

## PHOSPHATE ADSORPTION BY THE MIXED INORGANIC ION EXCHANGER BASED ON FE-MN HYDROUS OXIDES: EQUILIBRIUM AND FTIR STUDIES

CHUBAR N.<sup>1,2</sup>, SZLACHTA M.<sup>1,3</sup> and GERDA V.<sup>1,4</sup>

<sup>1</sup> Utrecht University, Department of Earth Science, Budapestlaan 4, 3584CD, The Netherlands, <sup>2</sup>School of Engineering and Built Environment, Glasgow Caledonian University, Cowcaddens Road 70, Glasgow, G40BA, United Kingdom, <sup>3</sup>Faculty of Environmental Engineering, Wrocław University of Technology, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland, <sup>4</sup>Faculty of Chemistry, Kyiv Taras Shevchenko National University, Volodymyrska Street 60, 01601, Kyiv, Ukraine

E-mail: malgorzata.szlachta@pwr.edu.pl

### ABSTRACT

Phosphorus greatly controls cycling, speciation and bioavailability of chemical elements in the environment, inside of living organisms and in many (treatment) technological vessels, and thus is of great interest to environmental and life scientists as well as chemical/environmental engineers. Adsorption is a major phosphate removal technological approach which is fully dependent on the development and application of new cost-effective and environmentally friendly adsorptive materials. It has been recently demonstrated that the mixed adsorbent based on Fe-Mn hydrous oxide (developed by the authors) is a promising material for the removal of inorganic anionic species. It is a stable, porous inorganic adsorbent which is easy to use in batch and column adsorption conditions. We report herein studies on its performance in the adsorptive removal of phosphate. These studies (based on batch adsorption characterisation of an adsorbent) were carried out as a function of pH (4, 6 and 8), phosphate concentration, contact time, adsorbent dose and temperature. The mechanism of phosphate adsorption was revealed by modelling the experimental results and FTIR studies. The results demonstrated that the Fe-Mn oxide based adsorbent is capable of functioning efficiently across a broad range of environmentally relevant pHs with an adsorptive capacity of up to 24 mg[P]/g. The pH effect of phosphate removal was typical for anion sorption, but not as sharp as is usually demonstrated by adsorbents of the same chemical nature based on individual metal oxides. The competitive adsorptive performance of Fe-Mn hydrous oxide to phosphate correlated well with the fast adsorption kinetics fitted to the pseudo-second order model. The adsorption rate constants were dependent on the initial phosphate concentration. FTIR studies showed that surface complexes of phosphate onto Fe-Mn hydrous oxide were pH dependent. At the investigated pH values, phosphate was bound to the surface via chemi-sorption mechanism. The investigated material is a promising adsorbent for phosphate removal and shall be recommended for testing in larger scale industrial facilities.

**Keywords:** adsorption, Fe-Mn hydrous oxide, isotherms, kinetics, phosphate, temperature and pH effects

### 1. Introduction

Phosphorus is an essential chemical element for all forms of life and is needed by every organism for growth and function. In the Earth's crust phosphorus mainly occurs in its maximally oxidized state, such as in inorganic phosphate minerals. As an important nutrient for life, phosphorus greatly influences the cycling of matter (carbon) on global and molecular-level scales. Most of the phosphorus remains within rocks, sediments, soils and within fractions of living biomass (EC Environment, 2015). Sorption of dissolved phosphate to various solid phases is a major process that controls the cycling of this essential chemical element in the biogeosphere. Environmental materials are seldom pure minerals. As a rule, they are

mixed/hybrid/composite materials containing both inorganic (such as clays and metal oxides) and organic phases. Understanding the role of various mineral phases (of various chemical composition and crystallinity) is of great interest in environmental science. Because phosphorus is the limiting nutrient, even a small increase in its concentration can cause a significant effect. Controlling phosphorus discharged from municipal and industrial wastewater treatment plants is a key factor in preventing eutrophication of surface waters. Among the few major processes applied for phosphate removal from water solutions, adsorption is the most environmentally friendly technological approach and the most selective method capable of removing phosphate to very low concentrations. Metal oxides, due to their chemical nature, have the highest affinity to dissolved phosphate and are capable of immobilizing it in the environment or removing it from water solutions. It has been recently recognized that adsorbents of complex structure (such as composite, hybrid or mixed materials of both inorganic and/or organic chemical nature) have great advantages over adsorptive materials based on individual compounds. In addition to their higher adsorptive performance, they are stronger mechanically, capable of functioning over a broader range of pHs and can remove a longer list of dissolved particles than individual compounds.

