Fe-Al-Mn Ternary Oxide Nanosorbent: Synthesis, Characterization and Phosphate Sorption Property

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ABSTRACT

In the present work, nanocrystalline Fe-Al-Mn ternary oxide nanosorbent was synthesized via impregnation method. X-ray diffraction (XRD), scanning electron microscope coupled with energy dispersive x-ray spectroscopy (SEM/EDX), Brunauer–Emmett–Teller (BET) technique and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the synthesized nanomaterial. The XRD results indicate the crystalline nature of the ternary oxide with a BET surface area of 49.53 m²g⁻¹. The optimum operating conditions to carry out sorption study such as pH, adsorbent dose, contact time, speed of agitation and initial phosphate concentration were found to be 3, 0.1 g, 16 h, 100 rpm and 30 ppm, respectively. Both Freundlich and Langmuir isotherm models fit the equilibrium data well with the latter model providing more fit to the experimental data. Kinetic data correlated well with the pseudo-second-order and Elovich models suggesting chemisorptions as the prevailing mechanism of phosphate sorption onto the nanosorbent. Thermodynamic studies resulted negative ΔG indicating the spontaneity of the sorption process. The Fe-Al-Mn ternary nanocomposite sorbent showed a sorption capacity of 38.46 mg g⁻¹ at pH 3. The sorption efficiency of the nanosorbent was found to be 99.5%. This adsorbent, with large sorption capacity and efficiency, is therefore a promising adsorbent for the removal of phosphate ions from aqueous systems.

Keywords: Sorption isotherm, phosphate, ternary oxides, kinetics, thermodynamics, desorption.

1. Introduction

Phosphorus is often present in low concentrations in wastewater almost solely as phosphates. It is an essential, often limiting, nutrient for growth of algal and other biological organisms in most ecosystems, however, excessive supply of phosphorus from wastewater into water bodies causes eutrophication [1-4]. Therefore, removing phosphate is crucial before discharging wastewater into water bodies.

Advanced treatments are typically required to remove phosphorus from wastewater especially at low concentration of the target analyte. Several techniques have been developed including physical processes (settling, filtration), chemical precipitation (with aluminum, iron and calcium salts), adsorption, reverse osmosis, constructed wetlands, and biological processes on biomass growth (bacteria, algae, plants) or intracellular bacterial polyphosphates accumulation [5-7]. Out of these, the adsorption processes are the simplest, very quick, and an economically viable alternative for removing inorganic pollutants [8, 9]. Chemical precipitation and biological removal are generally not able to meet the stringent effluent standards and reverse osmosis is of a high capital cost.

Phosphate sorbents synthesized with iron oxide that incorporate different metal oxides for high adsorption performance have been studied based on the fundamental assumption that multi component sorbents exhibit physico-chemical properties significantly different from those of their single component constituents that are believed to be primary reason for differences in sorption behavior between the multicomponent and their single counterparts [15]. Accordingly, Al (III), Cr (III), Cu (II), Mn (IV), Sn (IV), Ti (IV) and Zr (IV) [11-19] ions had been introduced into iron oxide to form bimetallic oxide adsorbents for phosphate sorption [20]. Although

extensive reports have been documented using binary oxide systems, very little is found in the literature regarding ternary oxide sorbents for phosphate sorption [21,22]. Furthermore, the ternary oxide systems reported in the literature are found to be amorphous in nature. To the best of the researchers' knowledge, there is still a paucity of information related to the synthesis, characterization and sorption property studies of Fe-Al-Mn ternary mixed oxide in nanocrystalline form for phosphate removal from wastewater. Recently, materials with nanostructure have gained special attention in the field of solute adsorption from the liquid phase due to small particle size, large surface area to volume ratio, high *in situ* reactivity and absence of diffusion resistance [15, 16, 23, 24].

In this work, we report the synthesis and phosphate sorption behavior of nanocrystalline Fe-Al-Mn ternary oxide sorbent. The synthesis involved a series of ternary oxides with different Fe/Al/Mn ratios and the one with the smallest particle size was selected and tested for phosphate sorption study. The sorption kinetics, sorption isotherms, regeneration and the influences of solution pH and coexisting anions on phosphate sorption were investigated. Phosphate sorption mechanism was also elucidated in the present paper. The results of this study provide additional insights on the fabrication of high performance sorbent for phosphate removal.

