

# REMOVAL OF POLYPHOSPHATES FROM WASTEWATER BY MAGNETIC COMPOSITE MINERAL SORBENTS

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**Keywords:** Composite magnetic sorbent, natural clay, magnetite, adsorption, magnetic separation.

Magnetic composite mineral sorbents based on saponite, spondyle, palygorskite clays and magnetite were created. The ability of magnetic sorbents to remove tripolyphosphate and hexametaphosphate from aqueous solutions has been studied for different adsorbate concentrations by varying the amount of adsorbent, temperature and shaking time. The kinetics of adsorption process data was examined using the pseudo-first-order, pseudo-second-order kinetics and the Boyd-Adamson internal diffusion kinetic models. The adsorption kinetics is best described by the pseudo second-order model with good correlation ( $R^2 \approx 1.00$ ). The experimental isotherm data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich equations. The experimental data well fitted to Langmuir isotherm model. It was found that calculated adsorption capacities of magnetic composites relatively tripolyphosphate ( $550\text{--}620 \text{ mg g}^{-1}$ ) and hexametaphosphate ( $670\text{--}730 \text{ mg g}^{-1}$ ) were good agreed with experimentally obtained values. The thermodynamic parameters, such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  were also determined. It was indicated that the adsorption of polyphosphates was feasible, spontaneous and exothermic in nature and the physical nature of the process was confirmed. Thus, cheap magnetic sorbents based on natural clays and magnetite, which not only quickly separated from the solution by magnetic separation, but effectively removed polyphosphates were obtained.

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## Introduction

Currently one of the major problems in wastewater treatment is the removal the biogenic elements, such as nitrogen and phosphorus, that cause eutrophication of water bodies.<sup>1</sup> Soluble phosphorus is the main limiting element that mostly affects the growth of vegetation of aquatic bodies. It is known that eutrophication of water is not observed at concentrations of phosphorus less than  $0.2 \text{ mg L}^{-1}$ .<sup>2</sup>

The main source of biogenic polluting substances of water bodies is municipal wastewater. Functioning of most urban wastewater treatment plants is based on traditional biotechnology, which provides a low degree of phosphates removal (20-30 %).<sup>3</sup> Especially polyphosphates, intensively used in the composition of household detergents and washing powders, are difficult to remove.<sup>4</sup>

Adsorption is the most promising method of disposal of contaminated wastewater. Recently, sorption materials of natural origin, such as clays acquired great popularity. Compared with traditional sorbents, clay minerals have a higher sorption capacity, greater mechanical and chemical resistance and lower cost. In particular, the clay materials were tested for the removal of phosphates. Clays has a sufficiently high sorption activity with respect to phosphate.<sup>5</sup>

The high sorption activity of clay sorbents was due to their colloidal dispersibility. In this regard, the problem of removing of spent sorbent particles from the aquatic environment arose. Also, it creates the risk of secondary water pollution.

To overcome this difficulty, the creation of the magnetic composites based on clays materials and magnetite ( $\text{Fe}_3\text{O}_4$ ) is proposed. The waste magnetic materials can be easily removed from the water after completion of the sorption process by magnetic separation. In addition, creation of composite sorbents based on clay minerals and magnetic iron oxide provides<sup>6</sup> aggregative stability of nanosized  $\text{Fe}_3\text{O}_4$ , due to its stabilization in the structure of clay matrix and high efficiency of composite sorbent based on cheap mineral raw materials.

Therefore, in this article the creation of magnetic composite mineral sorbents (MC) based clay minerals (saponite, spondyle clay, palygorskite) and magnetite  $\text{Fe}_3\text{O}_4$  is reported. The sorption, kinetic and thermodynamic laws of tripolyphosphate (TPP) and hexametaphosphate (HMP) removal from aqueous solutions by clay minerals, magnetite and composite sorbents based on them have been investigated.

## Experimental

### Synthesis of MC samples

Synthesis of MC by impregnation method was based on the process of physical adsorption of magnetic  $\text{Fe}_3\text{O}_4$  particles in the pores and on the surface of clay.<sup>7</sup> Magnetite in the form of magnetic fluid is produced by chemical deposition from a solution according to the Elmore method.<sup>8</sup> Saponite, spondyle clay, palygorskite (particle size less than 230 meshes ( $63 \mu\text{m}$ )) and magnetic fluid was stirred for 30 min. The resultant suspension was separated by the magnetic filter and dried at a temperature of  $60\text{--}80 \text{ }^\circ\text{C}$  for 24 h. Thus, samples of magnetic sorbents based on saponite (MCSp-2, MCSp-4, MCSp-7, MCSp-10), spondyle clay (MCSd-2, MCSd-4, MCSd-7, MCSd-10) and palygorskite (MCP-2, MCP-4, MCP-7, MCP-10) containing 2 wt., 4 wt., 7 wt. and 10 wt. of magnetite, respectively were obtained.