The authors recently developed a mixed inorganic ion exchanger based on Fe(III) and Mn(III) hydrous oxides and  $\text{MnCO}_3$  (Szlachta *et al.*, 2012). The material has been proved to be a promising inorganic adsorbent for the removal of toxic anions (Szlachta and Chubar, 2013) and is able to remove selenite via the chemi-sorption mechanism mainly by its amorphous phases (Chubar *et al.*, 2014). The objectives of the research shown in this work were to study the adsorption of phosphate in static adsorption conditions focusing on equilibrium isotherms, kinetics of adsorption, the influence of pH and temperature on the adsorptive performance; to model the equilibrium and kinetics experimental data and investigate the mechanism of phosphate adsorption by FTIR.

## 2. Material and methods

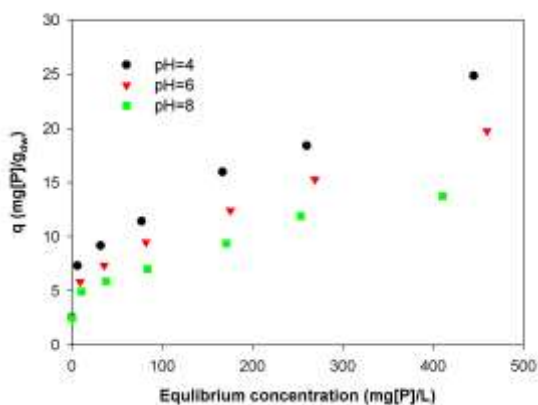
The hydrothermal precipitation approach in the presence of urea was used for the material preparation and was conducted in an Autoclave Suurmond BV as described in (Szlachta *et al.*, 2012). The resulting mixed inorganic adsorbent was composed of rhodochrosite ( $\text{MnCO}_3$ ) and subordinate maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) as well as amorphous phases of Fe(III) and Mn(III). The BET surface area of the material was  $124 \text{ m}^2/\text{g}$ , average pore diameter = 2.51 nm, true density =  $4.1 \text{ g}/\text{cm}^3$ ,  $\text{pH}_{\text{PZC}} = 4.5$ , anion exchange capacity = 4.73 meq/g. Batch adsorption studies were conducted at the adsorbent dose of 2 g/L and background electrolyte 0.01M  $\text{NaNO}_3$ . pH was adjusted with NaOH and  $\text{HNO}_3$ . Equilibrium adsorption isotherms were obtained by varying the initial concentration of phosphate from 20 to 500 mg[P]/L at a stable/adjusted pH and at a free drifting pH varying the temperature in a control orbital shaker. The effect of the adsorbent dose (0.5-5.0 g/L) on the removal efficiency and adsorptive capacity was studied at the initial concentration 50 mg[P]/L and adjusted pH 6. The pH effect was investigated at the initial concentration of 50 mg[P]/L and adsorbent dose of 2 g/L. The kinetics of the anion sorption by Fe-Mn hydrous oxide based adsorbent was defined at the initial concentration of 5 and 20 mg[P]/L and a free drifting pH. Adsorption was calculated from the difference of the initial and final/equilibrium concentration of the anions in the solution (Szlachta *et al.*, 2012). Equilibrium adsorption data were fitted to Langmuir and Freundlich models using the well-known linearized equations (Szlachta and Chubar, 2013). The data on the rate of phosphate adsorption by Fe-Mn hydrous oxide were described by the pseudo-second order model (Ho and McKay, 1999). The Fourier transform infrared spectra were recorded using a FTIR spectrometer Nicolet 6700 in the range  $400\text{-}4000 \text{ cm}^{-1}$ .

## 3. Results

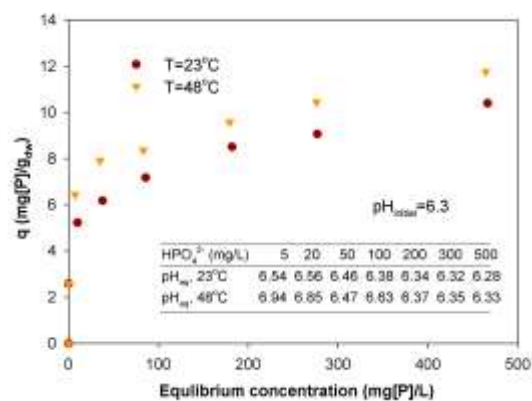
### 3.1. Equilibrium isotherms of $\text{HPO}_4^{2-}$ adsorption: pH and temperature effects

Both pH (Figure 1) and temperature (Figure 2) moderately influenced the removal performance of Fe-Mn oxide based adsorbent at equilibrium. The pH effect of phosphate adsorption was not sharp and was governed by its speciation at various pH ranges. At pH 4, the main phosphate

species was  $\text{H}_2\text{PO}_4^-$  (the most favourable phosphate species for adsorption) which resulted in higher adsorptive capacity at this pH, 25  $\text{mg[P]}/\text{g}_{\text{dw}}$ . At pH 6, when  $\text{H}_2\text{PO}_4^-$  was still strongly dominating over  $\text{HPO}_4^{2-}$ , adsorptive capacity was slightly lower, namely 20  $\text{mg[P]}/\text{g}_{\text{dw}}$ . Domination of  $\text{HPO}_4^{2-}$  at pH 8 resulted in a further decrease in adsorptive performance to 14  $\text{mg[P]}/\text{g}_{\text{dw}}$ . Increasing the temperature resulted in higher phosphate adsorption (Figure 2) and this regularity indicates that chemi-sorption was the ruling mechanism of this anion uptake by the investigated material.



