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Removal of 2,4-Dichlorophenoxyacetic Acid Using $Fe(OH)_3$ Based Complex Adsorbent

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The adsorbents based on $Fe(OH)_3$ containing SiO_2 and $Fe^{(0)}$ powders (denoted 3TP) were prepared and used for removal of 2,4-dichlorophenoxyacetic acid from water. The characteristics of this adsorbents were determined and indicated that the presence of SiO_2 and $Fe^{(0)}$ powders can enhance the amorphous structure of adsorbents, desired for the adsorption. The adsorption of 2,4-dichlorophenoxyacetic acid onto adsorbents was studied. The adsorption process occurs predominantly *via* chemisorptions of 2,4-dichlorophenoxyacetic acid onto adsorbents. The adsorption characteristics including kinetic thermodynamic parameters were examined. The experimental data shown that this is an endothermic, spontaneous adsorption process.

Key Words: $Fe(OH)_3$, Absorption, 2,4-Dichlorophenoxyacetic acid.

INTRODUCTION

The herbicide 2,4-dichlorophenoxyacetic acid with molecular formula $C_8H_6O_3Cl_2$ and mole mass of 221.04 g/mol has been widely applied to control broad-leaved weeds in farming. However, 2,4-dichlorophenoxyacetic acid is considered as moderately toxic and its allowable concentration is 100 ppb in drinking water. The International Agency for Research on Cancer (IARC) concluded that the phenoxy acid herbicides including 2,4-dichlorophenoxyacetic acid, 2-methyl-4-cholorophenoxy acid, 2,4,5-tricholorophenoxyacetic acid as a group were classified as a class 2B carcinogen-possibly carcinogenic to humans. On the other hand, 2,4-dichlorophenoxyacetic acid is a poorly biodegradable chemical that may persist for long time in the soil and groundwater. In Vietnam war, the herbicide agent orange contained 2,4-dichlorophenoxyacetic acid has been used extensively[1]. The 2,4-dichlorophenoxyacetic acid concentrations in the soils in some zones are much higher than allowable concentration. Based on these reasons many technologies have been developed for the removal of 2,4-dichlorophenoxyacetic acid from water, including photo catalytic degradation, ultrasound with photo-Fenton treatment, advanced oxidation processes, aerobic degradation, ozonation and adsorption[2-5]. In this article an adsorbent used for the removal of 2,4-dichlorophenoxyacetic acid from water based on the new complex adsorbent containing $Fe(OH)_3$, SiO_2 and $Fe^{(0)}$ is presented. The study goal is focused on the main factories such as effect of contact, initial concentration of 2,4-dichlorophenoxyacetic acid, temperature solution pH influencing on adsorption capacity of this new complex adsorbent. Besides, adsorption kinetic modeling, adsorption isotherm modeling, adsorption thermodynamics of this adsorption process would be also mentioned.

2,4-Dichlorophenoxyacetic acid is a member of the phenoxy family of herbicide, which includes: 2,4,5- Tricholorophenoxyacetic acid (2,4,5-T); 2-methyl-4-cholorophenoxy acid (MCPA); 2-(2-methyl-4-chlorophenoxy) propionic acids (MCPP), 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP); 2,4-dichlorophenoxybutyric acid (2,4-DB). 2,4-Dichlorophenoxyacetic acid abbreviated 1,4-D corresponding the molar formula $Cl_2C_6H_3OCH_2COOH$, with the following structure (Fig. 1).

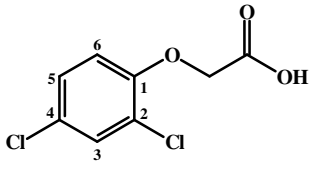

Fig. 1. Molecular structure of 2,4-dichlorophenoxyacetic acid

2,4-Dichlorophenoxyacetic acid is a yellow crystals, melting at 124 ºC, boiling at 160 ºC, having the solubility of 900 mg/L in water. 2,4-Dichlorophenoxyacetic acid is an acid with pK_a