### Adsorption kinetic

In kinetic studies, 1 g of each adsorbent was added into a flask with 100 mL of 200 mg L<sup>-1</sup> TPP solution or 400 mg L<sup>-1</sup> HMP solution. The sealed flasks were put in a shaker bath at 20±2 °C and shaken at 35 rpm for 15, 30, 60, 120 and 180 min. After the expiry of the specified time suspension was centrifuged at 3000 rpm for 5 min and residual (equilibrium) concentration of polyphosphates were determined by photometric method using a UV-5800PC Spectrophotometer.

### Adsorption procedure

Batch adsorption experiments were carried out by adding a fixed amount of sorbent (1 g) into a number of 250 mL stoppered glasses containing a 100 mL of different initial concentrations (50–10000 mg L<sup>-1</sup>) solution of tripolyphosphate or hexametaphosphate. The flasks were placed in a thermostatic water bath shaker (20±2 °C) and agitation was provided at 350 rpm for 60 min to ensure equilibrium was reached. After setting of adsorption equilibrium the suspension was separated in a field of centrifugal forces during 5 min at 3000 rpm. After adsorption experiments, the concentrations of phosphate in the solutions were determined by photometric method using a UV-5800PC Spectrophotometer.

The amount of adsorption at equilibrium,  $Q_{t(e)}$  (mg g<sup>-1</sup>), was calculated by eqn. (1),

$$Q_{t(e)} = \frac{(C_0 - C_e) \cdot V}{m}, \quad (1)$$

where

$C_0$  and  $C_e$  (mg L<sup>-1</sup>) are liquid-phase concentrations of TPP or HMP at initial and equilibrium, respectively,

$V$  (L) is the volume of solution and

$m$  (g) is the mass of sorbent used.

### Adsorption kinetic parameters

In the process of surfactants removal from aqueous solutions sorption kinetics is important to select the optimal conditions of water purification. It provides important information about the ways and mechanisms of sorption. As is well known, sorption process is complicated and multistage, therefore, traditional kinetic models are not always suitable to describe complex adsorption process. To describe the sorption kinetics in modern scientific literature the kinetic model of the pseudo-first order, pseudo-second order and diffusion Boyd-Adamson models are used, which reveal the influence of the chemical stage.<sup>9</sup>

The pseudo-first order model of the rate is the earliest sorption kinetics model (eqn. 2),<sup>10</sup> where  $Q_{t(e)}$  and  $Q_t$  is sorption capacity of surfactant, in mg g<sup>-1</sup>, at equilibrium and at time  $t$  and  $k_1$  is pseudo-first order model rate constant in min<sup>-1</sup>.

$$\frac{dQ_t}{dt} = k_1 \cdot (Q_{t(e)} - Q_t), \quad (2)$$

Eqn. (2) in the integration of boundary conditions of  $t = 0$  to  $t = t$  and  $Q_t = 0$  from to  $Q_e = Q_t$  takes the form of Eqn.(3).

$$\ln(Q_{t(e)} - Q_t) = \ln(Q_{t(e)}) - \frac{k_1}{2,303} \cdot t, \quad (3)$$

where  $Q_{t(e)}$  and  $Q_t$  are calculated as follows,

$$Q = \frac{(C_t - C_0) \cdot V}{m} \cdot 1000, \quad (4)$$

where

$C_0$  and  $C_t$  are the initial surfactant concentration and concentration of surfactant in solution at time  $t$ , respectively in mg L<sup>-1</sup>,

$V$  is model solution volume in L and

$m$  is the mass of sorbent sample in g.

For description of sorption process in aqueous solution the following pseudo-second order model of the rate is also used,<sup>11</sup> where  $k_2$  is pseudo-second order rate constant, (g mg<sup>-1</sup> min<sup>-1</sup>).

$$\frac{dQ_t}{dt} = k_2 \cdot (Q_{t(e)} - Q_t)^2, \quad (5)$$

The integrated form of the classical rate equation of pseudo-second order model is given by Eqn. (6).

$$Q_t = \frac{t}{\frac{1}{k_2 \cdot Q_{t(e)}^2} + \frac{t}{Q_{t(e)}}} \quad (6)$$

The analysis of primary kinetic curves was conducted using the equation for Boyd-Adamson internal diffusion kinetic model (Eqn. 7),<sup>12</sup>

$$F = \frac{\theta_t}{\theta_\infty} = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D \cdot \pi^2 \cdot n^2 \cdot t}{r^2}\right), \quad (7)$$

where

$\theta_t$  and  $\theta_\infty$  is the degree of sorbent saturation after  $t$  seconds and infinite time, respectively,

$F$  is the degree of equilibrium achievement,

$D$  is diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),

$r$  is sorbent particle radius (mm) and

$n$  is number of integers 1, 2, 3, 4, 5.