**Figure 1:** Isotherms of  $\text{HPO}_4^{2-}$  adsorption at pH 4, 6 and 8



**Figure 2:** Isotherms of  $\text{HPO}_4^{2-}$  adsorption at free drifting pH.

**Table 1:** Result of the data (Figures 1 and 2) fitting to Langmuir and Freundlich models.

| Solution            | Langmuir |          |       | Freundlich isotherm |      |       |
|---------------------|----------|----------|-------|---------------------|------|-------|
|                     | Q (mg/g) | B (L/mg) | $R^2$ | K (mg/g)(L/mg)      | n    | $R^2$ |
| pH 4                | 24.94    | 0.020    | 0.934 | 2.98                | 2.99 | 0.961 |
| pH 6                | 20.12    | 0.019    | 0.937 | 2.58                | 3.17 | 0.985 |
| pH 8                | 14.27    | 0.022    | 0.950 | 2.94                | 4.33 | 0.954 |
| T=23 °C, free drift | 10.27    | 0.057    | 0.987 | 3.77                | 6.46 | 0.991 |
| T=48 °C, free drift | 11.57    | 0.070    | 0.990 | 4.40                | 6.36 | 0.993 |

An increase in the temperature also resulted in higher affinity of Fe-Mn oxide based adsorbent reflected by the Langmuir higher affinity constant (see Table 1). The addition of acid and base during pH adjustments increased adsorptive performance of the material towards phosphate (adsorption is slightly higher at a stable pH than at a free drifting pH) and this observation is not novel. Many researchers have reported that an increase in the background electrolyte concentration also increases adsorptive performance of the other materials (Chubar *et al.*, 2005). Active participation of background electrolyte in surface reactions during pH adjustments resulted in lower fits of the data to Langmuir and Freundlich models, but theoretical and experimental data on the adsorptive capacity were the same (see Figure 1 and Table 1).

### 3.2. Effects of pH and adsorbent dose on phosphate removal

The pH effect at the broader range of pH values correlated with phosphate ion speciation in solution as described above (Figure 3). The removal performance of Fe-Mn hydrous oxide increased with a higher adsorbent dose (Figure 4). The adsorptive capacity at 2-5 g/L of the material was close even if the plateau was not achieved.

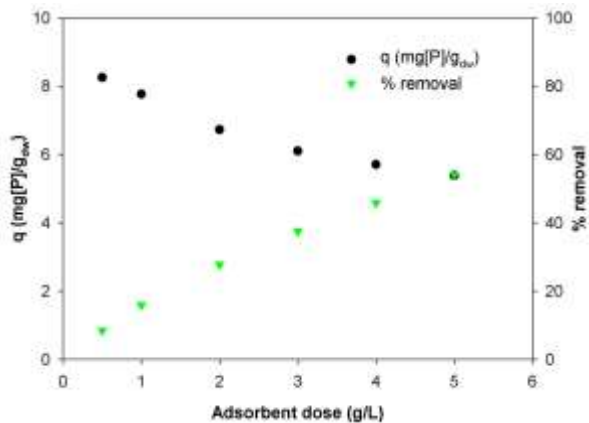


Figure 3: Effect of pH on  $\text{HPO}_4^{2-}$  adsorption.

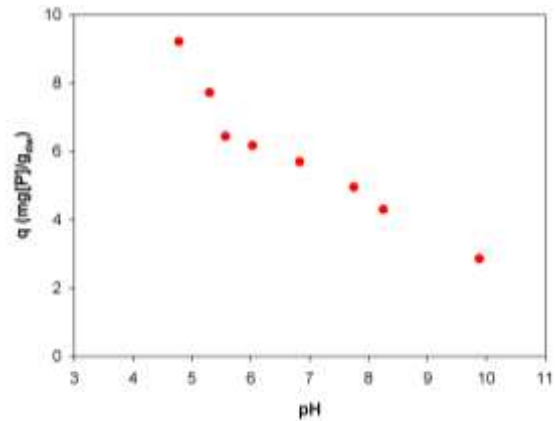


Figure 4: Effect of adsorbent dose on  $\text{HPO}_4^{2-}$  adsorption.

