Technical Note

Removal of phosphate by adsorption onto oyster shell powder — kinetic studies

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Abstract: Kinetic studies on the removal of phosphate by adsorption onto oyster shell powder have been investigated at 24 °C. The results showed that the equilibrium occurred in 10 min and the equilibrium data followed the Freundlich isotherm. Freundlich constants were found to be \( k_f \), \( 1.4 \times 10^{-2} \), and \( n \), 0.71. The phosphate removal was not influenced by pH over the range 5.0–10.5. Continuous agitation studies at 24 °C and 530 rpm reached equilibrium after 7.7 days, when 24 g dm\(^{-3}\) of oyster shell powder reduced the phosphate concentration from 50 to 7.0 mg dm\(^{-3}\). The Lagergren rate constant for the slow adsorption process was observed to be 3.81 \( \times 10^{-4} \) dm\(^3\) min\(^{-1}\). Comparison with calcium carbonate, GR grade, showed that oyster shell powder and CaCO\(_3\) behave more or less in the same way.

Keywords: phosphate; oyster shells; adsorption; kinetics; pH effect

INTRODUCTION

Removal and recovery of phosphate from wastewaters is important in the context of eutrophication in the receiving waters and the growing demand for nutrients to meet the needs of the increasing world population. Phosphate removal has been carried out by precipitation as calcium phosphate using calcium chloride or lime. Calcium phosphate exists in different forms: tricalcium phosphate, octacalcium orthophosphate, hydroxyapatite, monocalcium orthophosphate and dicalcium orthophosphate. However, this method produces excess chemical sludge and needs pH correction before the effluent can be discharged into receiving waters. These are eliminated in the adsorption process. Adsorbents used in the literature are composite adsorbents such as zirconium hydroxide supported on natural zeolite; clinoptilolite;2 magnesia clinker;3 half-burned dolomite;1 activated alumina with aluminum sulfate;4 red mud;5 ferric iron;6 fly ash;7 and hematite, bentonite, and bentonite–hematite systems.8 Polymeric ion exchangers9 and biological systems10,11 have also been investigated for the removal of phosphate.

Oyster shells are generated in large quantities in the marine food industry in Japan as well as in other countries. They are a rich source of calcium carbonate and it is well known that the latter is used not only as an adsorbent but also for alkalizing the wastewater in wastewater pre-treatment processes. Recycling waste oyster shells in the place of calcium carbonate may make the wastewater treatment process economical and works towards the goal of zero-emission. The raw oyster shell, however, is not a substitute for calcium carbonate. In this work, oyster shell powder (OSP) has been investigated for the removal of phosphate from water. The percentage calcium in OSP is 28%; the average particle size is 200 \( \mu \)m and the BET surface area is 237 m\(^2\) g\(^{-1}\). Kinetic studies have been carried out in this work to investigate the conditions for the effective and economic utilization of OSP.

MATERIALS AND METHODS

Powdered oyster shells were prepared by using high-pressure steam as follows: the apparatus consisted of a steam generator, a 0.5 dm\(^3\) reactor, a ball valve and a 20 dm\(^3\) product receiver. The generator supplied steam, which was compressed by a plunger pump, to obtain a stream of high-pressure steam that was then fed into the internal vessel and the constant temperature jacket of the reactor. The steam temperature controlled the reaction temperature and its internal pressure followed the saturated vapor pressure. For this study, 234 °C was chosen as the reaction temperature, giving a saturated vapor pressure of 3.0 MPa. After the shell sample was treated in the reactor for several minutes, the ball valve...
was released momentarily. Then the steam-exploded products (crushed solid and liquor) were collected from the receiver, washed with water and dried at 105 °C.