Criterion of Fourier is given by Eqn. (8), where  $B$ , the rate constant of diffusion is given by Eqn. (9).

$$\frac{D \cdot \pi^2 \cdot t}{r^2} = Bt, \quad (8)$$

$$B = \frac{D \cdot \pi^2}{r^2}. \quad (9)$$

By substituting the Eqn. (8) into the Eqn. (9) we get Eqn. (10),

$$F = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Bt n^2), \quad (10)$$

where

$Bt$  is the dimensionless parameter, which is the solution of task of diffusion in the solid part.

For experimentally obtained values of  $F$  the appropriate value of  $Bt$  is determined.<sup>13</sup> To confirm the diffusion limiting sorption process the construction of  $Bt$  versus  $t$  and  $-\ln(1-F)$  versus  $t$  are used. The linear dependence  $Bt$  on  $t$  evidences in favor of limiting internal diffusion. Linearity depending  $-\ln(1-F)$  on  $t$  can point to external diffusion mechanism or adsorption kinetics.

If dependence  $Bt = f(t)$  is linear the limiting stage of adsorption treatment is diffusion in sorbent phase. Slope of this line is equal to  $B$ , and then the average diffusion coefficient in the sorbent particle is,  $\text{cm}^2 \text{s}^{-1}$ .

$$D = \frac{B \cdot r^2}{\pi^2}. \quad (11)$$

### Adsorption isotherms models

The adsorption isotherms express the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Several isotherm models have been used to fit to the experimental data and evaluate the isotherm performance for polyphosphate adsorption. Langmuir, Freundlich, Temkin and Dubinin-Radushkevycha isotherms models have been employed in the present study.<sup>14</sup>

Langmuir adsorption isotherm quantitatively describes the formation of adsorbate monolayer on the external adsorbent pores surface. The model assumes equal adsorption energy on the surface of the sorbent. Based on these assumptions, the Langmuir model in the linear form is represented by the eqn. (12),<sup>15</sup> where  $C_{t(e)}$  is equilibrium concentration of surfactant ( $\text{mg L}^{-1}$ ) and  $K_L$  is constant of Langmuir equation ( $\text{L mg}^{-1}$ ).

$$\frac{1}{Q_{t(e)}} = \frac{1}{Q_t} + \frac{1}{Q_t \cdot K_L \cdot C_{t(e)}}, \quad (12)$$

Freundlich adsorption isotherm is used to describe adsorption on heterogeneous surfaces. According to this model, adsorption centers have different energies of interaction. Since active centers with maximum energy are saturated primarily. The linear form of Freundlich model is described by Eqn. (13),<sup>15</sup>

$$\log Q_{t(e)} = \log K_f + \frac{1}{n} \cdot \log C_{t(e)}, \quad (13)$$

where

$K_f$  is Freundlich equilibrium constant ( $\text{mg g}^{-1}$ ) and  $n^{-1}$  is parameter that indicates the intensity of interaction between adsorbent and adsorbate.

Temkin model takes into account the interaction between adsorbent and adsorbate. The model assumes that the heat of molecules adsorption in the layer will decrease linearly, not logarithmic with increasing degree of filling surface. The linear form of Temkin model is given in Eqns. (14) and (15),<sup>15</sup>

$$Q_{t(e)} = B \cdot \ln A_T + B \cdot \ln C_{t(e)}, \quad (14)$$

$$B = \frac{RT}{b_T}, \quad (15)$$

where

$A_T$  is Temkin equilibrium constant ( $\text{L g}^{-1}$ ),  
 $b_T$  is Temkin equations constant ( $\text{L g}^{-1}$ ) and  
 $B$  is constant of adsorption heat ( $\text{J mol}^{-1}$ ).

Dubinin-Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.<sup>9</sup> The model has often successfully fitted high solute activities and the intermediate range of concentrations data.

$$\ln Q_{t(e)} = -\beta \cdot \varepsilon^2 + \ln Q_{t(e)}, \quad (16)$$

Here  $\beta$  is Dubinin-Radushkevich equilibrium constant ( $\text{mol}^2 \text{K}^{-1} \text{J}^{-2}$ ) and  $\varepsilon$  is the Polanyi potential.

