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Note

The potential of phosphate removal from dairy wastewater and municipal wastewater effluents using a lanthanum-modified bentonite

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ABSTRACT

Adsorption is gaining interest as an effective advanced method for treatment of wastewater effluents with a high phosphorus concentration. The present work investigated the use of a bentonite–lanthanum clay (Phoslock®) which effectively reduced the amount of dissolved phosphate. Batch experiments were carried out in order to obtain adsorption equilibrium isotherms and kinetics with phosphate-spiked synthetic solutions. Different doses of Phoslock® clay were examined for their efficiency in removing phosphate from dairy wastewater and from two types of domestic wastewater treatment plant effluents (a sequenced batch reactor (SBR) and an activated sludge plant). The average maximum adsorption capacity ratio was 69 mg Phoslock® per 1 mg of phosphate removed from the phosphate-spiked synthetic solution. Nevertheless, a ratio of 100, 300 and 400 mg Phoslock® per 1 mg of phosphate was found for complete phosphate removal from the effluents of the dairy, the SBR and the activated sludge plant, respectively. The higher ratios are probably due to the presence of dissolved organic matter in the wastewater. Phosphate removal from the effluents was more efficient and faster with the increase in Phoslock® doses (up to 100% removal in the first 15 min for the dairy wastewater). This study shows that bentonite–lanthanum clay can be used to design an adsorption treatment process for phosphate removal from water and wastewater with a low hydraulic retention time and minimal infrastructure.

1. Introduction

Runoff from farmlands and accidental spills of toxic chemicals contribute to the pollution of lakes, rivers, and groundwater in many parts of the world by adding nutrients, including phosphorus. Phosphorus is a pollutant in aquatic systems because it promotes eutrophication which results in the bloom of aquatic plants, growth of algae and depletion of dissolved oxygen. Phosphorus removal from wastewater effluents, using chemical and biological treatments, has been widely studied. In many areas, municipal wastewater treatment plants must remove phosphorous in their treatment process, since a phosphorus concentration that exceeds 0.1 mg/L may accelerate eutrophication in natural habitats. Many studies compared phosphate uptake under aerobic and anoxic conditions (for example, Kerrn-Jespersen and Henze, 1993 and Meinhold et al., 1999). However, difficulties in ensuring long-term stable operation have also been recognized. Nonetheless, the reasons for failure of the biological phosphorus removal treatment are usually not identified (Barnard and Comeau, 2014).

The biological treatment process removes some phosphorus. However, in some cases precipitation of phosphorus as an insoluble compound is required in order to meet discharge regulations. Much attention has therefore been paid to chemical adsorptive removal of phosphorus from aqueous solutions. Many different materials for its removal from wastewater have been investigated, including fly ash and blast furnace slag (Agyei et al., 2002), metallic salts such as ferric sulfate, ferric chloride, aluminum sulfate, alunite, aluminum hydroxide and iron oxide tailings (Tanada et al., 2003; Özacar, 2003) and red mud (Liu et al., 2007). For example, removal rates Q_{max} (mg phosphate/g adsorbent) of 8.31 were found for modified palygorskite clay (Ye et al., 2006), 13.76 for fly ash (Cheung and Venkitachalam, 2000), 44.24 for blast furnace slag (Sakadevan and Bavor, 1998) and 93 for lithium intercalated gibbsite (Wang et al., 2007). However, most studies describe adsorption using a pure phosphate solution, when in fact it is already known that dissolved organic carbon, as found in wastewater and effluents, appears to be the strongest competitor for adsorption sites on various adsorbent materials (Teermann and Jekel, 1999; Genz et al., 2004).

In addition, phosphorus removal may be problematic when very high concentrations are present in the wastewater. For example, dairy wastewater usually contains more than 20 mg/L total phosphorus (Longhurst et al., 2000). This high concentration is a great challenge for wastewater treatment facilities which are designed to treat domestic wastewater, but which actually receive dairy wastewater in addition to the domestic wastewater. Most of the particulate phosphorus in these wastewater facilities is removed in settling tanks. However, this leaves

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the problem of high concentrations of dissolved phosphorus (mainly phosphate), as found in dairy wastewater. It is very difficult to remove dissolved phosphorous from the water using the general biological processes in wastewater treatment plants. Thus, pre- or post-treatment for dissolved phosphate removal using chemical adsorptive methods may be an economic and simple solution for such a task. Although many technologies for removing phosphorous from water were published in the past, the need remains for a relatively simple and safe technology that is efficient and less expensive compared to existing technologies.

Lanthanum has a known affinity for phosphorus. Studies have shown that phosphate precipitation by lanthanum was more effective over a wider pH range (4.5–8.5) than by either Fe(III) or aluminum salts. Lanthanum compounds have been used in water treatment processes because they are less expensive than other rare earth elements and lanthanum oxide's point of zero charge is higher than that of other well-known adsorbents (Shin et al., 2005; Li et al., 2009). The Phoslock® modified bentonite clay was developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organization) in order to significantly reduce the amount of dissolved phosphate present in the water column and in the sediment pore water of a water body. The Phoslock® contains lanthanum ions which are locked into the bentonite clay structure and designed to react with phosphate anion in water to form a highly insoluble and stable mineral named rhabdophane ($LaPO_4$) which its stability was proved under a wide range of pH, temperature, dissolved oxygen and phosphate levels (For more information see: Douglas et al., 2004; Robb et al., 2003; Ross et al., 2008; Haghseresht et al., 2009). Extensive laboratory and mesocosm trials demonstrated the effectiveness of Phoslock® in binding dissolved phosphate and sediment-released phosphate in lakes and rivers (Robb et al., 2003). Nevertheless, we know of only one study that showed phosphate removal from streams contaminated with domestic wastewater using the Phoslock® product (Haghseresht et al., 2009). That study examined contaminated river water. There is thus no knowledge on the effect of Phoslock® on phosphate removal from raw wastewater or from treated effluents. Actually, most of the literature describes adsorption studies of many different chemicals, using a pure phosphate solution, whereas Teermann and Jekel (1999) and Genz et al. (2004) stated that dissolved organic carbon, as found in wastewater and effluents, appears to be the strongest competitor for adsorption sites on various adsorbent materials. It is therefore of great interest to study the potential of this specially designed clay for its efficiency in phosphate removal from different types of wastewater.

