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Phosphate removal from solution using steel slag through magnetic separation

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Abstract

Steel slag with magnetic separation was used to remove phosphate from aqueous solutions. The influence of adsorbent dose, pH, and temperature on phosphate removal was investigated in a series of batch experiments. Phosphate removal increased with the increasing temperature, adsorbent dose and decreased with increasing initial phosphate concentrations, while it was at its peak at pH of 5.5. The phosphate removal predominantly occurred through ion exchange. The specific surface area of the steel slag was $2.09 \, m^2/g$. The adsorption of phosphate followed both Langmuir and Freundlich isotherms. The maximum adsorption capacity of the steel slag was 5.3 mg P/g. The removal rates of total phosphorus (TP) and dissolved phosphorus (DP) from secondary effluents were 62–79% and 71–82%, respectively. Due to their low cost and high capability, it was concluded that the steel slag may be an efficient adsorbent to remove phosphate both from solution and wastewater.
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1. Introduction

Phosphorus (P) is usually considered to be the limiting nutrient in relation to the eutrophication of water bodies. For this reason, wastewater treatment plants have to meet maximum P discharge limits. In China, these discharging limits vary from one plant to other, but a typical secondary effluent phosphorus target is between 1.0 and 2.0 mg P/L. The phosphate in treated wastewaters from municipalities and industries is less than 2.0 mg P/L; still it is responsible for eutrophication, which leads to short- and long-term environmental and aesthetic problems in lakes, coastal areas, and other confined water bodies. Minute concentrations of less than 0.03 mg P/L have been established as the criteria with respect to excessive algal growth in lakes and other confined water bodies

[1]. In order to meet effluent quality standards, further treatment of secondary effluent is required. Removal of phosphate from wastewaters has been conducted by chemical precipitation [2] or by biological treatment [3]. More effective methods for phosphate removal are chemical treatments including phosphate precipitation with calcium, aluminum and iron salts [4,5], however they are still subjected to high costs of maintenance and problems of sludge handling, its disposal, and neutralization of the effluent [6]. Various physical methods have been suggested including reverse osmosis, electrodialysis, contact filtration and adsorption [7]. Adsorption is comparatively handy and economical for this purpose. The application of low cost and easily available materials like fly ash [8,9], blast furnace slag [10–12], dolomite [13], dewatered alum sludge [14] and mesoporous structural material [15] have been widely investigated recently in wastewater treatment. The major advantage of using these materials or by-products for waster treatment is cost effectiveness.

The steel slag used in present study, is an industrial waste derived from a steel factory in Shanghai city, China. The steel

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slag is used as road materials after magnetic separation. The steel slag still contains certain amounts of iron oxides and alumina that may be effective in removing DP.

The objective of this work was to study the feasibility of using steel slag after magnetic separation as an adsorbent for phosphorus removal from wastewater. The effects of adsorption isotherms, adsorbent dosage, solution pH, contact time and temperature on removal of phosphate were evaluated in batch experiments using orthophosphate solutions. The column flow-through adsorption tests were conducted with secondary effluents from a wastewater treatment plant. Such work will contribute to optimize the phosphate removal process using the steel slag.

2. Materials and methods

2.1. Materials

The steel slag samples were procured from a steel plant in Shanghai city, China. The materials were air-dried and passed through a 2 mm sieve before the experiments.

Steal slag pH was measured in its solution with water using a 1:1 steel slag/water ratio. Exchangeable Ca was measured using a 0.1 M $BaCl_2$ solution following a 2 h equilibration. Reactive Al was estimated by extraction with 1 M $CuCl_2 \cdot H_2O$ [16]. Aluminum and Fe associated with organic matter were extracted with 0.01 M $Na_4P_2O_7$ [17]. Amorphous and crystalline forms of Al and Fe were dissolved in acidified 0.2 M $(NH_4)_2C_2O_4$ [18] and dithionite-citrate-bicarbonate (CDB) [19], respectively. Exchangeable Al was extracted with 1 M KCl. Total Fe and Al were determined by digestion in nitric-perchloric acid mixture. Iron and Al in the extracts were analyzed using ICP-MS (Agilent, 7500a, Japan). The properties and composition of steel slag are given in Table 1.