This approach was usually applied to distinguish the physical and chemical adsorption of organic pollutants. Its mean free energy per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by Eqn. (17), where  $\beta$  is denoted as the isotherm constant.

$$E = \frac{1}{\sqrt{2\beta}}, \quad (17)$$

Meanwhile, the parameter  $\varepsilon$  can be calculated as:

$$\varepsilon = RT \cdot \ln\left(1 + \frac{1}{C_{t(e)}}\right). \quad (18)$$

The impact of temperature is one of the most important factors that determine the effectiveness of sorption wastewater treatment. Adsorption removal of polyphosphates from aqueous solutions was determined at three temperatures (290, 323, 343 K). Fundamental thermodynamic parameters, like heat of sorption  $\Delta H^0$ , entropy  $\Delta S^0$ , and free energy of activation  $\Delta G^0$ , play an important role in predicting the adsorption behavior because these are strongly dependent on temperature.  $\Delta G^0$  was calculated according to the following equation,<sup>12</sup>

$$\Delta G^0 = -RT \cdot \ln K_D, \quad (19)$$

where

$R$  is the gas constant and

$K_D$  is equilibrium constant at the temperature  $T$ .

The numerical values of the equilibrium constant were calculated from:

$$K_D = \frac{C_{Be}}{C_{Ac}}, \quad (20)$$

where  $C_{Be}$  and  $C_{Ac}$  are the equilibrium concentrations of polyphosphates on adsorbent solid phase and in solution liquid phase, respectively,  $\text{mg L}^{-1}$ .

$\Delta H^0$  and  $\Delta S^0$  were evaluated using Van't Hoff equation as follows

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (23)$$

where,

$R$  is the gas constant ( $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ),

$T$  is solution temperature (K) and

$K_D$  is the distribution coefficient of the surfactant between the adsorbed layer and the solution.

The slope and intercept of the linear plot of  $\ln K_D$  versus  $T^{-1}$  were used to determine the values of  $\Delta H^0$  and  $\Delta S^0$ .

## Results

### Adsorption kinetic

Kinetic dependences of polyphosphates adsorption by minerals (saponite, spondyle clay, palygorskite), magnetite and composites on their base are presented on Figure 1.

### Isotherm data

Adsorption isotherms of tripolyphosphate (a, c, e) and hexametaphosphate (b, d, f) on clay minerals, magnetite and composites based on them are shown in Figure 2.

### Model fitting and kinetic parameters

In order to investigate rate-controlling steps that include mass transport and adsorption processes, kinetic models were used to test the experimental data. Table 1 presents the results of fitting of experimental data with pseudo-first-order, pseudo-second-order and Boyd-Adamson internal diffusion kinetics models using values of  $k_1$ ,  $k_2$ ,  $D$  and correlation coefficient ( $R^2$ ).

### Model fitting and adsorption isotherm parameters

To establish the mechanism of interaction between adsorbate and adsorbent the adsorption isotherms models were applied to obtained experimental data. The parameters of Langmuir, Freundlich, Temkin and Dubinin-Radushkevych adsorption isotherms are summarized in table 2.

### Thermodynamic parameters of adsorption

For determination of nature of polyphosphates sorption removal (physisorption or chemisorption) the thermodynamic patterns were analyzed. Values of thermodynamic parameters ( $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta G^0$ ) obtained at different temperatures during polyphosphate adsorption are given in table 3.

## Discussion

### Adsorption kinetic

According to the kinetic dependencies of polyphosphates removal from aqueous solutions (Figure 1) the equilibrium time was reached in 30 minutes for the magnetic composites MCSp-7 and MCSp-10. The purification of water model solutions of TPP and HMP by using the rest of composite sorbents and clay minerals was lasted for 60 min. Moreover, the percentages of polyphosphates adsorption for magnetic composites were in 1.5-2.0 times higher compared with native natural clays. If using nanosized magnetite as a sorbent the removal of TPP (40 min) was occurred faster compared with HMP (60 min).

### Isotherm data

The maximum sorption capacity of MCSp, MCSd and MCP in the disposal of polyphosphates was in the range of 490-570  $\text{mg TPP g}^{-1}$  and 610-810  $\text{mg HMP g}^{-1}$ , 500-550  $\text{mg TPP g}^{-1}$  and 660-820  $\text{mg HMP g}^{-1}$ , 490-540  $\text{mg TPP g}^{-1}$  and 650-790  $\text{mg HMP g}^{-1}$  respectively (Figure 2). The efficiency of removal of polyphosphates is directly proportional to the magnetite content in the composition of the composites.

The sorption capacities of native saponite, spondyle clay and palygorskite towards polyphosphates, as obtained from the sorption isotherms, are 2-3 times lower as compared with composites on their base.