### 3.3. Kinetics of phosphate removal and mechanism of its adsorption by FTIR

Adsorption was faster at the lower initial concentration of phosphate (5 over 20 mg/L) and the kinetics data were perfectly described by the pseudo-second order model (see the table on the Figure 5). During the first 300 minutes the rate of phosphate uptake was higher than the kinetics rate calculated for the entire investigated period of 1440 minutes. The rate constant decreased from 0.069 to 0.051 and from 0.009 to 0.005 g/mg-min for the 5 and 20 mg/L phosphate initial concentration.

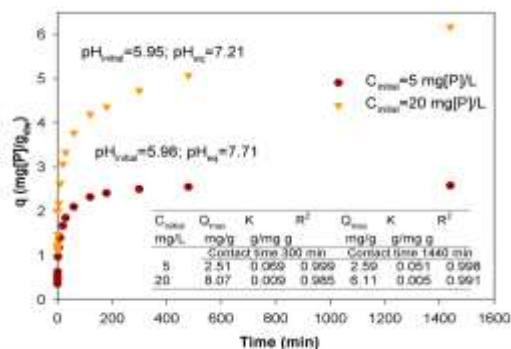


Figure 5: Kinetics of  $\text{HPO}_4^{2-}$  adsorption and pseudo-second order modelling.

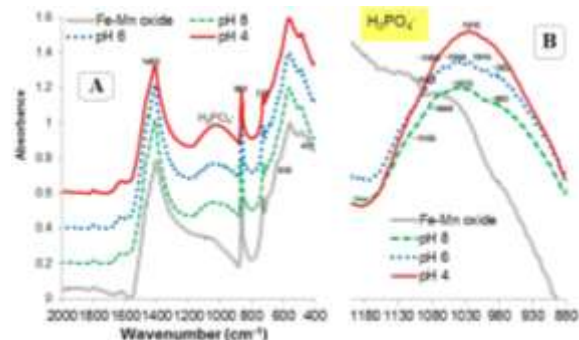


Figure 6: FTIR spectra of Fe-Mn and with adsorbed  $\text{HPO}_4^{2-}$  at pH 4, 6, 8

The bands at 1050 and 458 and 417  $\text{cm}^{-1}$  on the FTIR spectra (Figure 6) are to be attributed to the stretching mode of multicentered hydroxyl groups (M-OH). The presence of phosphate on the surface of adsorbent was clearly reflected by the new bands (Figure 6AB). It was found that the intensity of the sharp peak at 458  $\text{cm}^{-1}$  with characteristics of Fe oxide phase became very weak while the peak at 1050  $\text{cm}^{-1}$  completely disappeared. This indicates that complex reactions occurred between phosphate ions and hydroxyl groups of Fe(III) and Mn(III) oxide/hydroxides. The results of the FTIR analysis indicated that phosphate sorption on the Fe-Mn adsorbent occurred via replacement of surface hydroxyl groups (M-OH) by phosphate and the formation of inner-sphere surface complex (M-O-P) between phosphate and adsorbent. The result of the pH effect showed that a discernible pH increment occurred at pH 4-8 after phosphate adsorption on the adsorbent. This implies the release of hydroxyl groups from the surface of adsorbent into the solution. Overall, there are no distinguishing differences in phosphate surface complexes with a varying pH. The highest peak maxima of  $\gamma_3$  vibration which was significantly different from the maxima of phosphate in solution, 1006  $\text{cm}^{-1}$  (Arai and Sparks, 2001) shifted from 1015  $\text{cm}^{-1}$  at pH 4 to 1044 and 1035  $\text{cm}^{-1}$  at pH 7 and 8, respectively (Figure 6B). The broad band became more resolved at a higher pH and showed three peaks,

specifically at 1070, 1040 and 983  $\text{cm}^{-1}$ . They indicate molecular symmetry  $C_{2v}$  or lower and confirm the chemi-sorption mechanism of phosphate sorption by the inorganic ion exchanger. It has been postulated that monodentate or bidentate inner-sphere surface complex between phosphate (P-OH) and hydroxyl groups on Fe-Mn adsorbent (M-OH) might be formed (Shin *et al.*, 2004).

#### 4. Conclusions

The mixed adsorbent based on Fe-Mn hydrous oxide and  $\text{MnCO}_3$  demonstrated high removal efficiency to phosphate. The favourable phosphate removal properties of this adsorbent are due to its high affinity to  $\text{H}_2\text{PO}_4^-$  demonstrated by revealing the molecular-level mechanism of the interfacial processes. Fe-Mn oxide based adsorbent is capable of functioning across a broad pH range (4-8) with a high rate of phosphate uptake that is described by the pseudo-second order kinetic model. An increase in temperature resulted in higher phosphate adsorption indicating the chemi-sorption mechanism was responsible for its removal. Inner sphere complexation of phosphate to the surface of Fe-Mn hydrous oxide demonstrated by FTIR spectroscopy was governing the process at pH 4, 6 and 8.

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