Pergamon

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Cement and Concrete Research 33 (2003) 1109–1112

CEMENT AND CONCRETE RESEARCH

Removal of phosphate from wastewaters

Ensar Oğuz[a], Ahmet Gürses[b,*], Nurtaç Canpolat[b]

[a]Environmental Problems Research Center, Atatürk University, Erzurum 25240, Turkey
[b]Department of Chemistry, K.K. Eğitim Fakültesi, Atatürk University, Erzurum 25240, Turkey

Received 23 May 2002; accepted 2 January 2003

Abstract

Gas concrete waste was used to remove phosphate from aqueous solutions in this study. The influence of suspension pH, temperature, mixing rate, and gas concrete dosage on phosphate removal was investigated by conducting a series of batch adsorption experiments. In addition, the yield and mechanisms of phosphate removal were explained on the basis of the results of X-ray spectroscopy, measurements of zeta potential of particles, both values of BET–N_2 specific surface area, and images of scanning electron microscopy (SEM) of the particles before and after adsorption. In this study, phosphate removal in excess of 99% was obtained and it was concluded that wastes of gas concrete are an efficient adsorbent for the removal of phosphate. The removal of phosphate predominantly takes place by precipitation mechanism and the weak physical interactions between the surface of adsorbent and the metallic salts of phosphate.

Keywords: Concrete; SEM; Adsorption

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1. Introduction

The presence of trace amounts of phosphate (even less than 1 ppm) in treated wastewaters from municipalities and industries is often responsible for eutrophication, which leads to short- and long-term environmental and aesthetic problems in lakes, coastal areas, and other confined water bodies. Concentrations of less than 0.03 mg l^{-1} P have been established as the criteria with regard to excessive algae growth in lakes and other confined water bodies [1–4]. In order to meet effluent quality standards, further treatment of secondary effluent is required. In wastewater treatment technology, various techniques have been used for phosphate removal. Among these, chemical and biological methods have been successfully applied. Adsorption is one of the techniques which would be comparatively more useful and economical for this aim. The application of low-cost and easily available materials in wastewater treatment has been widely investigated during recent years. Chemical treatment is widely used for the removal of phosphate. Lime, aluminium sulphate (alum), and ferric chloride are the common precipitants used for phosphate removal; however, successful results were obtained by using powdered aluminium oxide [5–7], slag [8], fly ash [9,10], half-burnt dolomite [11], tamarind nut shell activated carbon [12,13], activated red mud [14,15], and aluminium [16].

Gas concrete, which is a building material, is included in the light concrete category. It is produced from different mixtures from silica, sand, cement, lime, water, and aluminium cake, which produce gas. One of the main advantages of phosphate removal by using gas concrete over the other chemical treatment methods is that it does not produce any chemical sludge. In addition, after gas concrete has been used in building works, its residues can easily be used to remove phosphate from wastewaters. In the present study, an attempt was made to investigate the phosphate removal potential of gas concrete under different environmental conditions by batch tests.

2. Materials and methods

Phosphate was removed by using a gas concrete batch reactor from a synthetic wastewater in this study. The grain size of the gas concrete used was between 2 and 0.063 mm. Gas concrete samples were washed with distilled water and then dried at 25 °C. The chemical composition of the gas concrete is given in Table 1.

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* Corresponding author. Tel.: +90-442-231-4007; fax: +90-442-236-0955.

E-mail address: ahmetgu@yahoo.com (A. Gürses).

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doi:10.1016/S0008-8846(03)00016-4

Table 1
Chemical composition of the gas concrete (as-received) component (wt.%)

SiO_2	Al_2O_3	CaO	Others
65	22	9.6	3.4

The standard phosphate solutions used in the experiments were prepared from anhydrous KH_2PO_4. The adsorption studies have been carried out at phosphate concentrations of 100 mg l^{-1} PO_4^{3-}. A given amount of gas concrete has been placed in 250-ml volumetric flasks and mixed with 50 ml of stock solution. The experiments have been carried out at different temperatures (20 and 55 °C) and pH values. pH adjustments have been done by using solutions of concentrated HCl and NaOH. The mixtures have been filtered prior to each measurement. Phosphate has been measured according to the Vanado Molybdo Phosphoric Acid Colorimetric Method [17]. The values of zeta potential of the particles were measured by using a microelectrophoresis cell (zeta meter 3.0+). The specific surface area of gas concrete particles was measured by using the BET–N_2 method.