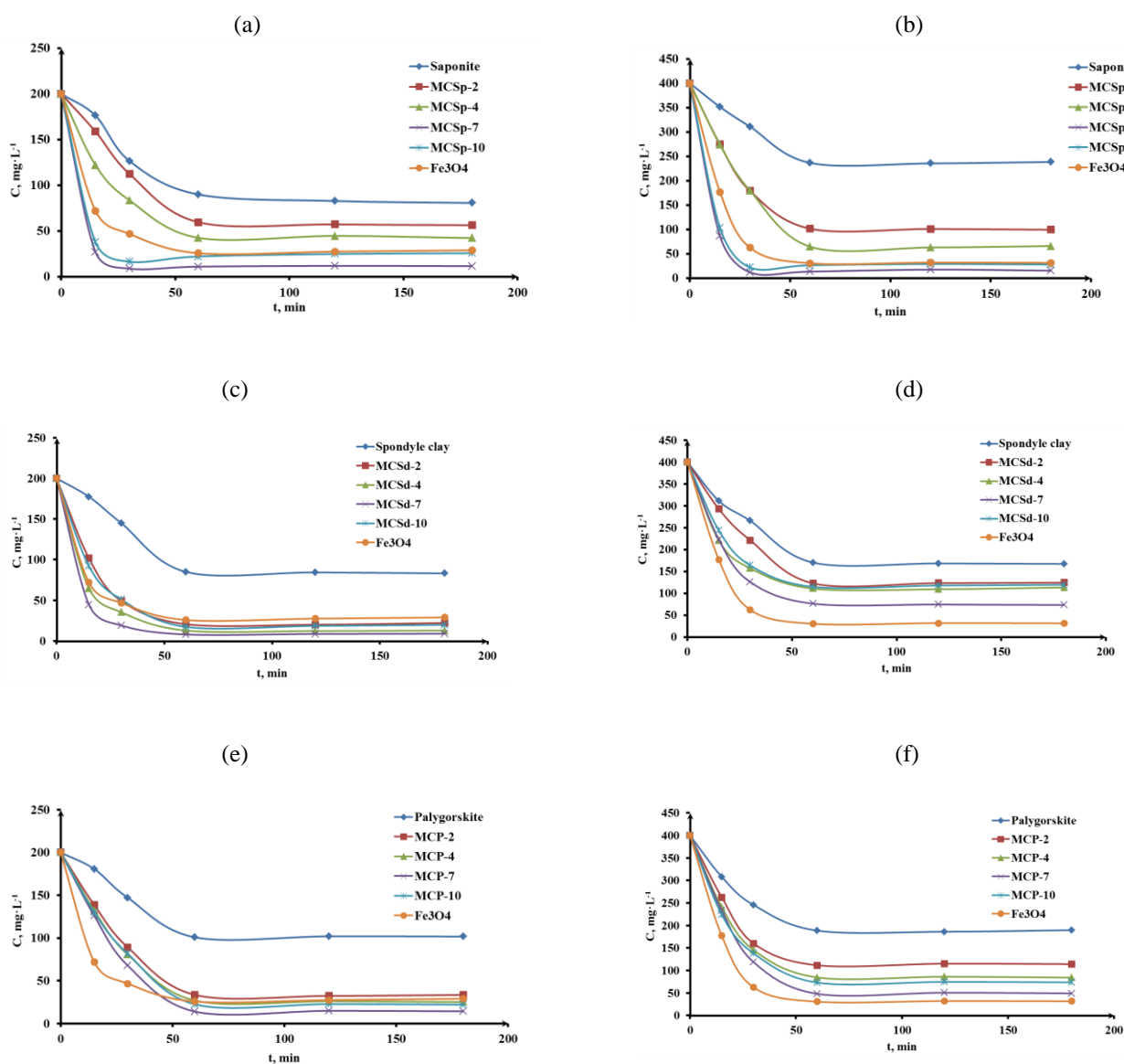
High sorption capacity relative to TPP (770 mg·g<sup>-1</sup>) and HMP (1200 mg·g<sup>-1</sup>) was inherent for nanosized magnetite received in the form of magnetic fluid. A significant magnetite sorption activity is guaranteed within one hour after the synthesis of magnetic fluid. Fe<sub>3</sub>O<sub>4</sub> is nonporous sorbent and the adsorption of pollutants takes place on the surface of its particles. Nanosized magnetite is prone to aggregation and is not stable over time. In forming micro particles due to aggregation the Fe<sub>3</sub>O<sub>4</sub> sorption capacity is reduced by an order. Thus, the nanosized magnetite stabilization on the surface of pores of clay minerals will provide the creation of composite sorbents with high sorption activity.

As can be seen from the figure 2, the highest sorption capacity towards TPP and HMP was achieved using magnetic composites MCSp-7, MCSd-7 and MCP-7, which contain magnetite in an amount of 7 wt. %.