2. Materials and Methods

2.1. Synthesis of nano sized Fe-Al-Mn ternary mixed oxides by impregnation Method

Impregnation method was used to synthesize nanocrystalline Fe-Al-Mn ternary mixed oxides [25]. 0.1 M nano sized Fe-Al-Mn ternary mixed oxides was prepared by impregnating MnO₂ with Al and Fe nitrate aqueous solution, then dried at 110 °C in an oven over night and further calcined at 300 and 600°C having different percentage of precursors [(Fe (NO₃)₃·9H₂O, Al

(NO_3)₃.9H₂O and MnO₂]. The percentage of iron, aluminum and manganese precursors varied in the range 80-90%, 8-15% and 0-10% respectively. The MnO₂ used here was synthesized by precipitation method [25]. All the chemicals and reagents used were analytical grade and used with no further purification.

2.2. Characterization

The structures of the as-synthesized nanomaterials were examined by powder X-ray diffraction (XRD) using X'Pert Pro PANalytical equipped with an X-ray source of a CuK α radiation (wavelength of 0.15406 nm) at step scan rate of 0.02 (step time: 1 s; 2 θ range: 5.0 – 90.4°). Sizes of the ternary oxide particles were calculated by Debye Scherrer equation [26]. The morphology and particle size distribution of the solids were determined by scanning electron microscopy (SEM) using a Hitachi TM1000 with EDX detector. N₂ adsorption isotherms were measured at -196 °C (77 K) on Micromeritics ASAP 2420 and the micropore surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The FTIR spectrum of the as-synthesized nanosorbent was determined using the KBr disc method using paraffin as diluent. The IR absorption pattern was recorded between 400 and 4000 cm⁻¹ using SHIMADZU (1730, Japan) spectrometer

2.3. Adsorption Studies

All sorption studies were carried out in Erlenmeyer flasks of 50 mL having adsorbent to solution ratio of 1:250 (0.1 g of metal oxide powder: 25 mL of 30 mg/L of KH₂PO₄ reacting solution). The pH of phosphate solution was adjusted using dilute HCl and NaOH solutions by using pH meter. The solution was separated from the adsorbent by filtration. Equilibration for all sorption experiments was done on a rotary shaker. Final concentrations of the phosphate ions were

estimated spectrophotometrically by the molybdenum blue method, monitoring the absorbance at 880 nm on UV–vis spectrophotometer (SP65). Influence of various experimental sorption parameters was studied and is described in the following subsections.

2.3.1 Effect of pH and Ionic strength

The effect of pH was studied in the pH range of 2 to 9 keeping the other parameters constant as follows: Sorbent dose 0.1 g L^{-1} ; initial phosphate concentration 30 mg L^{-1} ; shaking time 24 h; agitation speed 120 rpm. The effect of ionic strength was studied taking the initial phosphate concentration of 5 mg/L . The solution pH was adjusted from 2 to 10, the concentrations of NaNO_3 were 0.1, 0.01, 0.001 M, respectively, and the contact time was 8 h. In a separate experiment, the pH_{pzc} of the as-synthesized nanosorbent was determined by adding 100 mg of the nanosorbent into 250 mL beaker. 50 mL of 0.001M NaNO_3 was added and adjust to various pH ranging from 2-12 using dilute HNO_3 or NaOH solutions. The solution was equilibrated for 60 minutes in a mechanical shaker to determine the initial pH. Then, 1g of NaNO_3 was added to the above solution and further equilibrated for another 60 minute after agitation to measure the final pH. A plot of $\text{pH}_{\text{final-initial}}$ (Y-axis) versus pH_{final} (X-axis) was used to determine the point of zero charge where the graph intersects the X-axis.

2.3.2. Adsorbent dose

The influence of sorbent dose on phosphate sorption efficiency was studied by varying the dose from $0.05\text{--}2.00\text{ g L}^{-1}$ keeping the remaining parameters constant as follows: initial phosphate concentration 30 mg L^{-1} ; initial solution pH 3; shaking time 24 h; agitation speed 120 rpm.

