



Biogenic derived binary metal oxide as a reactive material for remediation of pyrophosphate contaminated aqua system



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ABSTRACT

Owing to the recent discovery about the potentials of pyrophosphate (PP) as a contributor to eutrophication, the ability of a binary metal oxide (BMO) as an adsorbent for PP removal from aqua system was investigated. The choice of a BMO was based on the synergy of the constituent metal oxides in sequestering ionic species. The binary metal oxide (BMO) of Ca and Fe, synthesized using a Gastropod shell, as precursor, exhibited high removal efficiency (>99%) for pyrophosphate (PP), irrespective of initial PP concentration studied (25–300 mg/L). The pseudo second order kinetic model had the best ($r^2 = 1.00$) fitting to the time-concentration profile data. The determination of the saturation index (SI) value of calcium pyrophosphate and application of the principle of constant solubility product affirmed the role of precipitation as a paramount factor in the PP removal process by BMO, in addition to the complex formation between any of the ionic species (i.e. Ca and Fe) in the system. The XRD analysis of the derived sludge revealed the formation of amorphous calcium pyrophosphate. Process variables optimization revealed that initial solution pH, organic load, and ionic strength had no negative impact on the PP removal efficiency. The results of the equilibrium isotherm analysis showed that the Freundlich isotherm equation gave the best description of the sorption process ($r^2 = 0.9109$) and the Langmuir monolayer sorption capacity (q_m , mg/g) value of 120.48 was obtained.

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1. Introduction

Early nineteenth century observations that phosphoric acid and its salts could be transformed into various forms led to the historic classification of phosphates into three types: orthophosphates, pyrophosphates and metaphosphates. The pyrophosphates and metaphosphates are now known as condensed phosphates, which are formed by repeated condensation (polymerization) of tetrahedral $[\text{PO}_4]$ units. This results in chains of tetrahedra, each sharing the O atom at one or two corners of the $[\text{PO}_4]$ tetrahedron. Diphosphate pyrophosphate, $\text{P}_2\text{O}_7^{4-}$ is the simplest condensed phosphate anion, formed by condensation of two orthophosphate anions. Condensed phosphates are polymers of phosphate connected through a phosphoanhydride bond and serve many biological roles, including storage of phosphate, a source of energy in anoxic environments, and the sequestration of multivalent cations [1].

Due to their wide applications, condensed phosphates were subjects of much investigation and controversy for over a century. Pyrophosphate (PP), as a dispersant, was widely used in industrial activities such as electroplating industry in which the effluent contained high concentrations of PP [2]. Condensed phosphates, especially ammonia polyphosphates, are widely applied as fertilizers to provide phosphorous to plants. Prior to the development of the ^{31}P NMR technology, most studies on phosphorus have focused exclusively on orthophosphate, which serves as the most important species of phosphorus in ecological systems [3]. The important role of PP in the phosphorus cycle has been neglected mainly because they are thought to be biologically unavailable without hydrolysis and some are even difficult to measure [4]. However, the recent innovation in ^{31}P NMR technology has made it possible to recognize the significance of PP [5,6]. Chung et al. [7] observed that mono-potassium phosphate and ammonium polyphosphate accounted for the largest quantity of phosphorus in soil leachates, serving as the potential reservoir for the nonpoint phosphorus sources. Sundareshwar et al. [5] reported that accumulation of pyrophosphate in coastal wetlands exceeded that of soluble orthophosphate. They further demonstrated that PP can be readily utilized by microbes in coastal wetland sediments in

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the presence of nitrogen and carbon and it can serve as a reservoir of orthophosphate.

As a result of several evidences on the role of PP as a potential contributor to the eutrophication in ecological systems, it is crucial to develop effective technology for the removal from aqua streams. Amongst the array of methods that have been developed, for the clean-up of the PP contaminated water, the adsorption technique has been recognized as an effective and promising method [8]. Consequently, an array of sorbents, e.g. ferrihydrite [4], aluminum hydroxide [9] and mesoporous magnesium oxide [10], have been investigated as potential sorbents for the remediation of PP contaminated aqua system.

Consequent upon the potential of mixed metal oxides, as advanced materials in the optical industry, ceramics, catalysts and adsorbents for environmental remediation [11–13], attention has focused on them as material of interest in diverse applications. In natural environment, single oxide minerals are scarcer than binary oxide, thus it is presumed that the interaction of particles in binary oxide systems possibly influences the adsorption mechanism of adsorbents produced from such systems [14,15]. Consequently, the oxyanions abstraction potentials of binary metal oxide (BMO) systems are being tested [16–20]. Thus far, the BMO of interest to researchers, for oxyanion abstraction, comprised of mainly transition metals; hence there is paucity of information on performance evaluation of mixed metal oxides of transition origin and alkali earth metals in this respect. Klabunde et al. [21] reported the enhanced performance efficiencies of mixed oxides of alkaline earth metal and transition metals in environmental remediation and surmised that such materials can be viewed as a new class of near stoichiometric chemical reagents. It was concluded that the large surface areas and enhanced surface reactivities, coupled with strategic addition of small amounts of catalytic transition metal ions make this a reality for a large number of environmental remediation chemistries [21].