### Adsorption kinetic models

In order to determine and interpret the mechanisms of polyphosphates adsorption processes onto MCSp-7, MCSd-7 and MCP-7 and major parameters governing sorption kinetics were fitted to the pseudo-first-order, pseudo-second-order and Boyd-Adamson internal diffusion kinetics models. The correlation coefficients for pseudo-second-order and kinetic model obtained for all the studied sorbents were relatively high. The  $R^2$  values for the plots of integrated form of rate equations were in the range 0.9874 – 0.9999 (Table 1).

It is clear from the accuracy of the model that the adsorption kinetic of the TPP and HMP onto magnetic composites is described by a pseudo second-order and that this interaction is significant in the rate-controlling step. Based on the rate constants of pseudo-second order model,  $k_2$ , the choice of magnetic composites mineral base was suggested. As follows, the TPP and HMP removal occurred most intense with application of composites based on saponite.

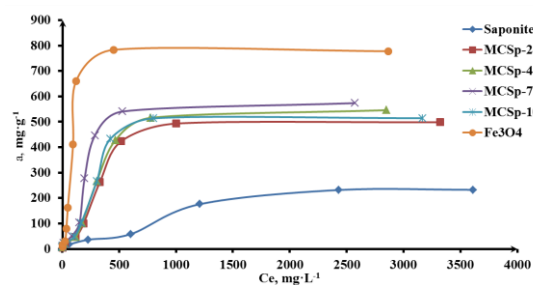


**Figure 1.** Dependences of the residual concentration of TPP (a, c, e) and HMP (b, d, f) of the duration of sorbents contact with water model solutions

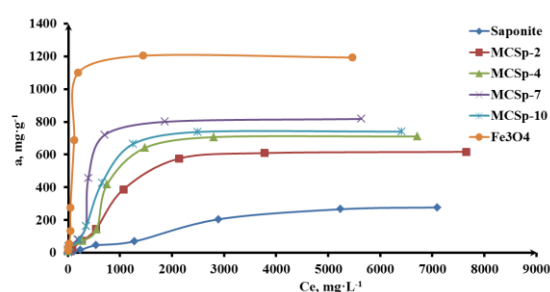


**Table 1.** Kinetic parameters and correlation coefficients of pseudo-first order, pseudo-second order and diffusion model of TPP and HMP adsorption by magnetic mineral sorbents

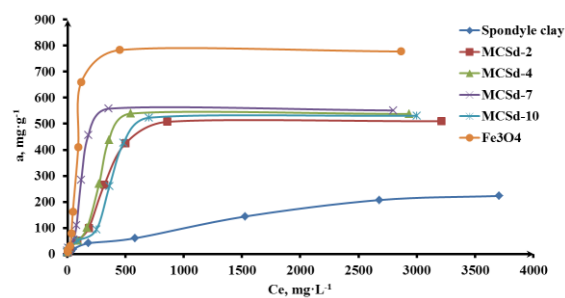
Kinetic model	Pseudo-first order model		Pseudo-second order model		Diffusion model		
	$k_1$	$R^2$	$k_2$	$R^2$	$R^2$	$D \cdot 10^6, \text{cm}^2 \cdot \text{s}^{-1}$	$R^2$
<b>TPP</b>							
Sample of polyphosphates							
MCSp-7	0.0205	0.4245	0.1266	0.9999	0.4245	1.517	0.5345
MCSd-7	0.0532	0.8217	0.0219	0.9997	0.5217	1.270	0.7754
MCP-7	0.1200	0.6312	0.0025	0.9874	0.6312	3.300	0.7199
<b>HMP</b>							
Sample of polyphosphates							
MCSp-7	0.0299	0.3053	0.0175	0.9996	0.3053	1.198	0.5343
MCSd-7	0.1092	0.8725	0.0031	0.9969	0.5725	2.890	0.7153
MCP-7	0.0815	0.9733	0.0029	0.9965	0.7733	1.970	0.8906



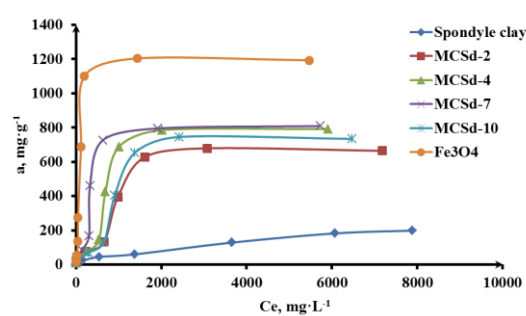
(a)