= 2.64. 2,4-Dichlorophenoxyacetic acid is manufactured from chloroacetic acid and 2,4-dichlorophenol, which is itself produced by chlorination of phenol. Alternatively, it may be produced by the chlorination of phenoxyacetic acid. 2,4-Dichlorophenoxyacetic acid is a chlorinated organic compound persisted by environment. The important chemical reaction of 2,4-dichlorophenoxyacetic acid includes pyrolysis converting various amine salts of 2,4-dichlorophenoxyacetic acid to the corresponding amides. Pyrolysis of 2,4-dichlorophenoxyacetic acid and its derivatives is likely to produce certain chlorodibenzodioxin (CDD) isomers. Besides, 2,4-dichlorophenoxyacetic acid is readily photodegraded.

EXPERIMENTAL

2,4-Dichlorophenoxyacetic acid with 98 % purity obtained from a China company. The stock solution of 2,4-dichlorophenoxyacetic acid was prepared by accurately weighing to obtain 100 mg/L-concentration in deionization water. The new complex adsorbent based on $Fe(OH)_3$, SiO_2 and Fe powders were prepared in the laboratory and its characterizations were measured by the suitable instruments. For synthesis of the new complex adsorbent, $FeCl_3$ solution 0.1 M from $FeCl_3.6H_2O$ (PA) and NH_4OH (25 %, PA), sodium silicate solution (Na_2O/SiO_2 = 11.02 ± 0.03 %), $Fe^{(0)}$ powders were used. The synthetic adsorbent is procedure was implemented basing on the method of Schwertmann and Cornell. A certain amount of solution of sodium silicate (200 g/L) premixed with ammoniacal solution was added to the reaction batch containing one liter of Fe(III)-solution (27g $FeCl_36H_2O$/L). The obtained mixture was vigorously stirred for 1 h to precipitate gel-like $Fe^{(III)}$-$Si^{(IV)}$ complexes and then allowed for to age for few hours. The precipitated slurry was washed and dewatered by decantation with deionization water until all the Cl^- ion amounts would be removed. Other obtained precipitate slurry was mixtured with a certain amount of iron powders to form the three-component adsorbent ($Fe^{(0)}$-$Fe^{(III)}$-$Si^{(IV)}$). For the both cases, the dewatered solids were dried at temperature between 120 and 250 ºC for the several hours. In this study, three types of the adsorbents based on FeOOH were prepared such as: FeOOH denoted 1PT; FeOOH with 10 % of SiO_2 denoted 2TP10 and FeOOH with10 % of SiO_2 and 10 % of $Fe^{(0)}$-powders denoted 3TP10. The characterization of the prepared adsorbents were determined by X-ray, SEM, BET methods.

Bath adsorption studies: Adsorption tests were performed in 250-mL Erlenmeyer flasks to evaluate the adsorption capacity of adsorbents. 5 g/L of adsorbent sample was loaded in the flask containing 200 mL of 2,4- Dichlorophenoxyl (2.4-D) solution with a different concentrations from 69 mg/L to 180.5 mg/L. The sample pH was then adjusted and measured. The flask with the tested sample was placed on a shaker with 180 rpm for 5 h. After adsorption period, the sample was filtered by 0.45-µm membrane filter and analyzed for remained 2,4-dichlorophenoxyacetic acid. The adsorption amount of 2,4-dichlorophenoxyacetic acid against time, the removal percentage of 2,4-dichlorophenoxyacetic acid, the adsorption capacity at equilibrium (q_e) were calculated by the expressions:

$$q_t = \frac{(C_0 - C_t)V}{G_a}, mg/g, \quad R = \frac{C_0 - C_t}{C_0} \times 100,$$

$$q_e = \frac{(C_0 - C_e)}{G_a} V, mg/g$$

Here, C_0 (mg/L) and C_t (mg/L) are liquid phase concentrations of 2,4-dichlorophenoxyacetic acid at the initial and time t, respectively; V(L) the sample volume; G_a the dried complex of adsorbent used; C_e (mg/L) is 2,4-dichlorophenoxyacetic acid concentration at the equilibrium.