The phosphate (PO_4^{3-}) stock solution containing 1000 mg P/L was prepared by dissolving potassium dihydrogen orthophosphate (KH_2PO_4) powders (analytical reagent grade) in distilled water. Phosphate working solutions in different concentrations were prepared by diluting the PO_4^{3-} stock solution with distilled water and 0.01 M KCl was used for adjusting its ionic strength. The pH of the PO_4^{3-} working solution was adjusted at 5.2 with 1 M HCl and 1 M NaOH solutions before adsorption experiments.

Table 1
Property and composition of the steel slag

Property and composition	Value (unit)	Property and composition	Value (unit)
pH	8.4	CDB Al	6.05 mg/g
Bulk density	1.5 g/cm^3	$CuCl_2$ Al	1.88 mg/g
Particle size	1–2 mm	Pyro Al	0.04 mg/g
SiO_2	96.78 mg/g	Pyro Fe	0.0004 mg/g
CaO	456.12 mg/g	KCl Al	0.0004 mg/g
Surface area	2.09 m^2/g	Exchangeable Ca	0.12 mg/g
Oxal Al	2.12 mg/g	Total Al	63.72 mg/g
Oxal Fe	1.67 mg/g	Total Fe	29.41 mg/g
CDB Fe	2.28 mg/g		

2.2. Analytical methods

The phosphate (PO_4^{3-}) was determined using an automated discrete analyzer (Seal Analytical Ltd., UK). The solution pH was measured using a pH meter (Model 250, ThermoOrin, USA).

2.3. Studies on isotherms and pH effects

Phosphate adsorption isotherm studies were carried out with different initial phosphate concentrations and 2 g/50 mL steel slag at 25 °C with initial pH of 5.2, at 200 rpm for 2 h. Nine initial phosphate concentrations (5, 10, 30, 50, 75, 100, 125, 150, and 200 mg KH_2PO_4/L), equivalent to (1.14, 2.28, 6.84, 11.40, 17.10, 22.79, 28.49, 34.19, and 45.59 mg P/L) were used during the experiment. The pH was maintained at a defined value of 5.2. The isotherm data on P adsorption were fitted to three two-parametric equations (Freundlich, Langmuir). With a similar procedure, the effect of pH (ranging from 3.5 to 11.5) on phosphate adsorption was examined in a series of experiments using the same initial phosphate concentration (22.79 mg P/L).

2.4. Effect of adsorbent dose

The effect of adsorbent dose on adsorption of phosphate was investigated with 50 mL phosphate solution containing 22.79 mg P/L under above similar conditions. Nine initial adsorbent concentrations (2, 4, 8, 16, 20, 40, 60, 80, and 100 g/L) were tested for phosphate removal.

2.5. Effect of initial phosphate concentrations

The effect of varying initial phosphate concentrations (11.40–45.59 mg P/L) on phosphate removal by steel slag was also investigated. The batch experiments were carried out using 2 g adsorbents in 50 mL phosphate solution under above similar conditions.

2.6. Effect of adsorption temperature

The effect of temperature on phosphate adsorption by steel slag was studied at different temperatures, i.e. 5, 25 and 45 °C. The data were obtained by using 2 g adsorbents in 50 mL solution containing 22.79 mg P/L under above similar conditions.

2.7. Removal of phosphate from secondary effluents

Column adsorption tests on phosphate removal were conducted at room temperature using a secondary effluent in Hangzhou city of Zhejiang province, China. The composition of wastewater taken from wastewater treatment plant effluent was as follows (mg/L each): DP = 0.7–2.2; TP = 1.0–3.4; chemical oxygen demand (COD) = 40–70; biological oxygen demand (BOD) = 20–30; suspended solids (SS) = 10–25. The adsorption columns made of PVC had an internal diameter 20 cm and a packet height of 20 cm steel slag (containing 6028.8 g of steel slag by weight). During tests, the secondary effluent was
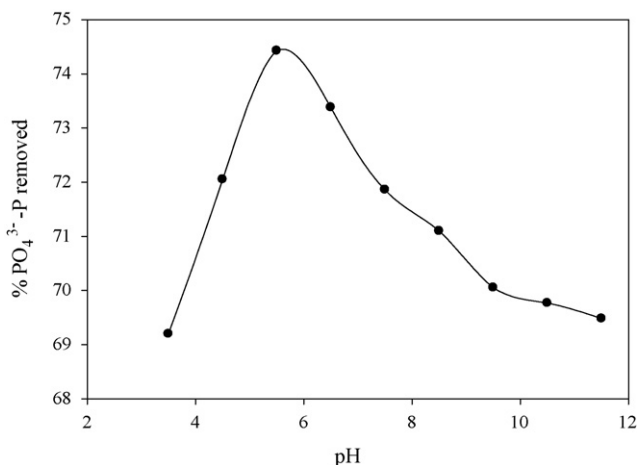
Fig. 1. Effect of pH on phosphate adsorption on steel slag (concentration: 22.79 mg P/L, adsorbent dose: 2 g/50 mL, temperature: 25 °C, stirring speed: 200 rpm, time: 2 h).