All experiments were carried out using a synthetic phosphate solution prepared from Na₃HPO₄ 2H₂O in deionized water. Both 10 and 50 mg dm⁻³ phosphate solutions were used. Both batch and continuous agitation methods were used for the studies. In the batch mode, phosphate solution (50 cm³) and OSP (1.2 g) was agitated at 115 rpm and 24 °C. After agitation for predetermined time intervals, the agitation was stopped, flasks were withdrawn and calcium and phosphate were analyzed accurately. Agitation of the 1 dm³ solution at 530 rpm continued for 9.7 days, with equilibrium being reached after 10.5 days. In the continuous agitation mode, phosphate solution (50 cm³) was agitated at 530 rpm and 24 °C. Aliquots (10 cm³) were withdrawn at predetermined time intervals, filtered through 0.45µm membrane filters and the phosphate and calcium were analyzed accurately. The volume of the solution was maintained constant by reintroducing after each sampling 10 cm³ of solution having a phosphate concentration identical to the previous sample. The effect of adsorbent dose was carried out using 10 and 50 mg dm⁻³ phosphate solution at pH 5 for 90 min at 115 rpm and 24 °C. The Freundlich isotherm was obtained using the adsorbent dose effect data. Some adsorption experiments were conducted in a batch mode using GR grade CaCO₃ for comparison with the OSP results.

Phosphate was estimated using the ascorbic acid method. Calcium was estimated using a modification of Hach’s method for estimation of hardness.

RESULTS AND DISCUSSION

Raw oyster shells did not show any removal of phosphate and it was only after treatment of the shells as described above (OSP) that any removal was obtained. Two equilibria were observed in the removal of phosphate by OSP, the first following fast processing after 10 min (Figs 1 and 2) and the second after slow processing for 7.7 days (Fig 3). In the fast process, with increased OSP dose, the percentage removal (Fig 4) and free Ca²⁺ increased, and the final pH approached 9.3 for an initial pH = 8.5. The equilibrium data for the fast reaction at 10 mg dm⁻³ phosphate concentration (R² = 0.6399) did not follow the Freundlich isotherm (Fig 5). However, equilibrium data for the fast reaction using 50 mg dm⁻³ phosphate solution did follow the Freundlich isotherm (R² = 0.8748) (Fig 6); with constants kᵢ = 19.47 and n = 1.02. The initial pH of phosphate solution did not influence the percentage removal over the initial pH range, 5.0–10.5, for OSP and CaCO₃. However, the amount of free Ca²⁺ in the solution after phosphate removal decreased and the final pH increased from 9.0 to 10.0 with increase in the initial pH. For the slow process, the amount of free Ca²⁺ was found to increase with agitation time.
and final pH remained at 8.4 for an initial pH of 8.5 (Fig 3). The Lagergren plots for the pseudo-first order fast ($R^2 = 0.9143$) and slow ($R^2 = 0.9898$) adsorption reactions were linear (figures not shown) with rate constants 0.2019 and $3\times10^{-3}$, respectively. Compared with CaCO$_3$ the percentage removal is slightly lower for OSP both at pH 5.0 and 6.8 (Figs 1 and 2). But Ca$^{2+}$ release is higher for OSP both at pH 5.0 and 6.8. In both CaCO$_3$ and OSP systems, Ca$^{2+}$ release is less at pH 6.8 compared with pH 5.0. At pH 8.5 both give the same removal (55%) and the same Ca$^{2+}$ release ($18\times10^{-3}$). In the continuous agitation mode, 1 dm$^3$ of water containing 50 mg dm$^{-3}$ phosphate required 24 g of OSP to reduce the concentration to 7.0 mg dm$^{-3}$ in 7.7 days. Based on published results and those obtained here, it can be shown that phosphate removal by OSP occurs by sorption through the binding of phosphate as amorphous calcium phosphate on the surface of OSP, which then slowly transforms into hydroxyapatite. The occurrence of two equilibria is shown as fast sorption from the start up to 10 min and then a slow transformation to hydroxyapatite. Further studies are required to confirm the nature of the calcium phosphate species formed finally on the OSP surface.

**CONCLUSION**

Kinetic studies on the removal of phosphate by sorption onto OSP have been investigated at 24°C. Phosphate can be removed by OSP and its removal is slightly lower than with CaCO$_3$. Sorption follows a pseudo-first order Lagergren rate equation. The equilibrium following fast sorption with a 50 mg dm$^{-3}$ phosphate solution moderately obeys the Freundlich isotherm. The initial pH does not have any effect on the removal of phosphate by OSP or calcium carbonate. Using OSP (24 g) with 1 dm$^3$ of phosphate solution containing 50 mg dm$^{-3}$ phosphate reduces the phosphate concentration to 7.0 mg dm$^{-3}$ in 7.7 days.

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**REFERENCES**