The change of 2,4-dichlorophenoxyacetic acid concentrations in the studied sample were measured by HPLC-equipment (HPLC Aligent, 1100, detector diode array USA) with the mobile phase of acetonitrile/water of 50/50.

RESULTS AND DISCUSSION

Characterization of the complex adsorbent based on $Fe(OH)_3$, SiO_2, $Fe^{(0)}$ powders: The surface morphology of the $Fe(OH)_3$ adsorbent containing SiO_2 (10 % w/w) and $Fe^{(0)}$ powders (10 % w/w) was measured using X-ray (D8 Advance Bruker AXS presented in Fig. 2. The spectra has shown that the obtained adsorbent is characterized by amorphous structure or poorly crystalline. Based on practice, the crystalline form of an adsorbent like goethite is not desired, because it has much less surface than amorphous form.

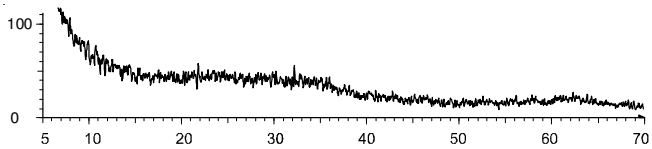

Fig. 2. X-ray spectra of the adsorbent of $Fe(OH)_3$, SiO_2 and $Fe^{(0)}$ powders

The surface morphology of the adsorbent of $Fe(OH)_3$, SiO_2 and $Fe^{(0)}$ powders was examined by SEM equipment compared with the adsorbents containing only $Fe(OH)_3$ and $Fe(OH)_3$ with SiO_2 (10 %) presented in Fig. 3 to evaluate the role of presented components in $Fe(OH)_3$ + 10 % SiO_2 + 10 % $Fe^{(0)}$ powders.

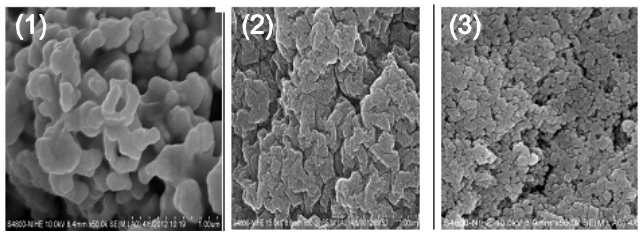

Fig. 3. SEM spectra of the adsorbents: 1 TP (1); 2 TP (2); 3 TP (3)

This SEM spectra shown that with the addition of SiO_2 and of $Fe^{(0)}$ to $Fe(OH)_3$ the surface characteristics of the complex adsorbents changed and gradually became to more poorly crystalline. This phenomena also coincides with a similar comment in the work[6].

Physical parameters of the complex adsorbents: The physical parameters such as specific surface area, porous volume, average diameters of the pores of adsorbents were

determined by BET method suggested by Stephen Brunauer, P.H. Emmet and Edward Teller. The obtained results is shown in Fig. 4 and Table-1. Fig. 3. SEM spectra of (1): $Fe(OH)_3$ (1PT); (2): $Fe(OH)_3$ + 10 % SiO_2(2PT10); (3): $Fe(OH)_3$ + 10 % SiO_2 + 10 % $Fe^{(0)}$ (3PT10).

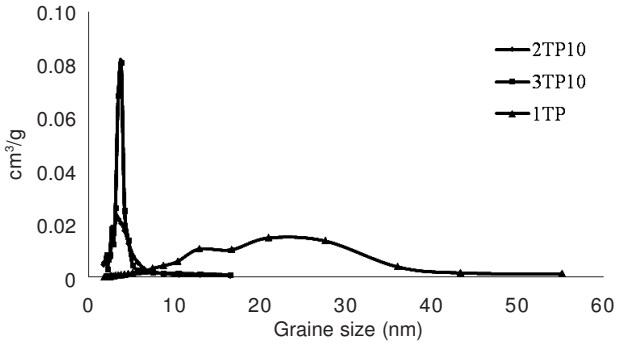

Fig. 4. Average diameters of adsorbents

The obtained experimental data have once again indicated that the presence of the addition of SiO_2 and $Fe^{(0)}$ powder to $Fe(OH)_3$ has caused enhancing significantly BET surface, porous volume and reducing average diameters of pores. This conclusion is consistent with the obtained SEM images (Fig. 3). The adsorbent 3 TP was selected for the study of 2,4-dichlorophenoxyacetic acid adsorption.