The main aim of the present study was to examine the phosphate removal efficiency from dairy wastewater and wastewater treatment effluents using Phoslock® under laboratory conditions, by studying its equilibrium properties and kinetics in batch experiments. These tests were conducted with synthetic pure phosphate solutions, with dairy wastewater and with municipal wastewater effluents from two different wastewater treatment plants (SBR and activated sludge plants).

2. Materials and methods

2.1. Study of adsorption isotherm

Lanthanum-modified bentonite was provided by a local representative of the Australian company Phoslock® Water Solutions Ltd. (PWS). Phosphate stock solution (200 mg/L) was prepared by dissolving KH_2PO_4 (Difco, analytical grade) in distilled water. The stock solution was diluted to obtain phosphate solutions with different concentrations. The adsorption isotherm were obtained by adding five levels (from 0 to 0.8 g) of the Phoslock® bentonite to 50 mL of a 200 mg/L phosphate solution in 250 mL borosilicate glass Erlenmeyer flasks (in triplicates). The experiment was carried out on an orbital shaker at room temperature (25 °C), and the pH remained 7.1 throughout the entire experiment. After 24 h, samples (triplicates) were taken from each bottle for phosphate concentration measurements. The quantity of adsorbed phosphate (adsorption capacity) was calculated from the decrease in the phosphate concentration of the solution.

2.2. Phosphate adsorption kinetics measurements in dairy wastewater

Phosphate adsorption kinetics in dairy wastewater were performed on dairy effluents (Keshet, Israel) that passed through a mechanical manure solids/liquid separation device and a primary sedimentation pond. The dairy effluents had a pH of 7.67, 3 mg/L nitrate, 110 mg/L ammonium, 221 mg/L chloride ions and 4 mg/L dissolved oxygen. The phosphate concentration was 8.33 ± 0.4 mg/L. For the kinetics experiments, different doses of Phoslock® (0–1000 mg) were introduced into 100 mL of dairy effluents in 250 mL borosilicate glass Erlenmeyer flasks. The flasks were stirred on an orbital shaker at 150 rpm at room temperature (25 °C). Samples (triplicates) were taken periodically from each bottle, centrifuged and analyzed for the phosphate concentration.

2.3. Phosphate adsorption kinetics measurements in domestic wastewater effluents

Phosphate adsorption kinetics in domestic wastewater treated effluents were carried out on two different effluent sources from two different wastewater treatment plants. One ("Meitzar") is an activated sludge technology wastewater treatment plant, and the other ("Dinur") is a SBR wastewater treatment plant. Both "Meitzar" and "Dinur" receive domestic wastewater together with large amounts of dairy wastewater throughout the year and suffer from a high phosphate concentration in their effluents. "Dinur" effluents had a pH of 7.38, 17.8 mg/L nitrate, 6.27 mg/L ammonium, 233 mg/L chloride ions and 5 mg/L dissolved oxygen. "Meitzar" had a pH of 7.26, 21.3 mg/L nitrate, 16.1 mg/L ammonium, 202 mg/L chloride ions and 6 mg/L dissolved oxygen. The phosphate concentration was 13.02 ± 0.47 and 4.82 ± 0.06 mg/L for "Meitzar" and "Dinur", respectively. For the kinetic experiments, different doses of Phoslock® (76, 153 and 306 mg for "Dinur" effluents and 207, 414 and 828 mg for "Meitzar" effluents) were introduced into 100 mL of effluent in 250 mL borosilicate glass Erlenmeyer flasks. These doses were calculated as follows: the initial phosphate amount (in mg) in the treatment bottles multiplied by 50, 100 and 200. The flasks were stirred on an orbital shaker at 150 rpm at room temperature (25 °C). Samples (triplicates) were taken periodically from each bottle, centrifuged and analyzed for the phosphate concentration.

2.4. Water physicochemical parameters

All chemical tests were performed according to Standard Methods (Rice et al., 2012). The colorimetric method using stannous chloride was used for determination of the phosphate concentration at 650 nm (GENESYS 20, Thermo Scientific). The adsorbent was eliminated by centrifugation at 6000 rpm for 6 min.

2.5. Statistical analysis

Two-way analysis of variance (ANOVA) followed by posttests was performed on all treatments containing different Phoslock® doses with GraphPad Prism version 6.05 (GraphPad Software Inc.), with mean differences regarded as significant at $p \leq 0.01$. Tukey's post-hoc tests were used for multiple comparisons between groups. All results presented in this study were found to differ significantly, with $p < 0.01$, except for the results of the treatments containing 500 and 1000 mg Phoslock® in the dairy wastewater experiments.