3. Results and discussion

The effect of temperature on the removal of phosphate was investigated as a function of contact time. The results were then plotted in Fig. 1. From this figure, it has been determined that 10 min of contact time is enough to remove a considerable amount of phosphate present in aqueous solution at all temperatures. Fig. 1 also shows that the removal of phosphate does not depend on temperature. This result indicates that the removal of phosphate is mainly based on physical interactions (physisorption). The effect of mixing rate on the removal of phosphate was studied for various contact times. The results are given in Fig. 2. This figure shows that the yield increases with increasing time, but the rate of mixing has no effect on the yield. This suggests that the diffusion of phosphate ion from the solution to the surface of adsorbent and into the pores occurs easily and quickly since the mixing rates at different times give similar results.

In order to see the surfaces of particles after and before adsorption, scanning electron microscopy (SEM) images for the samples of the raw and treated adsorbents were obtained. These micrographs are presented in Figs. 3 and 4. A representative experiment under the given conditions—such as 20 °C, pH ≈ 11, a contact time of 1 h, a mixing rate of 150 rpm (min^{-1}), and an initial phosphate concentration of 100 mg l^{-1}—was carried out to obtain the micrograph in

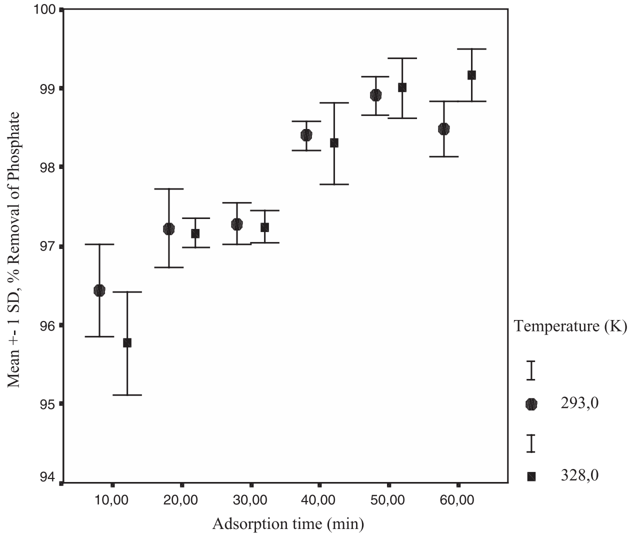

Fig. 1. The effect of temperature on phosphate removal with gas concrete (Co: 100 mg l^{-1}; pH: 11.5; mixing rate: 150 rpm).

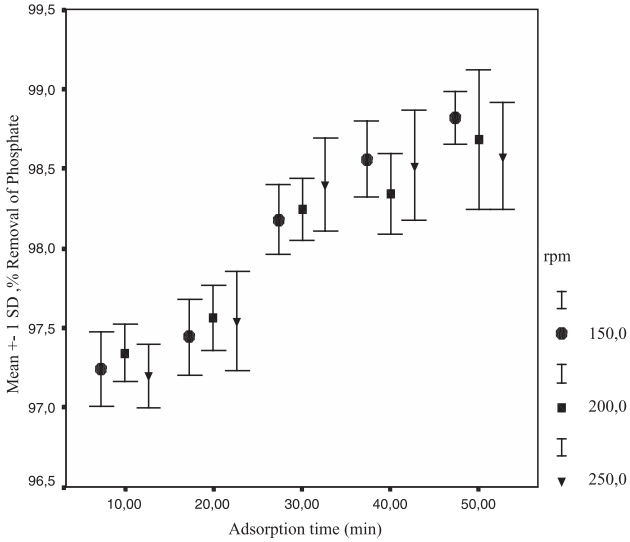

Fig. 2. The effect of mixing rate on phosphate removal with gas concrete (Co: 100 mg l^{-1}; pH: 11.5; *T*: 20 °C).

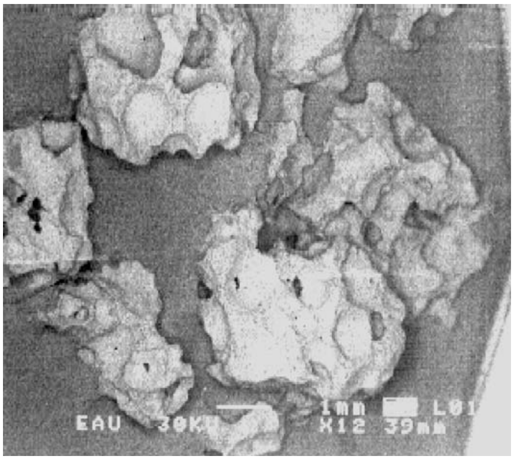

Fig. 3. SEM micrograph of the particles of gas concrete before adsorption (Co: 0 mg l^{-1}; pH: 11.5; *T*: 20 °C; mixing rate: 150 rpm).