127 2.3.3. *Agitation speed*

128 The impact of agitation speed was investigated by varying the speed of the shaker in the range
129 50-200 rpm keeping the remaining parameters constant as follows: sorbent dose 0.1 g L^{-1} ; initial
130 phosphate concentration 30 mg L^{-1} ; initial solution pH 3; shaking time 24 h.

131 2.3.4. *Initial phosphate concentration*

132 The effect of phosphate concentration was determined considering the following initial
133 phosphate ion concentration: 10, 20, 30, 50, 100, 150 and 200 mg/L keeping other parameters
134 constant as follows: sorbent dose 0.1 g L^{-1} ; initial solution pH 3; agitation speed 100 rpm;
135 shaking time 16 h.

136 2.4. *Adsorption Isotherm*

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among the liquid and solid phases based on a set of assumptions that are related to the heterogeneity or homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate species. In order to construct adsorption isotherms for the adsorbent, experiments were carried out by varying the initial phosphate ions concentration from 10 to 200 ppm and with the adsorbent dose of 0.1g. The following optimum parameters were kept constant during the study: pH 3; shaking time 16 h; agitation speed 100 rpm.

2.5. Thermodynamics of adsorption

Thermodynamic parameters shed valuable insight into feasibility and spontaneity nature of the adsorption process [27]. By plotting the graph $\ln K_c$ versus T^{-1} , the values of ΔH and ΔS were estimated from the slopes and intercepts and on the basis of this, the spontaneity of the process was assessed. Based on the above approach, the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated for the sorbent. Accordingly, the thermodynamic parameters were studied using the following optimum conditions: sorbent dose 0.1g ; initial phosphate concentration 20-200 mg L⁻¹; initial solution pH = 3; and equilibration time 16 h; agitation speed 100 rpm; temperature 30-60 °C.

2.6. Kinetics study

Adsorption is time dependent process and it is very important to know the rate of the process and evaluate the adsorbent in removing phosphate from aqueous system. The following optimum operating conditions were employed for the kinetic study: sorbent dose 0.1g

L⁻¹; initial phosphate concentration 30 mg L⁻¹; initial solution pH 3; shaking time 1/2-48 h; agitation speed 100 rpm.

2.7. Selectivity of phosphate adsorption

The selectivity of phosphate adsorption experiment was done according to the method described elsewhere [28] by keeping all parameters at optimized value. The effect of common coexisting ions such as: Fluorides, chloride, sulfate, nitrates and carbonate on the sorption of phosphate was investigated. 30 mg L⁻¹ solutions of the ions were prepared from their respective salts sodium fluoride, sodium chloride, sodium sulfate, sodium nitrate and sodium carbonate.

2.8. Desorption of phosphate

Phosphate desorption was conducted using phosphate loaded powder sample. 0.1 g of Fe–Al–Mn ternary mixed oxide of phosphate loaded powder was added into each flask containing 25 mL of deionized water. 0.1 M NaOH or 0.1 M HCl solutions were used to adjust pH of the solution from 2-9. The solutions were agitated at optimized values, filtered and analyzed for phosphate ions according to the method described previously [20]. The quantity of desorbed phosphate ions was determined by the amount of phosphate ions in the solution after each desorption experiment was performed

3. Results and discussion

3.1. Synthesis and characterization

Ten series of Fe-Al-Mn samples were synthesized and their structure examined by XRD. The diffraction patterns exhibited in all cases the presence of hematite (Figure S1). No peak was