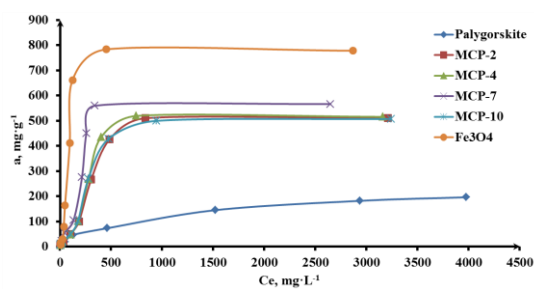
(b)



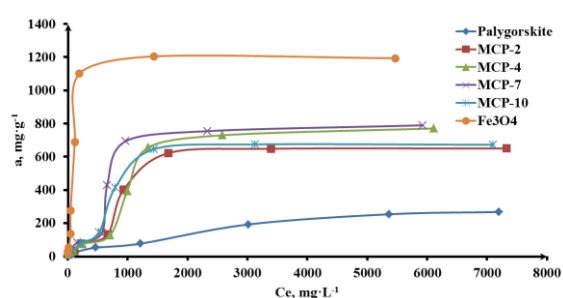
(c)



(d)



(e)



(f)

**Figure 2.** Adsorption isotherm of TPP (a, c, e) and HMP (b, d, f) on sorbents samples

The kinetic data of polyphosphates sorption were analyzed by Boyd-Adamson diffusion kinetics model. As noted in table 1 correlation coefficient of dependence  $-\ln(1-F)=f(t)$  were significantly lower compared to  $R^2$  of  $Bt=f(t)$ . Thereby, the assumption about the possibility of limiting sorption process of purification in the internal diffusion field was not confirmed. The values of diffusion coefficient are found to be on the order of  $10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for all the investigated sorbent samples, so the pore diffusion in this study was not significant.

### Adsorption isotherms models

The adsorption isotherms express the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature.

Several isotherm models as Langmuir, Freundlich, Temkin and Dubnin–Radushkevich adsorption isotherm model have been used to fit to the experimental data and evaluate the isotherm performance for polyphosphate adsorption onto MCSp-7, MCSd-7 and MCP-7.

The conformity of adsorption data (Table 2) to the Langmuir isotherm ( $R^2 \approx 1.00$ ) could be interpreted as a homogeny adsorption process, leading to monolayer binding. So, the relatively uniform energy distribution of active adsorption sites on the pores surface of composites was achieved. The theoretical maximum adsorption capacities of magnetic composites containing magnetite in an amount of 7 wt. % were calculated by Langmuir equation. It was found that calculated adsorption capacities were good agreed with experimentally obtained values.

**Table 2.** Adsorption isotherm parameters and correlation coefficient of TPP and HMP adsorption by MC sorbents

Sample Sorbent	TPP					
	Langmuir isotherm			Freundlich isotherm		
	$R^2$	$K_L, \text{L} \cdot \text{mg}^{-1}$	$Q_{t(e)}, \text{mg} \cdot \text{g}^{-1}$	$R^2$	$K_f, \text{mg} \cdot \text{g}^{-1}$	$n$
MCSp-7	0.9959	0.0070	625.0000	0.9211	2.0674	1.5163
MCSd-7	0.9986	0.0179	555.5556	0.8995	3.1925	1.9212
MCP-7	0.9935	0.0085	588.2352	0.9204	1.8360	1.3763
Sorbent	Temkin isotherm			Dubinin-Radushkevich isotherm		
	$R^2$	$A_T, \text{L} \cdot \text{g}^{-1}$	$B, \text{J} \cdot \text{mol}^{-1}$	$R^2$	$E, \text{kJ} \cdot \text{mol}^{-1}$	$Q_{t(e)}, \text{mg} \cdot \text{g}^{-1}$
	MCSp-7	0.7072	0.2528	78.6020	0.3693	0.7906
MCSd-7	0.6648	1.2674	60.9900	0.5208	1.5811	156.1004
MCP-7	0.7366	0.1871	88.7370	0.3835	0.5000	131.0659
Sample Sorbent	HMP					
	Langmuir isotherm			Freundlich isotherm		
	$R^2$	$K_L, \text{L} \cdot \text{mg}^{-1}$	$Q_{t(e)}, \text{mg} \cdot \text{g}^{-1}$	$R^2$	$K_f, \text{mg} \cdot \text{g}^{-1}$	$n$
MCSp-7	0.9981	0.0049	733.3333	0.9273	2.4051	1.6906
MCSd-7	0.9989	0.0063	814.3011	0.9277	2.2235	1.6000
MCP-7	0.9938	0.0025	678.1200	0.9444	1.5300	1.4100
Sorbent	Temkin isotherm			Dubinin-Radushkevich isotherm		
	$R^2$	$A_T, \text{L} \cdot \text{g}^{-1}$	$B, \text{J} \cdot \text{mol}^{-1}$	$R^2$	$E, \text{kJ} \cdot \text{mol}^{-1}$	$Q_{t(e)}, \text{mg} \cdot \text{g}^{-1}$
	MCSp-7	0.7337	0.1707	108.96	0.4796	0.4082
MCSd-7	0.7576	0.1362	116.24	0.3851	0.4082	205.5933
MCP-7	0.7604	0.0547	126.17	0.4502	0.1581	209.1391