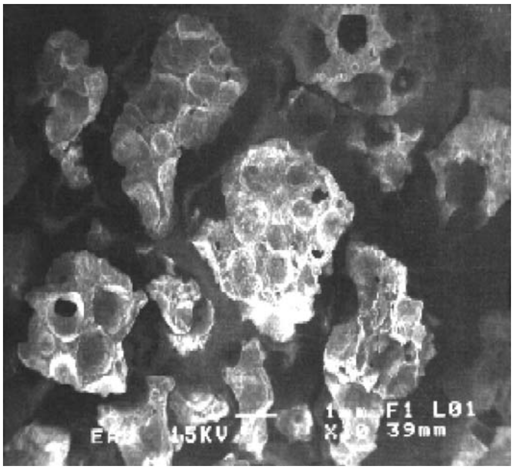

Fig. 4. SEM micrograph of the particles of gas concrete after adsorption (Co: 100 mg l^{-1}; pH: 11.5; *T*: 20 °C; mixing rate: 150 rpm).

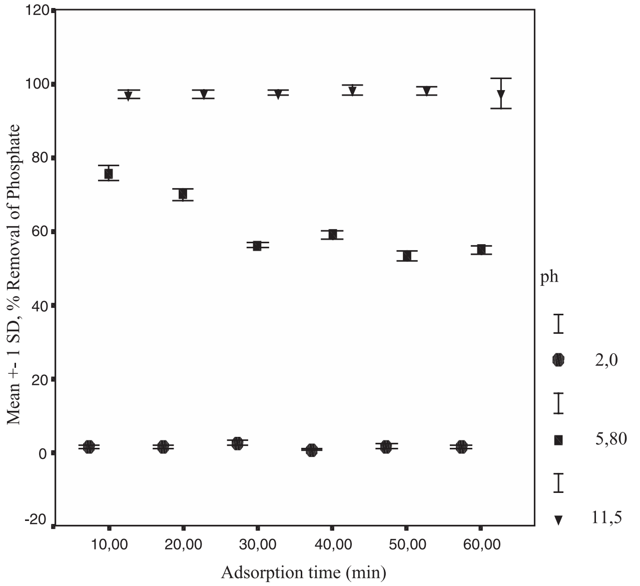

Fig. 6. The effect of pH on phosphate removal with gas concrete.

Fig. 4. In this experiment, almost 99% of the phosphate in the aqueous solution has been removed.

The micrograph obtained after adsorption indicates that the pores of the particles of the adsorbent have been opened. However, the specific surface area of the particles for the sample in Fig. 4 was measured to be 17.0 $m^2\ g^{-1}$, whereas the specific surface area of the raw sample was 22.0 $m^2\ g^{-1}$. This decrease can be attributed to the fact that the slightly soluble phosphate salts of aluminium and calcium ions filled the pores of the adsorbent. In addition, the results of X-ray analysis in Fig. 5 clearly reveal the presence of these salts on the structure of adsorbent after adsorption process.

The variation of removal of phosphate with suspension pH was investigated for several contact times. Furthermore, the zeta potential of adsorbent particles was measured for various pH values. The results are given in Figs. 6 and 7, respectively. The removal of phosphate has never been observed near pH 2. As pH increases, the removal of phosphate also significantly increases. From Fig. 7, it can be seen that at low pH, particles have negative zeta potentials values, but at high pH values, the zeta potentials of particles are zero. This clearly shows that the removal of phosphate predominantly takes place by precipitation mechanism and the weak physical interactions between the surface of adsorbent and the metallic salts of phosphate. At the pH range of 2–6, phosphate removal probably occurs with ion exchange mechanisms of phosphate hydrolysis products ($H_2PO_4^-$, HPO_4^{2-}). In this range, the fact that the surface charge does not change confirms the mecha-