attributable to either alumina or manganese. This may due to small percentage of MnO_2 ($< 3\%$, as witnessed by the EDX) and the amorphous structure of alumina. In fact, crystallized alumina such as $\beta\text{-Al}_2\text{O}_3$ might present under thermal treatment at 800°C where as $\alpha\text{-Al}_2\text{O}_3$ might present under thermal treatment at 1000°C [20, 26]. Increased crystallite size with increased calcinations temperature is also witnessed in this study (Table 1). From the as-synthesized ternary oxide samples, the one with the smallest crystallite size (22.53 nm) was found to be C3 (90% Fe, 8% Al and 2% Mn) as shown in Table 1. The XRD pattern of this sample is depicted in Figure 1. The peaks at 2θ values corresponding to 24, 33, 36, 41, 49.5, 54.5, 63, 64.5, 72.5 are all associated with hematite. The SEM micrographs of the selected (C3) as-synthesized nanomaterial are displayed in Figure 2. Aggregates of nanorods of a wide range of sizes are obtained for the ternary crystals. EDX analyses included in Figure 2 confirmed the presence of all the three metals considered in the relatively wider range: 86.4-94.5% (Fe), 2.0-13.6% (Al) and 0-3.5% (Mn) revealing the heterogeneous nature of the nanosorbent. The average values of all the readings of the C3 micrographs, however, resulted 90.8% Fe, 7.8% Al and 1.4% Mn in close agreement with the theoretical composition of C3 shown above. The average specific surface area of the selected Fe-Al-Mn nanosorbent (C3) was found to be $49.53\text{ m}^2\text{g}^{-1}$ indicating the moderately high specific surface area of the as-synthesized nanopowder. Lu et al.[21], reported a much higher BET specific surface area of $303\text{ m}^2\text{g}^{-1}$ in contrast to our findings for the Fe-Al-Mn trimetalic oxide they synthesized. However, XRD and TEM results confirmed the amorphous nature of their ternary system. As one might expect, amorphous materials in general exhibit higher specific surface area than crystalline ones as the two parameters are reciprocally related unless the as-synthesized material involves phase change during calcinations. [20].

The FTIR spectra of the naked sorbent and the phosphate-loaded sorbent are depicted in Figure 3. The bands observed in both cases are more or less similar except additional peaks appeared in the phosphate loaded spectrum. The bands at 3439 cm^{-1} correspond to O-H stretching vibrations and the peaks at 1631 cm^{-1} may be attributed to bending vibrations of adsorbed H_2O [20-22]. The peaks at 563 cm^{-1} and 480 cm^{-1} correspond in both cases to M-O stretching vibrations. The bands observed at 1380 cm^{-1} could be assigned to the adsorbed carbonate, because the adsorption tests were carried out open to the atmosphere. For a spectrum after phosphate adsorption additional peaks at 1051 and 1078 cm^{-1} were observed owing to the P-O stretching modes indicating the adsorption of phosphate on the surface of the nanosorbent [20]. The bands at 2920 and 2844 cm^{-1} are responsible for the symmetric and asymmetric C-H stretching vibrations respectively the appearance of which could be attributed to the presence of residual paraffin used as diluent [23].

3.2. Effect of pH

Figure 4 shows the effect of pH on the adsorption of phosphate. The highest adsorption was attained under acidic conditions (pH 3) and decreased with increase in solution pH. This lower pH causes the mixed oxide surface to carry a more positive charge (protonation of sorbent surface) as evidenced from the pH_{pzc} of the as-synthesized sorbent, which is 6.6. The sorbent is presumed to exhibit positive charge at $\text{pH} < \text{pH}_{\text{pzc}}$ and negative charge at $\text{pH} > \text{pH}_{\text{pzc}}$ (Figure 5). Increased protonation is thought to increase the positively charged sites, enlarge the attraction force existing between the sorbent surface and the phosphate anions and thus would more significantly attract the negatively charged monovalent H_2PO_4^- ions in solution and therefore increase the amount of sorption at lower pH. Higher pH value causes the surface to carry more negative charges and thus would significantly electrostatically repulse the negatively charged

species in solution, hence the fall in the sorption of phosphate at higher pH [29-31]. The phosphate adsorption mechanism of Fe-Al-Mn ternary oxide nanosorbent was investigated by evaluating the ionic strength effect on the adsorption behavior. Figure 6 demonstrates that the phosphate adsorption showed no consistent decreasing trend with increase in ionic strength. Especially at the optimum pH the trend found was contrary, increased in phosphate sorption with increased ionic strength from 0.001 to 0.1 mol L⁻¹. It is well known that anions adsorbed by outer-sphere association are strongly sensitive to ionic strength where as anions adsorbed by inner-sphere association either show little sensitivity to ionic strength or greater phosphate adsorption with increasing ionic strength [39]. Based on this finding, it can be concluded that phosphate anions may be specifically adsorbed on the Fe-Al-Mn ternary oxide nanosorbent via forming inner-sphere surface complexes.