continuously pumped from a storage tank to the PVC column downward at a flowrate of approximately 8.37 mL/min using a peristaltic pump. This was equivalent to a space velocity of approximately 60 cm/day in the column. The effluent from the column was collected daily in a bottle as an average daily sample for DP and TP analysis.

3. Results and discussion

To study the influence of pH on the phosphate adsorption capacity of steel slag, experiments were performed at various initial solution pH values, in range of 3.5–11.5. The obtained results were shown in Fig. 1. It was found that the amount of phosphate adsorbed at pH 5.5 was the greatest. The phosphate adsorption by the steel slag had a direct relation with solution pH, i.e. the amount of phosphate adsorbed onto steel slag decreased with decreasing or increasing pH.

The surfaces of Fe and Al metal oxides of steel slag consist mainly of oxygen atoms and hydroxyl groups. It is primarily the hydroxyl group that determines the chemical properties (acid–base character) and the reactivity of these surfaces [20]. Phosphate cannot be ion exchanged onto steel slag under alkaline or acidic conditions. This is likely attributed to the fact that a higher pH causes the steel slag surface to develop more negative charges and thus would more significantly repulse the negatively charged species in solution. Under acidic conditions, the adsorptive capacity decreases due to a higher solubility of Al and Fe oxides [21]. Therefore, the lower adsorption of phosphate at higher pH values resulted from an increased repulsion between the more negatively charged PO_4^{3-} species and negatively charged surface sites. That is why the maximum phosphate adsorption occurred at pH 5.5.

The relation between the amounts of phosphate adsorbed and steel slag dose is shown in Fig. 2. It is apparent that the phosphate removal rate in solution increased with increasing steel slag dose for a given initial phosphate concentration. This result was anticipated because increasing adsorbent doses provide greater surface area. It is evident that for the removal of 22.79 mg P/L
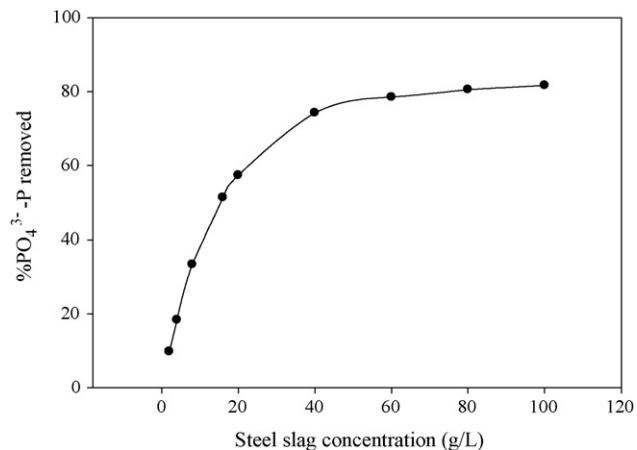

Fig. 2. The effect of steel slag on the efficiency of phosphate removal (concentration: 22.79 mg P/L, pH: 5.2, temperature: 25 °C, stirring speed: 200 rpm, time: 2 h).

phosphate in 50 mL solution, a minimum steel slag dosage of 40 g/L was required (Fig. 2).