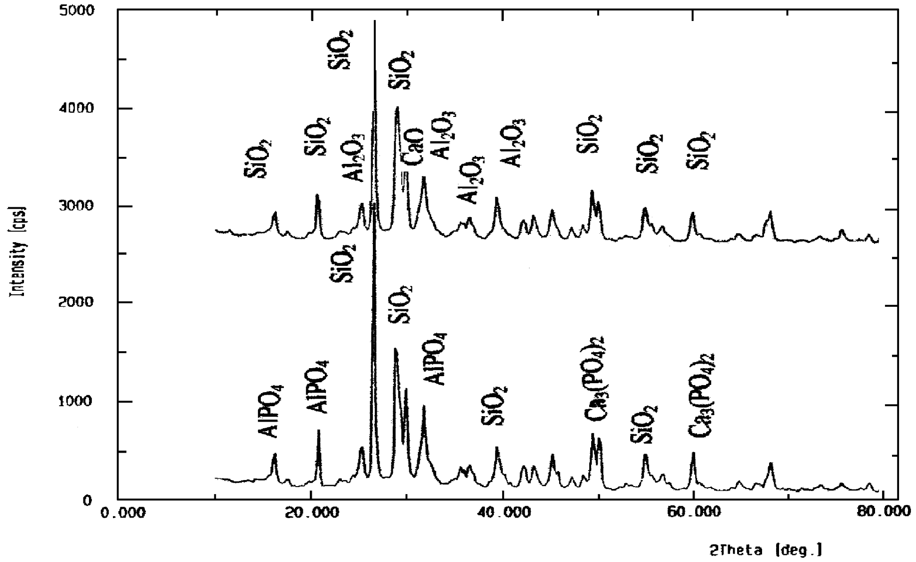

Fig. 5. X-ray diffraction diagram of the gas concrete before and after adsorption (Co: 100 mg l^{-1}; pH: 11.5; *T*: 20 °C; mixing rate: 150 rpm).

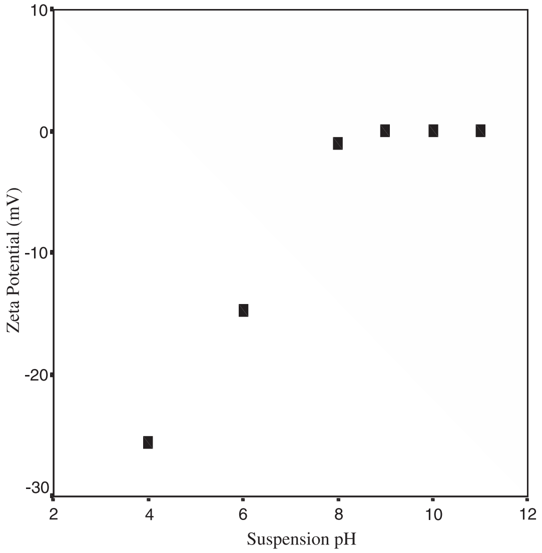

Fig. 7. Variation of the values of zeta potential of the particles with suspension pH.

nisms suggested below. At high pH, it is suggested that the process of the removal of phosphate takes place through the following reactions steps:

$$\mathrm{Ca(OH)_{2(s)}} \rightleftharpoons \mathrm{Ca^{2+}_{(aq)}} + \mathrm{2OH^{-}_{(aq)}};$$

$$\mathrm{3H_2O_{(l)}} + \mathrm{Al_2O_{3(s)}} + \mathrm{2OH^{-}_{(aq)}} \rightleftharpoons \mathrm{2Al(OH)^{-}_{4(aq)}} \qquad (1)$$

$$\mathrm{Al(OH)^{-}_{4(aq)}} + \mathrm{PO^{3-}_{4(aq)}} \rightleftharpoons \mathrm{AlPO_{4(s)}} + \mathrm{4OH^{-}_{(aq)}};$$

$$\mathrm{3Ca^{2+}_{(aq)}} + \mathrm{2PO_4^{3-}} \rightleftharpoons \mathrm{Ca_3(PO_4)_{2(s)}} \qquad (2)$$

The predominant intermediate product in this process is $AlPO_4$ because the solubility value (7.94×10^{-10} mol l^{-1}) for $AlPO_4$ is lower than that of $Ca_3(PO_4)_2$ (7.14×10^{-7} mol l^{-1}). The results of X-ray analysis (Fig. 5) also suggest that the main product adsorbed onto the surface of the adsorbent in this work is $AlPO_4$.

4. Conclusion

The results of this study indicate that gas concrete is an effective adsorbent for removal of phosphate contained in aqueous solutions. Phosphate removal ratios of 99% were obtained. It was found that the amount of phosphate adsorbed on gas concrete depends on pH and mixing rate of the solution. Gas concrete can be regenerated at lower pH values (1–3) after phosphate removal. Thus, obtained concentrated phosphate solution can be used as a source of recycled phosphate, which can be used for fertilizing in agriculture.

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