The present study aimed at incorporating oxide of iron into the framework of growing particles of CaO to produce complex binary oxides of alkaline earth and transition metals. The shell of African land snail (*Achatina achatina*) (SS) shall serve as the precursor for the derivation of the alkaline earth metal oxide (CaO) because of the chemical and mineralogical assemblage. Gastropods have worldwide distribution from the near arctic and antarctic zones to the tropics and very striking in its extraordinary diversification of habitats. Large tons of Gastropod shell are discharged annually, as waste from food processing industries, which made it a low cost and abundant material that could be harnessed for CaO synthesis. The choice of iron as the transition metal to be incorporated onto the CaO matrix was predicated on the substantial affinity of oxides of iron for anionic pollutants [22–24], from contaminated waters. Furthermore, they are environmentally benign, chemically stable over a wide pH range, and cost effective.

At present, the BMO shall be synthesized, characterized and assessed as a functional reactive material for PP capture from aqua system. The time-concentration profile shall be studied to derive the PP uptake mechanism and the kinetic parameters. The sorption process variables (pH, ionic strength and organic load) shall be optimized by method of continuous variations and data for process scale-up shall be obtained via equilibrium isotherm studies.

2. Materials and methods

2.1. BMO preparation and characterization

Solution of CaCl₂ was derived from the SS, as previously described in our earlier discourse [25]. The alkaline earth-transition metal bimetallic oxide material was prepared, as previously described [20], by the sol-gel method, using FeCl₃·5H₂O as the source of Fe thus: mixed solutions containing the

appropriate mass ratios of Ca:Fe (1:1) was prepared and stirred to obtain even mix. The mixture was titrated slowly, under vigorous stirring, at the rate of 0.833 ml/min with 1 M NaOH for 8 h and the precipitate formed was allowed to gelate in the mother liquor for 24 h and then washed several times with deionised water. The washed precipitate was kept in the drying oven at 100 °C for 24 h, and then calcined in the furnace at 1100 °C. The crystallinity and mineralogical assemblage of the material were determined via X-ray diffractometer. The surficial morphology and elemental composition were determined by scanning electron microscope (SEM) equipped with energy dispersive analysis of X-ray (EDAX) and thermogravimetric analysis was carried out in TG analyzer. Textural characteristics were determined using nitrogen absorption procedure, to determine the specific surface area and the pore diameter using an ASAP Micrometrics instrument. The pH_{pzc} was determined via a batch equilibrium procedure described by Milonjić et al. [26].

2.2. Sorption studies

Sorption mechanism and kinetic parameters were evaluated by the addition of 2.0 g of BMO into a liter of the PP solution, prepared from sodium pyrophosphate decahydrate (Na₄P₂O₇·10H₂O), of varying concentrations that ranged between 25 and 300 mg/L. In order to reduce the effects of hydrolysis, all PP solutions were freshly prepared prior to each study. Experiment was conducted at room temperature, typical of a tropical region. The mixture was stirred at 200 rpm in thermostatic shaker between 0, and 4 h, of sorption, centrifuged and the supernatant was analyzed for residual PP.

The equilibrium isotherm analysis of the sorption process was conducted by contacting 50 mL solution of known PP concentration that ranged between 25 and 300 mg/L with 0.1 g of sorbent. The mixture was stirred at 200 rpm in thermostatic shaker for 1 h, samples were removed, centrifuged and the supernatant was analyzed for residual PP.

The effects of process variables were evaluated via optimization of such process variables thus: the effects of pH was investigated by varying the pH of the initial PP solution between pH 7 and 12; the effects of ionic strength was tested in NaCl solutions of the following concentrations (%): 0, 0.05, 0.1, 0.2, 0.5 and 1, equivalent to ionic strengths (mol/L) of 0, 0.0085, 0.017, 0.0342, 0.085 and 0.17; while organic interference was simulated by the addition of humic acid (HA) of concentrations that ranged between 10 and 80 mg/L into a solution of PP of known concentration.

The residual PP was determined by immediately filtering a portion of the mixture through a 0.45 μm membrane filter made of cellulose acetate for analysis according to the standard method [27]. In brief, the concentration of PP was obtained by direct colorimetric reading of a spectrophotometer at a wavelength of 880 nm after preliminary acid hydrolysis of the PP and subsequent conversion to orthophosphate. The amount of PP sorbed per unit mass of the BMO (in mg/g) was calculated using the mass balance procedure.

3. Results and discussion

3.1. Sorbent characterization

The mineralogical assemblage of the BMO was elucidated by matching the diffractogram (Fig. 1) with the database of the JCPDS data and the results obtained showed that the compounds synthesized is a complex oxide of calcium and iron Ca₂Fe₂O₅. Peaks at different 2θ values, 11.9°; 17.0°; 32°; 33°; 33.5°; 46.5°, synonymous with the Ca₂Fe₂O₅ were identified.

The surface microstructures (Fig. 2a) of the BMO, obtained from SEM analysis showed that it is made up of well-defined closely

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