Adsorption characteristics of 2,4-dichlorophenoxyacetic acid on the complex adsorbent (3PT): The adsorption properties of an adsorbent are expressed through the adsorption capacity and the factories influencing on the adsorption including contact time, solution pH, temperature, initial concentration and adsorption kinetics, thermodynamics. These properties are very important for designing treatment system of 2,4-dichlorophenoxyacetic acid contaminated wastewater that are also studied in detail.

TABLE-1
PHYSICAL CHARACTERISTICS OF ADSORBENTS

Adsorbent	BET surface (m^2/g)	Porous volume (cm^3/g)	Average diameter of pors (nm)
1 TP	26	0,092	14,2
2 TP	270	0,227	3,0
3 TP	350	0,569	3,5

Influence of contact time on the adsorption equilibrium: The effect contact time on adsorption equilibrium is shown in the Fig. 5.

The obtained experimental data have shown that the adsorption equilibrium of systems was done during the contact times being 200-300 min. At 300 min, the removal percentages of 2,4-dichlorophenoxyacetic acid were 97.4 % (series 1), 87.4 % (series 2) and 82.5 % (series 3). The adsorption equilibrium process taking place relatively slowly indicates that the adsorption onto the complex adsorbent may occurs *via* physicochemi sorption of 2,4-dichlorophenoxyacetic acid.

Effect of temperature on 2,4D adsorption: The temperatures of 25 ºC, 35 ºC and 40 ºC were chosen for study of their influence on the adsorption of 2,4-dichlorophenoxyacetic acid. The experimental data were shown in the Table-2.

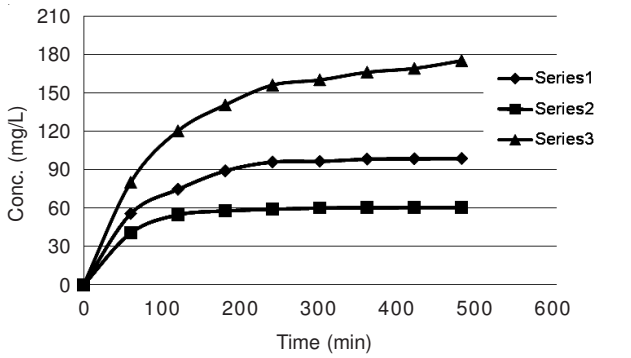

Fig. 5. Effect of contact times on 2,4-dichlorophenoxyacetic acid adsorption, system containing 5 g/L of adsorbent (3PT), pH = 4.5, temperature of 25 ºC, concentrations of 2,4-dichlorophenoxyacetic acid 112 mg/L (series 1) 69.0 mg/L (series 2); 185.5 mg/L (series 3)

TABLE-2
EFFECT OF TEMPERATURE ON THE REMOVAL PERCENTS OF 2,4-DICHLOROPHENOXYACETIC ACID

Samples	Components of solutions	pH	Temp. (ºC)	R (%)
M1	3TP 5 mg/L, 2,4-D 112 mg/L	4.5	25	87.0
M2	3TP 5 mg/L, 2,4-D 112 mg/L	4.5	35	89. 6
M3	3TP 5 mg/L, 2,4-D 112 mg/L	4.5	40	91.5

The data have indicated that with increasing temperature from 25 to 40 ºC the removal percentages of 2,4-dichlorophenoxyacetic acid increase from 82.5 to 91.5 %. The increase of removal percentages of 2,4-dichlorophenoxyacetic acid in the samples demonstrated again the adsorption occurring predominantly *via* chemisorptions and it is an endothermic process.

Effect of pH on 2,4-dichlorophenoxyacetic acid adsorption: The solution pHs of 4.5; 7.0; 9.0 were selected to indicate the influence of pH on removal percentages of 2,4-dichlorophenoxyacetic acid. The experimental data were presented in Table-3.