Experiments were conducted to study the effect of varying initial phosphate concentrations (11.40–45.59 mg P/L) on phosphate removal by steel slag. Fig. 3 indicates that all curves have the similar shape. The phosphate adsorption percentage increased with increasing contact time and attained equilibrium at variable time according to the initial concentrations of phosphate. The removal percentage decreased with the increasing initial phosphate concentrations from 76.16% for 11.40 mg P/L phosphate to 73.03% for 45.59 mg P/L phosphate. The higher uptake at lower concentrations might be due to higher ratio of initial number of phosphate moles to the available surface area at higher initial concentrations; hence fractional adsorption was dependent on the initial phosphate concentration. For a given adsorbent dose, the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of phosphate, thus resulting in a decrease in the percentage removal corresponding to an increase in initial adsorbate concentration [22,23].
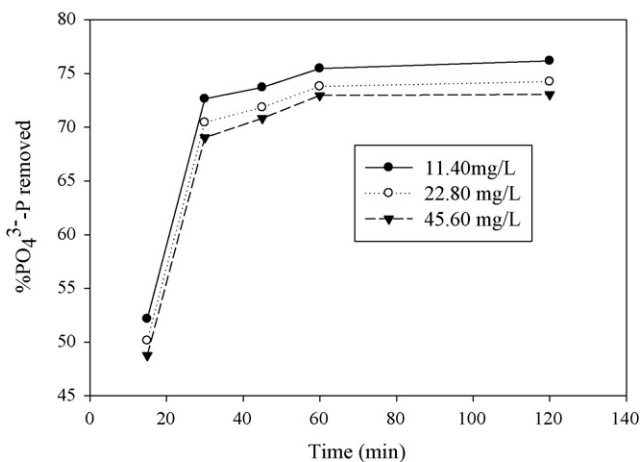

Fig. 3. Adsorption of phosphate on the steel slag as a function of initial phosphate concentration (adsorbent dose: 2 g/50 mL, pH: 5.2, temperature: 25 °C, stirring speed: 200 rpm, time: 2 h).

Table 2
Langmuir and Freundlich isotherm parameters

Langmuir	
Q_m (mg P/g)	5.3
b (L/mg P)	0.015
R^2	0.9988
Freundlich	
K	0.088
n	1.117
R^2	0.9998

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [24]. The estimated model parameters with the correlation coefficient (R^2) for both Langmuir and Freundlich models are shown in Table 2. According to the coefficients of Langmuir isotherm the maximum adsorption capacity of steel slag was 5.3 mg P/g.

The effect of temperature on the removal of phosphate was investigated as a function of contact time. The phosphate removal rates were 72.19, 74.22 and 76.52% at 5, 25 and 45 °C, respectively. The results show that phosphate adsorption increased with the increasing temperature because an increase in the solution temperature resulted in the increased concentrations of $FePO_4$, $AlPO_4$ and $Ca_3(PO_4)_2$ in the solution, it was suggested that the precipitation of metallic salts such as Al^{3+}, Fe^{3+} and Ca^{2+} was less effective as a result of the electrostatic attraction between adsorbate and adsorbent which affected the phosphate removal from aqueous solution. This result indicates that the phosphate removal was mainly based on physical interactions and was not due to the chemical precipitation of metallic salts such as Al^{3+}, Fe^{3+} and Ca^{2+} on the steel slag.

Another column flow-through adsorption test was carried out for 30 days using a secondary effluent in Hangzhou city of Zhejiang province, China. The influent pH was maintained in range of 7.0–7.5 with a corresponding effluent pH of 7.2–8.0 during the test. The dissolved TP and DP concentrations in the influent and effluent were measured daily. The experimental results are shown in Fig. 4. It can be seen that both TP
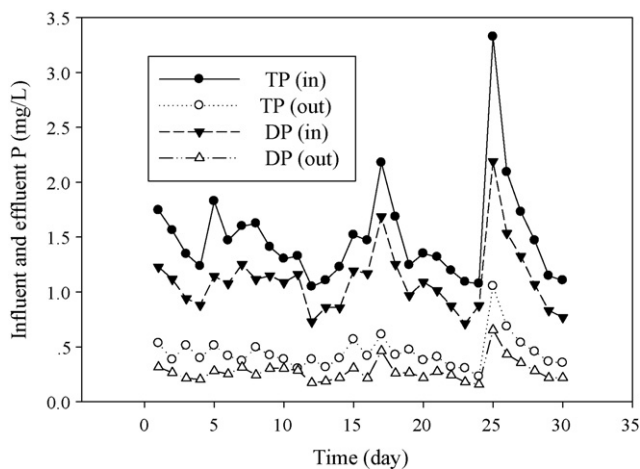