3.3. Effect of adsorbent dose

The result of adsorbent dose study is shown in Figure 7. It was observed that the removal efficiency increased from 64.36% to 97.73% with an increase in adsorbent dose from 0.01 to 0.1 g. This can be attributed to the number of sorption sites available for sorbent-solute interaction. It is also observed that, with a further increment of adsorbent dose from 0.1 to 2 g, the increase of percent of sorption was less significant. Thus, the adsorbent dose was maintained at 0.1 g in all the subsequent experiments.

3.4. Effect of agitation speed

Figure 8 illustrates the effect of agitation speed on phosphate sorption by the Fe-Al-Mn nanosorbent. The graph showed increasing phosphate sorption from 98.7 to 99.1% with speed of

agitation up to 100 rpm. This evidences the importance of perturbing the solution containing phosphate ions to a certain extent to enhance the contact between the sorbent and the analyte. It has been investigated that the mass transfer rate increases with increase in stirring speed. This is because of decreasing the boundary layer thickness with increase in stirring speed which results in a reduction of surface film resistance [32]. However, beyond this optimum agitation speed, the sorption efficiency decreased due to desorption of the already sorbed phosphate ions as the result of vigorous shaking.

3.5. Effect of phosphate concentrations

The influence of initial phosphate ion concentration on the removal efficiency of the adsorbent is illustrated in Figure 9. It was carried out by varying the initial phosphate concentration from 10 to 200 mgL⁻¹ while keeping other parameters constant: pH 3, adsorbent dose 0.1 g, agitation speed 100 rpm and contact time of 16 h. The removal efficiency of the phosphate ion decreased from 99.52% at 30 mgL⁻¹ to 73.81% at 200 mgL⁻¹. This can be explained by the fact that in case of low concentrations, the ratio of the initial number of moles of solutes to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration and consequently higher adsorption yields were obtained [20]. However, at higher concentrations, most of the adsorption sites could be occupied by ions and the available sites of adsorption would become fewer, hence the percentage removal of phosphate ions which depends up on the initial concentration could decrease.

3.6. Adsorption isotherms

The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms. For this, both Freundlich and Langmuir models were employed to describe the experimental results of phosphate ions adsorption. Experiments on phosphate adsorption isotherm were conducted with different initial concentration of phosphate at room temperature keeping all other parameters at optimum conditions. The results of phosphate adsorption isotherm on the nanosized adsorbent are illustrated in table 2.

The linear Langmuir adsorption model is expressed as,

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

From the plot of C_e/q_e vs. C_e , Figure 10, a straight line was obtained with a slope value of 0.026 giving Q_o values of 38.46 mg g⁻¹ and an intercept of 0.079 giving b value of 0.329. The feasibility of the isotherm can be tested by calculating the dimensionless constant, R_L expressed as:

$$R_L = \frac{1}{1 + b C_o} \quad (2)$$

As can be seen in table 2, R_L values are in between 0 and 1 indicating a favorable adsorption. This means that phosphate ions in solution have tended to be adsorbed on the Fe-Al-Mn binary oxide nanosorbent. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. The linearized form of the equation is:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

299

300 Plotting $\log q_e$ versus $\log C_e$ (Figure 11) provides a straight line with a slope of 0.344 and an
301 intercept of 1.051. The value of $1/n$ lying between 0 and 1, which is 0.344 and the n value lying
302 between 1 and 10, which is 2.907, shows a favorable condition for sorption [33]. The Langmuir's
303 and Freundlich's curves were interpreted with respect to correlation coefficient (R^2), a statistical
304 measure of how well the regression line approximates the real data point (table 2). In this study,
305 the sorption isotherm of the Fe-Al-Mn ternary oxide nanosorbent showed better fit to both
306 isotherms though the value of R^2 is relatively higher for Langmuir's equation than the Freundlich
307 (i.e. 0.9877 versus 0.9588, respectively). This indicates that each sites of the adsorbent can
308 accommodate one molecule of phosphate ion or can be characterized by supporting surfaces of
309 different affinity (heterogeneity of surfaces which may be from doping of aluminum).

310

311 *3.7. Kinetics of Adsorption*

312 The study of adsorption kinetics is very useful for understanding the involved mechanisms and
313 also for the design of future large scale adsorption facilities. Many models are used to fit the
314 kinetic adsorption experiments. The most used ones are the pseudo-first order, pseudo-second
315 order, Elovich and intra-particle diffusion models [34,35] and these models are used in our study.