TABLE-3
EFFECT OF SOLUTION- pH ON 2,4 DICHLORO-PHENOXYACETIC ACID

Samples	Components of solutions	PH	Temp.	R (%)
M1	3TP 5 mg/L, 2,4-D 112 mg/L	4.5	25 ºC	82.5
M2	3TP 5 mg/L, 2,4-D 112 mg/L	7.0	25 ºC	67.9
M3	3TP 5 mg/L, 2,4-D 112 mg/L	9.0	25 ºC	56.2

With the solution pHs increasing the removal percentages of 2,4-dichlorophenoxyacetic acid reduce from 82.5 % (pH = 4.5) to 67.9 % (pH = 7.0) and 56.2 % (pH = 9.0). The solution pH influences the properties of both adsorbate and adsorbent. Due to the pK_a of 2,4-dichlorophenoxyacetic acid being 2.64, in the studied solution pH (> pK_a) 2,4-dichlorophenoxyacetic acid molecules are dissociated and a greater percentages of them are in the ionized form, $Cl_2C_6H_3OCH_2COO^-$. At the high solution pH (pH = 9) the surface of the complex adsorbents become more negatively charged, so the removal of 2,4-dichlorophenoxyacetic acid reduced. At the low solution pH (pH = 4.5), the removal percentages of 2,4-dichlorophenoxyacetic acid increased may be due to the two reasons that will be discussed in the following item.

Role of $Fe^{(0)}$ powders in the complex adsorbents: The presence of $Fe^{(0)}$ powders in the complex adsorbents may cause

the their adsorption capacity from solutions, mainly in pH acid range. In solution there is a corrosion of iron powders by the reactions:

$$Fe^{(0)} + 2H^+ \rightarrow Fe^{2+} + H_2$$

$$Fe^{(0)} + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2.$$

The presence of Fe^{2+} in solution after the long contact time causes precipitation of $Fe(OH)_2$ and $Fe(OH)_3$ that can enhance the adsorption of 2,4-dichlorophenoxyacetic acid from solution.

Besides, maybe there is reaction between iron powders and 2,4-dichlorophenoxyacetic acid as follows:

$$Cl_2C_6H_3OCH_2COO^- + H^+ + Fe^{(0)} \rightarrow H\ (Cal)C_6H_3OCH_2COO^- + Fe^{2+} + Cl^-$$

Molecules in the form of $H\ (Cal)C_6H_3OCH_2COO^-$ (dechlorinated forms) due to the reduced molecule size are more easily adsorbed than original form.

Effect of initial concentration of 2,4-dichlorophenoxyacetic acid on adsorption: As given in the Fig. 4. The initial concentrations of 2,4-dichlorophenoxyacetic acid changed caused increasing the adsorption rate, equilibrium adsorption capacity and reducing the removal percentages of 2,4-dichlorophenoxyacetic acid. The obtained data were consistent with theory of the heterogeneous adsorption process. The increase in equilibrium adsorption capacity may be due to the utilization of all available active sites for adsorption. At higher 2,4-dichlorophenoxyacetic acid concentration there are a large mass transfer driving force and increased number of collision between 2,4-dichlorophenoxyacetic acid molecules and adsorbent as suggested[7].

Adsorption isotherm modeling: The $Fe(OH)_3$ adsorbent containing SiO_2 and $Fe^{(0)}$ is a mixed adsorbent and in amorphous form. The surface of this adsorbent is heterogeneous that it is in favour of the assumption of multilayer formation of adsorption. For this reason, the Feundlich empirical equation was selected for examining adsorption isotherm. The Freundlich equation is as follows:

$$q_e = K_F C_e^{1/n}$$

Here q_e is equilibrium adsorption capacity, mg/g, K_F (mg/g) and n are Freundlich constants related. When C_e concentration is 1 mM/L, the K_K value is q_e, equilibrium adsorption capacity of an adsorbent. The values of K_F, n must be determined by experiment based on the equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

The plotting $\log q_e$ *vs.* $\log C_e$ (Fig. 6) allows determining K_F and 1/n.