Fig. 4. Phosphorus removals from secondary effluent through steel slag column.

and DP after the tailings column were largely reduced compared to their influent concentrations. The reduction of TP was caused by infiltration removal of particulate P (PP) through the steel slag layer. The decrease of DP was mainly attributed to the phosphate adsorption on the tailings. PP was smaller than DP which was the main form of TP in the secondary effluent. During the column flow-through tests, it was observed that the column packed with steel slag was not clogged while operating at small flowrate, bigger particle size and little suspended solid from secondary effluent. This observation suggested that steel slag was also a good filter bed for P from secondary effluent adsorption.

Acid oxalate reagent is known to dissolve short-range order (amorphous) components. These forms of Fe and Al correlated positively with P sorption in acid soils [25,26]. Relative to the other forms of Fe and Al, the contribution of crystalline Fe and Al–P sorption was expected to be smaller. Reden and Pratt [27] reported that crystalline Fe and Al hydrous oxides adsorb 10–100 times less P than their amorphous counterparts. Relatively higher correlation of CDB-Al with P sorption for the soil samples studied was attributed to the fact that CDB extracted both amorphous and crystalline Fe and Al oxides [28]. That is why the steel slag still kept higher Phosphate adsorption capacity of 5.3 mg P/g under lower total Fe and Al content through magnetic separation.
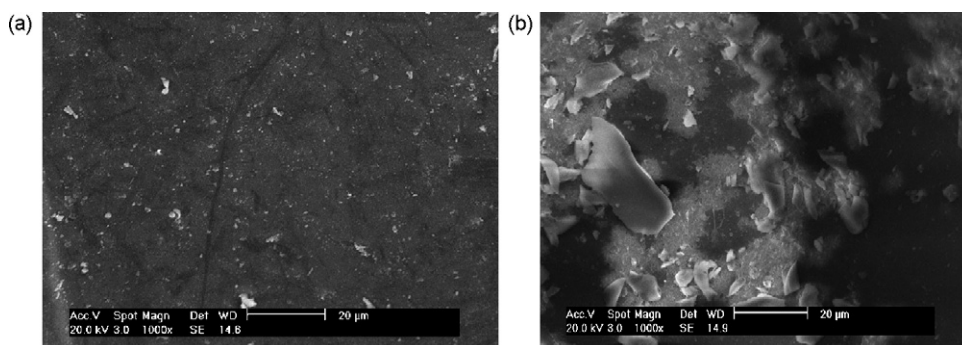

Fig. 5. SEM micrograph of the particles of steel slag before (a) and after (b) phosphate adsorption (concentration: 22.79 mg P/L, adsorbent dose: 2 g/50 mL, pH: 5.2, temperature: 25 °C, stirring speed: 200 rpm, time: 2 h).

In order to study the particles surfaces before and after adsorption, scanning electron microscopic (SEM) images for the samples of the raw and treated adsorbents were obtained. These micrographs are presented in Fig. 5. A representative experiment under the given conditions such as 25 °C, pH 5.2, a contact time of 120 min, a stirring speed of 200 rpm, and an initial phosphate concentration of 22.79 mg P/L were carried out to obtain the material shown in the micrograph. In this experiment, almost 74% of the phosphate in the aqueous solution was removed. The micrograph obtained after adsorption indicated that the pores of the particles of the adsorbent have been covered with adsorbate.

4. Conclusions

Present study indicates that steel slag may be an effective adsorbent for phosphate removal from secondary effluents as well as solution after magnetic separation. The steel slag showed good performance for phosphorus removal. The maximum adsorption capacity of steel slag was 5.3 mg P/g. Due to its low cost and high adsorptive capacity, the steel slag possess the potential to be utilized for cost-effective removal of phosphorus from wastewater. It was also found that the phosphate removal efficiency by steel slag depended on pH, initial phosphate concentration, adsorbent doses and temperature. Long-term performance characteristics of steel slag need to be evaluated further before it can be recommended for critical applications requiring guaranteed performance.

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