

PHOSPHATE REMOVAL FROM REAL WASTEWATER USING MAGHEMITE BEADS

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ABSTRACT

The present study aimed at research of phosphate adsorption onto poly(vinyl-alcohol) PVA alginate beads in comparison with maghemite modified beads from wastewater. The characterisation of material was performed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction. The influence of pH and the quantity of maghemite nanoparticle was studied.

The results of phosphate adsorption onto PVA-alginate beads showed 45 % of initial PO_4^{3-} concentration removal from wastewater while the maghemite PVA-alginate beads showed better adsorption activity at 70 % of initial PO_4^{3-} removal. The optimal dose was determined at 0.9 g of PVA-M beads (containing 0.01 g maghemite) added to the 50 mL wastewater. The efficiency of phosphate removal from wastewater was relatively low due to content of coexistent anions, including SO_4^{2-} , CO_3^{2-} , NO_3^- and Cl^- , which compete with phosphate for the binding sites, hindering PO_4^{3-} to form inner sphere complexes.

Keywords: *maghemite beads, phosphate removal, wastewater*

INTRODUCTION

Orthophosphate PO_4^{3-} represents an important macronutrient in aquatic environment, but overgrowth of algae causes dissolved oxygen depletion. Sorption processes show potential for phosphate removal from wastewater by offering advantages, such as low sludge production, simple operation, etc. [1].

Different natural immobilisation media have been used for biomatrix immobilisation, nevertheless alginate is still one of the most frequently used carriers [2]. Sodium alginate is

one of the most studied natural polymers for metal ions removal [3]. Alginate is known to be fragile and cannot be recycled [1]. Immobilisation of one polymer to another is a common practice in production of durable beads [4]. Maghemite nanoparticles are incorporated with alginate and poly(vinyl-alcohol) PVA to enhance the ability of bead as a biosorbent. The immobilization of maghemite is simple and cost effective. PVA-M-beads were used for efficient removal of cesium from wastewater [5].

The synthesis of nanostructure magnetic materials has become a particularly important area of research because of its potential applications in the field of water remediation [6]. Further studies are required to compare the PO_4^{3-} removal by using iron oxides [6]. It was reported that Fe_3O_4 has the potential to remove toxic elements such as arsenic from water [7]. Authors also claim that it is still rare to find the investigation of removal/recovery of phosphate by using Fe_3O_4 . Therefore, the present study aimed at efficient adsorption of phosphate from wastewater onto PVA alginate beads in comparison with maghemite modified beads, which is the novelty of present study. The aim of the research was to study the influence of other compounds in wastewater on phosphate removal as well as the influence of concentration of maghemite in beads. Iron oxide based nanoparticles are purposely incorporated with alginate and PVA to enhance the efficiency of pollutant removal [8].

EXPERIMENTAL

Preparation of maghemite nanostructures

Nanoparticles were prepared by a topotactic transformation of a $\gamma\text{-FeO(OH)}$. Firstly, the 2 mM $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution was prepared in 100 mL of de-oxygenated milli-Q water. The solution was exposed to Ar (300 mL/min) for 30 min. 2 mL of pyridine was poured into the solution and again exposed. After 1 h the oxygen gas flew at 300 mL/min through the reaction mixture for 15 min, followed by oxygen flow of 50 mL/min (for 3 h). The solid to $\gamma\text{-FeO(OH)}$ product was centrifuged and washed several times with distilled water. The dehydroxilation of the $\gamma\text{-FeO(OH)}$ was performed in a furnace at 280 °C for 1 h in air. In Figure 1 maghemite nanostructure in a weigh boat is seen.



Figure 1. Maghemite nanostructure

Preparation of PVA beads

PVA solution was prepared by dissolving 24 g of PVA in 200 mL flask in Millipore water at 120° C for 3 h. Separately alginate solution was prepared by dissolving 2 g of alginate in 40 mL water. Both solutions were poured together. White beads were formed by using plastic transfer pipette.

The same procedure was used for preparing PVA alginate beads with maghemite (PVA-M-beads). Into the prepared solution 0.2 g of maghemite was added. Beads were kept in the solution containing 2 % CaCl_2 and 6 % boric acid for 24 h. Then beads were rinsed and kept in Millipore water as seen from Figure 2.



Figure 2. Maghemite PVA-alginate beads in Millipore water

Material characterisation

The samples were characterized by a Fourier transform infrared spectroscopy (FTIR). Spectrophotometer IRAffinity-1 (Shimadzu) was used. For X-ray diffraction (XRD) a Bruker D5005 diffractometer (Siemens) was used ($\text{Cu-K}\alpha$ radiation with 2θ from 20° to 70° at a scan rate of 2°/minute).

Adsorption in real wastewater samples

The real wastewater samples were taken from the inflow into the local wastewater treatment plant. The COD (chemical oxygen demand) was determined at 760 mg/L, BOD (biochemical oxygen demand) at 310 mg/L and TSS (total suspended solids) at 325 mg/L. Representative samples were taken after 24 h of sampling. The initial phosphate concentration was measured and adsorption on PVA beads was performed.