From this plot, the parameters of K_F and n have been determined and are 12. 02 and 3.47 respectively. The experiments were repeated with the same amounts of adsorbents and 2,4-dichlorophenoxyacetic acid but at 35 and 40 ºC. The equations obtained were fitted with Freundlich expression, are $\log q_e = 0.33x + 1.18$ and $\log q_e = 0.36x + 1.21$, respectively. The K_F and n values at the different temperatures are given in Table-4.

The obtained experimental data showed that the adsorption process of 2,4-dichlorophenoxyacetic acid onto the complex adsorbent (3 TP) suggested is according to the Freundlich isotherm model.

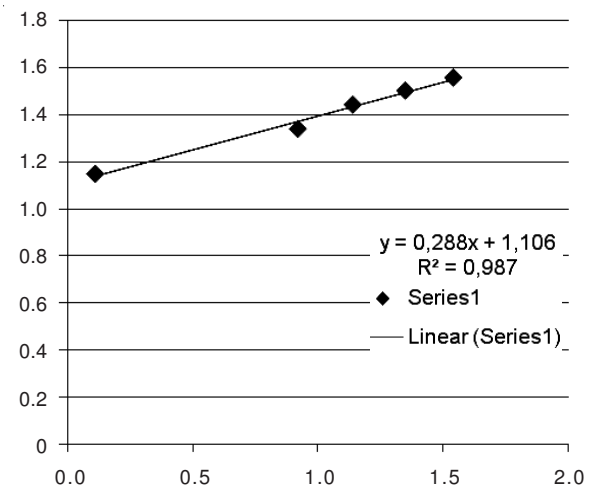

Fig. 6. Adsorption isotherm of 2,4-dichlorophenoxyacetic acid onto 3 TP, at 30 ºC

TABLE-4
FREUNDLICH ISOTHERM MODEL PARAMETERS

Parameters	30 ºC	35 ºC	40 ºC
K_F	12.02	15.13	16.21
n	3.5	3.0	2.77

Adsorption kinetic modeling: The dependence of the adsorption capacity of 2,4-dichlorophenoxyacetic acid on the time was presented in Fig. 7. The adsorption kinetic curve of this adsolute may be described by pseudo first-order and pseudo second-order expressions including:

The pseudo first-order expression: $\frac{dq}{dt} = k_{1ad}(q_{eq} - q)$, or in the integrated form is $\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1ad}}{2.303}t$.

The pseudo second-order expression: $\frac{dq}{dt} = k_{2ad}(q_{eq} - q)^2$, or in the integrated form is $\frac{t}{q} = \frac{1}{k_{2ad}q_{eq}^2} + \frac{1}{q_{eq}}t$.

Here, q_{eq}, q are denoted for adsorption capacity of 2,4-dichlorophenoxyacetic acid at the time $t = \infty$ and time t, respectively.

k_{1ad}, k_{2ad} are denoted for the rate constants corresponding to pseudo first-order and pseudo second-order reaction kinetics, respectively.

The values of these parameters may be determined by plots based on the experimental data.

Based on the view points of adsorption on solid phase, the pseudo first-order kinetic model is generally applicable over the initial 20-30 min of the sorption process. By this reason, the pseudo second-order kinetic model was selected to study the adsorption process of 2,4-dichlorophenoxyacetic acid on the complex adsorbent. The experimental data were presented in Fig. 7. The obtained data shown that the second-order kinetics were applicable for the adsorption process of 2,4-dichlorophenoxyacetic acid on the complex adsorbent. Based on these plots, the adsorption constants of k_2 (g/mg min) were determined to equal 5.3×10^{-4}; 5.1×10^{-4} and 5.8×10^{-4}, respectively. The adsorption rate constants with a small change when changing the initial concentrations of 2,4-dichlorophenoxy-

acetic acid have demonstrated the hypothesis of pseudo-second-order kinetic model to be correct given (Fig. 7).

