Jr., 2001). A study on water and wastewater quality in Blantyre, Malawi, revealed phosphate concentrations ranging from 0.63 to 5.50 mg/L in some streams and effluent from some wastewater treatment plants (Sajidu et al., 2007). This indicates need for phosphate removal during wastewater treatment in an effort to prevent eutrophication of stagnant water bodies onto which the effluent is discharged. Conventional methods for phosphorus removal from wastewater include biological uptake and chemical precipitation using iron and aluminum salts. Despite biological uptake and chemical precipitation being established methods, problems are encountered owing to poor operation stability or high economic costs. There has been growing interest in search for low cost materials that can be used for phosphate removal during wastewater treatment. A lot of studies have been done on phosphate removal using low cost materials such as blast furnace slags (Johansson and Gustafsson, 2000; Kostura et al., 2005;), alunite (Ozacar, 2006), calcite (Karageorgiou et al., 2007), iron oxide tailings (Zheng et al., 2004), flyash (Can and Yildiz, 2006; Chen et al., 2007), bauxsol (Akhurst et al., 2006), red mud (Pradhan et al., 1998; Huang et al., 2008) and sludge from Fuller's earth production (Moon et al., 2007). The above listed low cost materials removed phosphate ions from aqueous solutions either through adsorption on iron and aluminum (hydr)oxides or precipitation of phosphate salts by $Ca^{2+}$and

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Fe^{3+} ions. Amongst iron oxide minerals that have strong affinities for phosphate ions, goethite is the most studied owing to its role in nutrient adsorption and desorption in soils. Adsorption of phosphate on goethite is attributed to a ligand exchange reaction on the adsorbent surface, in which the phosphate ion is exchanged with surface structural hydroxyl groups (Russell et al., 1974). Phosphate adsorption on goethite proceed mainly via formation of innersphere bidentate complexes, $(FeO)_2PO_2(H)$ from pH 3.5 to 8.0 with abundance of a monodentate complex, $FeOPO_3(H)_{1,2}$, increasing with increasing pH and decreasing phosphate surface coverage (Zhong et al., 2007). In their study on phosphate adsorption on hematite, Elzinga and Sparks (2007), reported surface complexes bound in a monodentate (bridging) fashion as well as those coordinated as monodentate mononuclear complexes to the hematite surface. Similarly, anion adsorption on aluminum oxide surfaces proceeds through formation of ion-pairs with positively charged surface sites or by ligand exchange with surface hydroxyls (Goldberg et al., 1996).

Reactions between phosphate species and iron and aluminum salts during chemical precipitation are complex and not fully understood, however the primary reaction appears to be the combining of orthophosphate with the metal cation (Hammer and Hammer Jr., 2001). Investigations on phosphate removal using calcium containing materials such as fly ash and calcite have shown that phosphate precipitates with calcium as apatites, especially hydroxyapatites $\{Ca_5(PO_4)_3{\cdot}OH\}$ (Johansson and Gustafsson, 2000; Karageorgiou et al., 2007; Moon et al., 2007).

This paper reports on removal of orthophosphate species from aqueous solutions by kaolinite obtained from Linthipe, Malawi, investigating key process parameters.

2. Materials and methods

2.1. Preparation and characterization of kaolinite samples

Kaolinite samples used in this study were obtained from kaolin deposits located at Linthipe in Dedza district Malawi. The clay samples have chemical composition given in Table 1 as determined by the Geological Survey Department of Malawi (GSoM). Prior to use, the samples were further sun-dried for 48 h and ground by a traditional pestle and mortar followed by sieving through a 60-mesh size sieve. Clay samples prepared in this way are referred to as raw Linthipe kaolinite (RL-Ka). Acid treatment of the kaolinite samples was achieved by addition of 100 mL hydrochloric acid (0.3 mol/dm^3) to a 200 g clay sample, ensuring thorough mixing in the process. This was followed by drying of the wet clay in a sample-drying oven (Gallenkamp OVL 570 010 J) at 50 °C for 7 h, crushing of the clay blocks, and sieving through a 60-mesh size sieve. Samples prepared in this way are referred to as treated Linthipe kaolinite (TL-Ka).