316 *Pseudo-first-order kinetics model*

317 This model was suggested by Lagergren (1898) for the sorption of solid/liquid systems. It can be
318 expressed as:

$$319 \quad \log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} \quad (4)$$

320 *Pseudo-second-order kinetics model*

321 If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption
322 kinetic rate equation after integration is expressed as:

$$323 \quad \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (5)$$

324 *Elovich model*

325 The Elovich equation is given as follows:

$$326 \quad \frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (6)$$

327 The integration of the rate of equation with the same boundary conditions as the pseudo-first and
328 second order equation becomes the Elovich equation

$$329 \quad qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

330 Where α is the initial sorption rate (ng/g min), and the parameter β is related to the surface
331 coverage and activation energy for chemisorptions (g mg^{-1}).

332 *Intraparticle diffusion model*

333 In the liquid–solid system, the diffusion rate of phosphate k_m can be calculated from the following
334 equation:

$$335 \quad q_t = k_m t^{0.5} \quad (8)$$

336 where k_m ($\text{mg g}^{-1} \text{min}^{0.5}$) is the rate constant.

337 The kinetics of phosphate sorption from aqueous solutions onto the Fe-Al-Mn mixed oxide
338 nanosorbent is depicted in Figure 12. Cumulative P sorbed with time followed, in general, an
339 initial rapid sorption of P occurring at the available surface sites followed by a slower sorption
340 that was still continuing after 48 h equilibration time as the result of phosphate diffusion into the
341 matrix of the nanosorbent [36]. Kinetic parameters and coefficient of determination (R^2) for the
342 various kinetic models are also shown in Table 3. The pseudo-first-order equation appeared to fit

well for the first 16 h, however, the data deviated from calculated values as time increases (Figure 13). In addition, the difference between experimental (7.395 mg g^{-1}) and theoretical (1.83 mg g^{-1}) adsorbed masses at equilibrium is very high. As a consequence, adsorption of phosphates onto Fe-Al-Mn nanosorbent is not an ideal pseudo-first-order reaction. For the pseudo-second-order model, the correlation coefficient was the highest ($R^2 = 0.9999$) of all the models considered in this study (Figure 14 and Table 3). Furthermore, the difference between the experimental ($q_e=7.395 \text{ mg g}^{-1}$) and theoretical ($q_{ecal}=7.46 \text{ mg g}^{-1}$) adsorbed masses at equilibrium is very small (less than 1%). This indicates that chemisorption or chemical bonding between adsorbent active sites and phosphate might dominate the adsorption process. One of the most useful models for describing such ‘activated’ chemisorption is the Elovich equation. The Elovich equation, which has been shown to be useful in describing chemisorptions on the adsorbents, give a good account of sorption of phosphate with R^2 values of 0.961 (Figure 15) consolidating the results obtained above using pseudo second order kinetic model. The plot for intra-particle diffusion (Figure 16), q_t vs $t^{1/2}$ showed relatively poor correlation coefficient ($R^2 = 0.715$) indicating that this model did not fit the sorption process [37].

3.8. Selectivity of Phosphate Adsorption

The selectivity of phosphate sorption onto the Fe-Al-Mn nanosorbent in the presence of individual or mixed competing ions was found to follow the order: sulfate> mixed anions> nitrate> hydrogen carbonate> chloride> fluoride (Figure 17). The most competing ion was found to be fluoride ion. However, the amount of phosphate adsorbed on the Fe-Al-Mn ternary mixed oxide in the presence of all anions considered was relatively higher indicating the good

sorption ability of the nanosorbent in the presence of these competing ions. The fact that the drop in sorption ability of the nanosorbent was only 0.45% even in the presence of the most competing ion such as fluoride makes this nanosorbent a promising material for phosphate removal from aqueous system or real waste water. In our previous work, we reported a relatively higher drop (2%) in phosphate sorption in the presence of fluoride ion by Fe-Al nanosorbent [20]. In this report we witnessed increased phosphate selectivity when Mn is introduced into the Fe-Al binary system to form Fe-Al-Mn ternary nanocomposite evidencing the higher phosphate selectivity of the ternary system compared with the its binary congener.