The solution pH condition was adjusted to 7.0 with 0.1 M of HCl using a portable pH-meter (WTW Multi 3410, Germany). The reaction vessels were then homogeneously shaken in an orbit shaking incubator at 250 rpm with controlled temperature at 20 °C for different time periods of 20, 40, 60 and 240 min and the analyses on phosphate were performed.

The samples were immediately filtered using a filter with an opening of 0.45 µm; the phosphate concentrations in the filtrates were then analysed using an Agilent Spectrophotometer. Removal efficiency of phosphate removal (E) is calculated following equation (1):

$$E = (c_i - c_f) / c_i \cdot 100 \quad (1)$$

where c_i is initial concentration and c_f is final phosphate concentration.

RESULTS AND DISCUSSION

The results of material characterisation

The FTIR spectrum of maghemite nanostructure is illustrated in Figure 3. A characteristic adsorption band at 559 cm⁻¹, which can be attributed to the Fe–O bond of maghemite, was observed.

The XRD spectrum in Figure 4 confirmed the formation of maghemite. The XRD graph showed good crystallinity, with sharp peaks. The patterns can also be seen at 30, 35 and 57

on 2-Theta-Scale which is typical for maghemite structure [9].

PVA-M-beads contained 0.1 g maghemite /100 g PVA- alginate. BET, pore radius and pore volume were determined at 9.38 m²/g, 1.4 mm and 7.42·10⁻² cm³/g, respectively. The removal efficiencies of phosphate removal achieved with PVA beads was 97.9 % and PVA-M-beads 98.5 %, respectively are reported elsewhere [10].

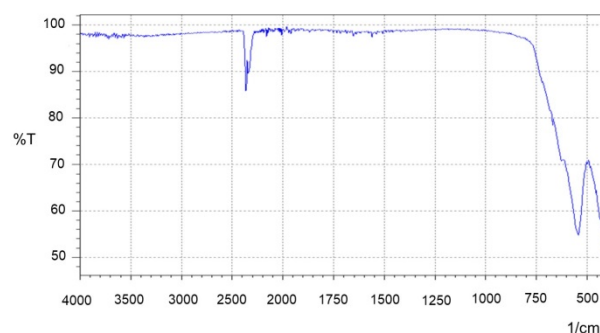


Figure 3. FTIR spectrum of maghemite

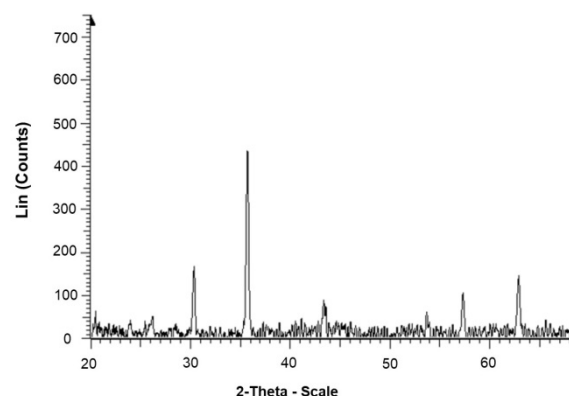


Figure 4. The XRD pattern of maghemite

The results of experiments using real wastewater

Samples of real wastewater were taken from local wastewater treatment plant. Initial concentration was 5 mg/L PO₄³⁻. The optimum dosage of PVA was determined at 0.45 g beads in 50 mL or 0.005 g maghemite per 0.45 g PVA-M-beads in 50 mL were added.

The efficiency was determined with PVA and PVA-M-beads. The results are presented in Table 1. After 240 min the efficiency of PO₄³⁻

removal increased. However, the results are much worse compared to those with model solutions. At the same amount of beads the removal percentage was lower. PVA-M-beads were more efficient than PVA beads which is in accordance with model solution results [10].

Table 1. Comparison of removal efficiency with PVA and PVA-M-beads

<i>t</i> , min	<i>E</i> (PVA-M), %	<i>E</i> (PVA), %
20	30.4	23.5
40	32.5	31.5
60	35.5	33.5
240	43.8	36.7

The maximum allowed concentration in municipal wastewater is determined at 2 mg/L PO_4^{3-} [10]. It was calculated that the concentration of phosphates remained above statutory value. The exchange of OH^- ions and phosphate in wastewater was low due to presence of other negative ions which have higher affinity to OH^- ions than PO_4^{3-} [11]. Municipal and industrial wastewaters always contain coexistent anions, including SO_4^{2-} , CO_3^{2-} , NO_3^- , F^- , Br^- , I^- and Cl^- , which may compete with phosphate for the binding sites [5]. The decrease in PO_4^{3-} adsorption with an increase in pH might be mainly due to electrostatic attraction. Strong competition occurs between PO_4^{3-} species ($H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-}) and hydroxyl (OH^-) ions at higher pH, creating strong repulsions between phosphate and hydroxyl ions that reduces adsorption [1]. The introduction of HCO_3^- also hinders phosphate adsorption. In the next step pH was measured in order to compare this value with the optimum one. The results are presented in Table 2. It can be seen that the initial pH value was 7.87 and it is alkaline. pH value was measured every 10 min. Small pH value increase was noticed, but it stabilised after 40 min. The presence of CO_3^{2-} caused the pH to rise, resulting in decrease of PO_4^{3-} removal due to repulsions between phosphate and hydroxyl ions [5].