2.2. Potentiometric titration

RL-Ka samples (0.1 kg) were saturated with sodium by repeatedly suspending them in 1 mol/dm^3 $NaNO_3/HNO_3$ solution at pH 3. After centrifugation of the suspension (using a Hettich Roxita/AP centrifuge), the supernatant was discarded and replaced with fresh solution. This was done up until when the supernatant solution pH had dropped to pH 3. This was followed by repeated suspension of the samples in non-acidified $NaNO_3$ and centrifugation up until when the supernatant pH value approached 5. At this point, the samples were repeatedly suspended in 0.1 mol/dm^3 $NaNO_3$ and centrifuged until a stable pH was registered. A Thermo Ross Sure Flow combination electrode (Orion 8172) suitable for pH determination in suspensions was used through out the study along with a Mettler-Toledo SevenMulti meter. Na-saturated clay stock suspensions were stored at pH 5.2–5.8 in sealed centrifuge bottles. Pretreatment of the RL-Ka samples assisted in removing calcium carbonates that could have interfered during the titration, besides saturating the clay with sodium.

Table 1
Chemical composition of Linthipe kaolinite.

Parameter	Composition (wt.%)
SiO_2	46.7
Al_2O_3	33.8
Fe_2O_3	2.0
CaO	1.1
MgO	0.26
$K_2O + Na_2O$	0.28

Suspensions of 6.0 g sample/L were used for the potentiometric titrations. The RL-Ka suspension (25 mL) was titrated with 0.0236 mol/dm^3 nitric acid and 0.0200 mol/dm^3 NaOH stepwise using a Metrohm 775 Dosimat titrator equipped with a Metrohm 806 exchange unit. The pH reading was recorded after equilibration of each step (30 min). During the titration the flask containing the suspension was covered with a parafilm to minimize formation of carbonates at pH greater than 6. A blank titration (excluding the clay) was run following the same procedure. The apparent proton surface charge density, $\sigma_{H,titr}$, was calculated using the equation:

$$\sigma_{H,titr} = M_{soln}\left\{([H^+]_b - [H^+]_s) - \left(\frac{K_w}{[H^+]_b} - \frac{K_w}{[H^+]_s}\right)\right\}$$

where M_{soln} is the mass of electrolyte solution (per unit dry mass) equilibrated with the clay, $[H^+]$ is the solution proton concentration, K_w is the dissociation product of water, and the subscripts s and b refer to sample and blank solutions, respectively (Scroth and Sposito, 1997). The point of zero net proton charge (p.z.n.p.c.) was determined as the *x*-intercept on a plot of net proton surface charge density against pH.

2.3. Standard solutions

A standard phosphate stock solution (1000 mg/L) was prepared by dissolving an appropriate amount of analytical grade anhydrous KH_2PO_4 (Glassworld, SA) in distilled water. Intermediate standard solutions (100 mg/L) were prepared by diluting the stock solution with distilled water. The intermediate standard solutions were used in obtaining desired phosphate concentrations. Similarly, carbonate standard solutions were prepared from Na_2CO_3 (Glassworld, SA) whilst sulphate, calcium (Ca^{2+}), and magnesium (Mg^{2+}) standard solutions were prepared by dissolving anhydrous Na_2SO_4 (ACE, SA), $CaCl_2$ (SAARCHEM, SA), and $MgCl_2$ (Glassworld, SA) salts, respectively, in distilled water.

2.4. Phosphate removal experiments

Defined masses of RL-Ka or TL-Ka were weighed into centrifuge tubes to which was added a defined volume of either 0.1 mol/dm^3 $NaNO_3$ or distilled water followed by a defined volume of 100 mg/L standard phosphate solution to make a total of 10 mL. Depending on parameters under study, defined volumes of 100 mg/L standard solutions of species of interest were added before introduction of the phosphate solution with adjustments made to added volumes in order to obtain a total volume of 10 mL. An appropriate amount of nitric acid (0.02 mol/dm^3) or sodium hydroxide (0.02 mol/dm^3) was added to the clay suspension to adjust pH to a certain value. The mixture was shaken for a defined period of time using a Griffin flask shaker then centrifuged at 2500 rpm. The supernatant (2–3 mL) was passed through a Titan, 0.45 μm, PES, membrane filter