The result shows that the value of Freundlich adsorption isotherm parameter  $n$  is greater than unity for all analyzed sorbents indicating that the polyphosphates is favorably adsorbed on MC samples. The magnitude of Freundlich constant indicates easy uptake of TPP and HMP from aqueous solution.

### Adsorption thermodynamics parameters

The values of thermodynamic parameters, i.e.  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ , are used to determine the spontaneous nature of the processes and provide essential information evaluating adsorbent practicability.

**Table 3.** Thermodynamic parameters for TPP and HMP adsorption by magnetic mineral sorbents

Sorbent	T, K	$\Delta G^0$ , J·mol <sup>-1</sup>	$\Delta H^0$ , J·mol <sup>-1</sup>	$\Delta S^0$ , J·mol <sup>-1</sup> ·K <sup>-1</sup>
<b>Sample</b>		<b>TPP</b>		
MCSp-7	293	-4787.0	-32110.7	-93.3
	323	-1989.4		
	343	-124.3		
MCSd-7	293	-6575.4	-32021.8	-86.8
	323	-3969.9		
	343	-2233.0		
MCP-7	293	-5176.3	-34740.0	-100.9
	323	-2149.3		
	343	-131.3		
<b>Sample</b>		<b>HMP</b>		
MCSp-7	293	-3889.7	-38247.6	-117.3
	323	-371.9		
	343	1973.4		
MCSd-7	293	-4301.9	-27713.0	-79.9
	323	-1904.8		
	343	-306.8		
MCP-7	293	-7241.7	-38492.8	-106.7
	323	-4041.9		
	343	-1908.8		

The values of  $\Delta G^0$  obtained at all temperatures were negative, indicating that the adsorption of polyphosphates onto MCSp-7, MCSd-7 and MCP-7 is a spontaneous and favorable process in nature.

The calculated activation energy of anionic SAs sorption by magnetic composites was approximately 5 kJ·mol<sup>-1</sup>, which confirmed the physical nature of the process. Furthermore, activation energy values lower than 40 kJ·mol<sup>-1</sup> indicated diffusion control processes.<sup>16</sup>

The negative value of  $\Delta H^0$  was confirmed the exothermic nature of TPP and HMP adsorption. The increasing  $\Delta G^0$  values with increasing temperature testified that the adsorption of SAs becomes unfavorable at higher temperature because the process does not require energy to take place. The negative value of  $\Delta S^0$  corresponds to decreasing of degree of freedom in the system as a result of adsorption of the TPP and HMP molecules.

It can be concluded that the adsorption mechanism is dominated by physic sorption, in keeping with the finding that the adsorption is rapid and more spontaneous at the temperature corresponding to the normal conditions of the experiment.

## Conclusions

Effective magnetic composite sorbents MCSp, MCSd and MCP with a content of magnetite from 2 to 10 % wt. based on cheap mineral raw material have been prepared. The sorption capacities of the resultant magnetic composites containing magnetite 4-7 %wt. towards TPP and HMP were

1.5-2.0 times higher compared with native natural clays. In our opinion, this effect is caused by changes in the porous structure of natural clay minerals and stabilization of magnetite nanoparticles on pores surface.

The adsorption kinetics of polyphosphates removal by magnetic composites can be predicted by pseudo-second-order kinetic model. The values of diffusion coefficient are found to be on the order of 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> for all the investigated sorbent samples, so the pore diffusion in this study was not significant. Sorption isotherms were best adjusted to the Langmuir model. This means that magnetic composite sorbents have a homogeneous surface. Thermodynamic studies showed that polyphosphates adsorption was spontaneous and endothermic nature. Estimated thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$  i  $\Delta S^0$ ) of TPP and HMP sorption by magnetic mineral sorbents indicated that the sorption process was physical.

As a result, cheap magnetic sorbents based on natural clays and magnetite for polyphosphates removal from wastewater were obtained. Magnetic composite sorbents were successfully precipitated from purified water by magnetic separation that guaranteed the elimination of risk of secondary water pollution. The results of the present investigation indicated that effective and low-cost magnetic composite could be employed as an alternative to commercial adsorbents for the removal of polyphosphates from water bodies.

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