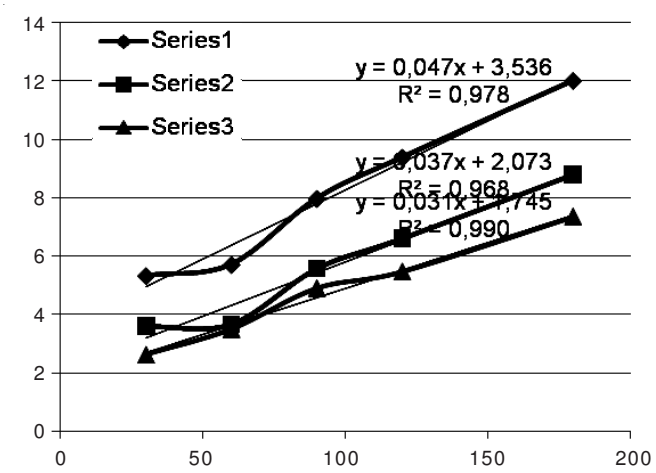

Fig. 7. Plots of pseudo-second-order kinetic models, 2,4-dichlorophenoxyacetic acid concentrations are 1159.0 (series3); 128.5 (series 2) and 112 (series 1) mg/L, respectively.

Determination of activation energy: The adsorption process of 2,4-dichlorophenoxyacetic acid onto complex adsorbent (3 TP) take place under pseudo-second-order model, so its rate constants k_2 let's determine the activation energy by expression:

$$k_2 = A\exp(-\frac{E_a}{RT}), \quad \ln k_2 = \ln A - \frac{E_a}{RT}$$

where, A: constant, R (8.314 J/mol K): the gas constant; T: the absolute temperature. By the plot of $\ln k_2$ *versus* 1/T the activation energy E_a were determined listed in Table-5.

TABLE-5
THERMODYNAMIC PARAMETERS
OF ADSORPTION PROCESS

Parameters	69 mg/L	112 mg/L	128.5 mg/L
K_2	5.310^{-4}	5.810^{-4}	6.210^{-4}
Ea (kJ/mol)	11.63	12.34	11.92

Obtained E_a values indicated that adsorption process corresponds to physico-chemisorptions way[8].

Determination of thermodynamic parameters: The thermodynamic parameters such as standard free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) can be determined by experimental data to elucidate the adsorption process based on the following equation:

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

The K_c values were determined based on the expression as follows:

$$K_C = \frac{C_{ep}}{C_e}$$

where, C_{eq}, C_e are concentrations of 2,4-dichlorophenoxyacetic acid (mg/L) on the adsorbents and in solutions at equilibrium times. By obtained experimental data the equation of $\ln K_c$ has found out: $\ln K_c$ = -1804 X + 2213. Based on this equation the values of ΔH^o, ΔS^o and ΔG^o, are -14.99 kJ/mol; 0.018 kJ/mol.K and -9.52 kJ, respectively. The obtained experimental thermodynamic parameters have shown that adsorption process of 2,4-dichlorophenoxyacetic acid onto the complex adsorbents (3TP) corrsponds to spontaneous and endothermic process. This process is consistent with the case of 2,4-dichlorophenoxyacetic acid adsorption on activated cacbon powders[9]. This results may demonstrate the increase of the adsorption rate of 2,4-dichlorophenoxyacetic acid with temperature increased.

Conclusion

The adsorbents based on $Fe(OH)_3$ containing SiO_2 and $Fe^{(0)}$ powders (denoted 3TP) were prepared and used for removal of 2,4-dichlorophenoxyacetic acid from water. The characteristics of this adsorbents were determined and indicated that the presence of SiO_2 and $Fe^{(0)}$ powders can enhance the amorphous structure of adsorbents, desired for the adsorption. The adsorption of 2,4-dichlorophenoxyacetic acid onto adsorbents (3TP) was studied. The adsorption process occurs predominantly *via* chemisorptions of 2,4-dichlorophenoxyacetic acid onto adsorbents. The adsorption characteristics including kinetic thermodynamic parameters were examined. The experimental data shown that this is an endothermic, spontaneous adsorption process.

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