3.9. Thermodynamics of Adsorption

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equations:

$$\Delta G = -nRT \ln K_c \quad (9)$$

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{-\Delta S^\circ}{R} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

Where R (8.314 J/molK) is the gas constant, T (K) is the absolute temperature and K_c is the standard thermodynamic equilibrium constant defined by q_e/C_e .

The values of ΔH° and ΔS° can be estimated by plotting the graph of $\ln k_c$ versus T^{-1} (Figure 18) from the slopes and intercepts respectively. Table 4 shows the negative values of ΔG° indicating the spontaneity of the phosphate sorption process. The decrease in ΔG° with increase temperature indicates more efficient sorption at higher temperature. For phosphate ions travel

through solution and reach the sorption sites, it is necessary for them first to be stripped out (at least partially) of their hydration shell, this process requires energy input. The positive value of ΔS° suggests increased randomness at the solid/solution interface and may suggest some structural changes in adsorbents [38].

3.10. Desorption of Phosphate

According to the results of desorption studies (Figure 19), the amount of phosphate desorbed increased with the increase of pH. When pH value is 4 only 2.21% phosphate was desorbed whereas when the pH reached 9, 47.54% was leached into the liquid. This indicates that chemisorptions might be involved. Only the phosphate ions that are adsorbed by physisorption and ion exchange that are presumed to desorb easily whereas the phosphate ions that are chemisorbed are presumed to be less labile making the desorption process a bit time consuming [39].

$$\% \text{ Desorption efficiency} = \frac{\text{Desorbed}}{\text{Adsorbed}} \times 100\% \quad (12)$$

Where, Desorbed refers to the concentration of the phosphate ion after the desorption process
Adsorbed = $(C_o - C_e)$ for each recovery process.

4. Conclusion

Phosphate removal is important in the control of eutrophication of water bodies and sorption is one of the promising approaches. For this purpose, Fe-Al-Mn ternary oxide nanosorbent was synthesized by impregnation method. The material was investigated by means of XRD, SEM-EDX, BET and FTIR. From XRD study the Fe-Al-Mn ternary oxide was confirmed

nanocrystalline. The SEM-EDX analyses evidenced a heterogeneous surface comprising all the three metals. The FTIR spectrum after phosphate sorption exhibited additional peak at 1051 cm^{-1} attributed to the bending vibration of adsorbed phosphate. The phosphate removal by this oxide was highly pH dependent, maximum retention of phosphate occurred at pH-3. Pseudo second-order reaction rate model adequately described the kinetics of sorption of phosphate with high correlation coefficient ($R^2 = 0.9999$) and its theoretical equilibrium capacities q_{ecal} (7.46 mg/g) fit well with experimental data q_e (7.395 mg/g). Both the pseudo second order and Elovich kinetic models evidenced chemisorption as the prevailing mechanism of phosphate sorption. The sorption isotherms of phosphate ions were analyzed using both Freundlich and Langmuir isotherm models with the latter showing a better fit to the experimental data. The negative values of ΔG^0 indicate that the phosphate adsorption process is spontaneous. The Fe-Al-Mn ternary oxide nanosorbent has shown high selectivity towards phosphate ions and coexisting ions such as, sulfate, nitrate, hydrogen carbonate, chloride and fluoride did not greatly interfere in the uptake of phosphate. The as-synthesised nanocrystalline sorbent showed relatively high sorption efficiency (99.5%) and large adsorption capacity (38 mg/g) make it potentially attractive material for the removal of phosphate from aqueous systems.

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551 **Table1** Designation of percentage composition, calcinations temperature, and XRD results of
 552 the as synthesized powders.

Sample code	Percentage (%) composition			XRD results		
	Fe	Al	Mn	2 θ (degree)	β (degree)	D (nm)
1(300°C) C1	90	10	0	33.141	0.338	24.52
2(300°C) C2	85	10	5	33.220	0.341	24.32
3(300°C) C3	90	8	2	33.280	0.368	22.53
4(300°C) C4	80	15	5	33.309	0.283	29.30
5(300°C) C5	80	10	10	33.340	0.358	23.17
1(600°C) C6	90	10	0	33.369	0.225	36.86
2(600°C) C7	85	10	5	33.357	0.332	24.98
3(600°C) C8	90	8	2	33.357	0.362	22.97
4(600°C) C9	80	15	5	33.560	0.317	26.18
5(600°C) C10	80	10	10	33.424	0.339	24.47

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554 **Table 2** Langmuir and Freundlich isotherm constants for phosphate adsorption by Fe–Al–Mn
 555 ternary mixed oxide sorbent.