The experiments were done at different pH values 5, 6 and 7. Differences in PO_4^{3-} concentrations at 240 min were negligible in

wastewater at all three pH values as seen from Figure 5. The final concentration was measured at 1.5 mg/L PO_4^{3-} .

Table 2. pH value in municipal water

<i>t</i> , min	pH (PVA-M)	pH (PVA)
0	7.87	7.87
20	8.10	7.99
40	8.14	8.03
60	8.18	8.06
240	8.18	8.06

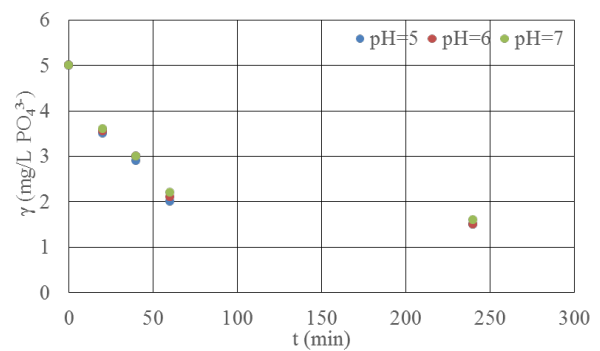


Figure 5. Phosphate concentrations during adsorption on PVA-M-beads in wastewater at different pH

Due to the lowest HCl consumption needed for pH adjustment, the optimum pH was determined at 7. The wastewater pH was adjusted to 7 and the experiments were done again with the same mass of beads 0.45 g in 50 mL wastewater. The phosphate concentration was measured after 20, 40, 60 and 240 min. The results are seen from Figure 6.

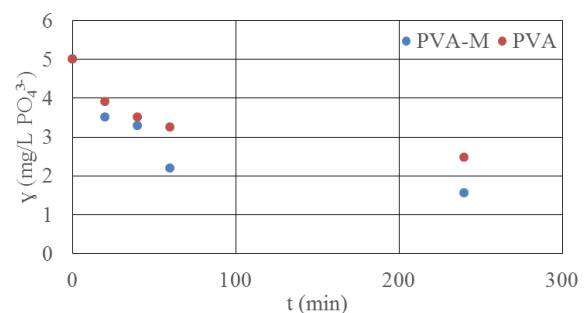


Figure 6. Phosphate concentrations in wastewater after treatment at pH = 7

From Figure 6 it is seen that the concentration of PO_4^{3-} decreased from 5 mg/L below 2 mg/L after 240 min and the concentration is very

close to 2 mg/L after 60 min. At shorter contact times PO_4^{3-} is not removed sufficiently.

The larger decrease in PO_4^{3-} adsorption onto maghemite particles could be reduced due to inner-sphere complexation between anions and surface groups [11].

PVA- beads gave worse results and the concentration did not decrease below statutory value. Nanosized material, such as PVA-M-beads always showed better contact between adsorbents with phosphate than PVA- beads in accordance with another study [12]. It could be concluded that alginate beads modified with maghemite are promising for the application of phosphate removal in real systems while PVA-beads did not give satisfactory results.

Another experiment was conducted with the doubled mass 0.9 g of PVA-M beads (containing 0.01 g maghemite) added to the 50 mL aliquot of the same sample of real wastewater. The adsorption of PO_4^{3-} did not change significantly. The concentration decreased from 5 mg/L to 1.5 mg/L PO_4^{3-} after 240 min which represents 70 % PO_4^{3-} removal. No significant changes in removal efficiencies were noticed compared with lower beads amount.

The adsorbent surface contains a fixed number of binding sites, many of which remain occupied in wastewater with other anions, such as SO_4^{2-} , which form outer complexes with beads [12]. Due to repulsion between SO_4^{2-} and PO_4^{3-} , the concentrations of PO_4^{3-} did not decrease as much as in model solution, where inner sphere complexes were formed during PO_4^{3-} elimination in accordance with literature [1].

CONCLUSION

The phosphate adsorption onto poly(vinyl-alcohol) PVA alginate beads from wastewater in comparison with maghemite modified PVA alginate beads was evaluated. The influence of

pH and the quantity of maghemite nanoparticle in PVA alginate beads was studied.

In the real wastewater samples, the pH value was very important, while at neutral pH the phosphates could be removed below statutory value but only with maghemite modified beads. The removal efficiency was 70 % of initial PO_4^{3-} concentration. The efficiency of phosphate removal from wastewater was relatively low due to content of coexistent anions, including SO_4^{2-} , NO_3^- and Cl^- , which compete with phosphate for the binding sites.

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