Adsorbent	Langmuir model				Freundlich model		
	Q _o (mg/g)	b	R _L	R ²	K _f	1/n	R ²
Fe–Al–Mn ternary oxide	38.46	0.329	0.092	0.9877	11.25	0.344	0.9588

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557 **Table 3** The values of parameters and correlation coefficients of kinetic models

	k	q _e (mg/g)	R ²	α	β	K _i (min ⁻¹)	C
Pseudo-first order	0.239	1.83	0.9867	-	-	-	-
Pseudo-second order	0.576	7.46	0.9999	-	-	-	-
Elovich model	-	-	0.9612	-7.2	0.5040	-	-
Intra-particle	-	-	0.7150	-	-	0.2955	5.8568

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559 **Table 4** Thermodynamic parameters for phosphate adsorption onto nano- sized adsorbent.

T(K)	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS (J/molK)
303	-3692	+43.259	+155.214
313	-5129		
323	-7444		
333	-8195		

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Figure 1 XRD pattern of Fe-Al-Mn ternary nanocomposite

Figure 2 SEM micrographs with EDX analyses of Fe-Al-Mn (C3) nanocrystals

Figure 3 FTIR Spectrum of nano sized ternary mixed oxide sorbent before and after adsorption .

Figure 4 Effect of solution pH on the removal phosphate onto ternary mixed oxide ($C_o = 30$ mgL⁻¹, adsorbent dose = 0.1 g, agitation speed = 120 rpm and t = 24 h)

Figure 5 pH_{pzc} of as-synthesized Fe-Al-Mn ternary oxide nanosorbent

Figure 6 Effect of ionic strength on phosphate sorption by Fe-Al binary oxide nanosorbent (initial phosphate concentration 5 mg/L and adsorbent load 0.1 g/L)

Figure 7 Effect of adsorbent dose on the removal of phosphate ($C_o = \text{mgL}^{-1}$, pH =3, agitation speed = 120 rpm and t = 24 h)

Figure 8 Effect of speed of agitation on the removal of phosphate ($C_o = 30 \text{ mgL}^{-1}$, pH = 3, dose = 0.1 g and t = 16 h)

Figure 9 Effect of initial concentration of phosphate on the removal of phosphate (At pH = 3, adsorbent dose = 0.1 g, agitation speed = 100 rpm and contact time 16 h

Figure 10 Langmuir adsorption isotherm of phosphate by Fe-Al-Mn ternary oxide sorbent at pH = 3.

Figure 11 Freundlich isotherm for phophate adsorption onto ternary mixed oxide sorbent
(pH=3; T=25 °C; adsorbent dose = 0.1 g; and t=16 h)

Figure 12 Kinetics of Adsorption on the removal of phosphate ($C_o = 30$ mg/L, pH = 3, adsorbent dose = 0.1 g and agitation speed = 100 rpm)

Figure 13 Plot of the pseudo-first order model ($C_o = 30$ mg/L, pH = 3; dosage = 0.1 g and agitation speed = 100 rpm)

Figure 14 Plot of the pseudo-second order model ($C_o = 30$ mgL⁻¹, pH = 3; dosage = 0.1 g and agitation speed = 100 rpm)

Figure 15 Plot of the Elovich model (At $C_o = 30 \text{ mgL}^{-1}$, $\text{pH} = 3$; adsorbent dose = 0.1 g and agitation speed = 100 rpm)

Figure 16 Plot of the intra-particle model (At $C_o = 30 \text{ mg/L}$, $\text{pH} = 3$; adsorbent dose = 0.1 g and agitation speed = 100 rpm)

Figure 17 Effect of anions on phosphate adsorption

Figure 18 Plot of $\ln K_c$ Vs T^{-1} for phosphate adsorption (pH = 3, dose = 0.1 g, agitation speed = 100 rpm, Contact time = 16 h, $C_o = 30 \text{ mgL}^{-1}$)

Figure 19 Effect of pH on desorption of phosphate at varied pH