Investigation of sorption mechanism of methylene blue, congo red and tannic acid from aqueous solutions onto magnetic composite sorbent obtained from alkaline pretreated spent coffee grounds

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Abstract. In this article, a novel magnetic composite material obtained from alkaline pretreated spent coffee grounds was used for investigating of the sorption mechanism of methylene blue, congo red and tannic acid from aqueous solutions. In order to clarify mechanisms were analyzed the adsorption kinetics models (external and internal diffusion; chemical kinetics (pseudo-first order, pseudo-second order); intraparticle diffusion) and the adsorption thermodynamics. The results showed that the sorption of all studied sorbates was controlled by a mixed diffusion model and a pseudo-second order and diffusion rate revealed three stage of the mass transfer. The adsorption process of methylene blue, congo red and tannic acid onto $Fe_3O_4/PVA/APSCGs$ sorbent was spontaneous and endothermic. Based on the results, it was concluded that the mechanism for removal of the studied sorbates by adsorption onto $Fe_3O_4/PVA/APSCGs$ sorbent may be assumed both physisorption and chemisorption.

1 Introduction

Many organic compounds like dyestuffs and aromatic compounds are commonly found in textile, paper, leather, plastics, food, cosmetics, and other industries. The toxic effects of these organic contaminants on human health, and the environment requires their efficient removal from contaminated water, and this topic becomes environmentally important [1].

Methylene blue (MB) is a cationic dye. It is found in almost textile for coloring. MB can cause toxicities for animals and humans, for example: if ingested, then MB causes convulsions, dyspnea, irritation to the skin, vomiting, and diarrhea [2].

Congo red (CR) is an anionic dye. It is found in the textile, paper, printing, leather industries, etc. It is a skin, eye, gastrointestinal, and respiratory irritant [3].

Tannic acid (TA) is a natural phenolic compound. It is found in most surface water, drinking water, and wastewater from plant medicine, paper and leather industries. TA has toxicity to aquatic organisms, such as algae, phytoplankton, fish, and invertebrates [4].

Recently, in order to solve technical problems related to the separation and regeneration of sorbents after adsorption process, various methods have been used like precipitation, coagulation, filtration or magnetic separation [5]. Particularly, magnetic separation technique is an effective method for separation of samples after adsorption using an external magnetic field [6]. To improve the potential application of magnetic separation techniques in the environment, new magnetic composite materials have to be developed based on the low-cost sorbents, in there, spent coffee grounds (SCGs) are a solid waste that is interested because the approach reduces the environmental and financial costs of disposal [7].

According to data publication, the magnetic composite sorbent obtained from spent coffee grounds (SCGs) has a high adsorption capacity towards organic dyes. Zuorro et al. [8] studied using magnetic coffee silverskin for methylene blue adsorption from aqueous solutions with a maximum adsorption capacity of 556 mg/g. Safarik et al. [9] studied magnetic coffee grounds for dyes removal (acridine orange, crystal violet, malachite green, Congo red, Bismarck brown Y, and safranin O) and obtained the adsorption capacities from 9.34 to 73.4 mg/g. Safarik et al. [10] studied magnetically responsive composite materials from coffee grounds for Bismarck brown Y and safranin O removal, the adsorption capacity reaching 49.3 and 146.6 mg/g, respectively.

However, there is still no study devoted to the sorption mechanism of pollutants from aqueous solutions onto this magnetic composite sorbent. The purpose of this article was to study the sorption mechanism of organic dyes (methylene blue, congo red) and aromatic compounds (tannic acid) onto magnetic composite sorbents based on alkaline pretreated spent coffee grounds.

2 Experimental

Materials. SCGs were collected after brewing of Vietnamese commercial milled Robusta coffee and then

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the samples were washed with distilled water to remove dirt and color, and dried at 105 °C for 5 hours in a convection oven. The chemicals for the preparation of magnetite (Fe_3O_4) particles: $FeCl_3.6H_2O$, Na_2SO_3, NH_4OH 25%, Polyvinyl alcohol (PVA) (M.W.: 146000-186000, degree of hydrolysis: 99.5%), and the sorbates such as Methylene blue (M.W.: 319.85 g/mol), Congo red (M.W.: 696.68 g/mol), Tannic acid (M.W.: 1701.21 g/mol).

Preparation of magnetic composite sorbent. The magnetic composite sorbent (Fe_3O_4/PVA/APSCGs) based on alkaline pretreated spent coffee grounds (APSCGs) and particles Fe_3O_4 was prepared via dispersed method. To obtain this composite sorbent, the Fe_3O_4 particles were dispersed in PVA 2% solution. Then, the sample was heated to 80°C and added in APSCGs at 4:1 ratio of APSCGs/Fe_3O_4. Composite was collected by a magnet and sieved via a mesh size 315 μm.

Adsorption kinetics. The adsorption kinetics of sorbates onto Fe_3O_4/PVA/APSCGs sorbent were studied in the change of the contact times to the adsorption capacity [11]. For each experiment, the samples (0.1 g) were mixed with 50 mL solutions sorbates of MB (0.15 mmol/L and 0.30 mmol/L), CR (0.07 mmol/L and 0.14 mmol/L) and TA (0.03 mmol/L and 0.06 mmol/L). The experiments were performed at room temperature and pH 9 (MB), pH 5 (CR), pH 4 (TA). The concentration of sorbates in solutions was determined by spectrophotometric method using a SPECORD 210Plus spectrophotometer (Germany) at absorbance 666 nm (MB), 500 nm (CR), 275 nm (TA).

The amount of adsorbed sorbates onto the magnetic composite q_e (mmol/g) was calculated following to:

$$q_e = \frac{C_0 - C_e}{m}.V \qquad (1)$$

Where C_o (mmol/L) is the initial concentration of sorbates, C_e (mmol/L) is the equilibrium concentration of sorbates after adsorption, V (L) is the volume of solution and m (g) is the weight of sorbent.

Adsorption thermodynamics. To investigate adsorption thermodynamics, adsorption isotherms were constructed at different temperatures 298 – 318 K [12]. Batch experiments were performed at different initial concentrations of sorbates with values of pH 9 (MB), pH 5 (CR), pH 4 (TA). After that, the samples were incubated in the water-batch thermostat for 8 hours. The concentration of sorbates in solutions was determined by spectrophotometric method.

3 Results and discussion

Investigation of the preparation and characterization of Fe_3O_4/PVA/APSCGs sorbent prepared from alkaline pretreated spent coffee grounds have been published in our articles [13, 14]. The results showed that the APSCGs have a significant amount of functional groups as carbonyl, carboxyl, hydroxyl on Fe_3O_4/PVA/APSCGs surfaces and these functional groups can be potential adsorption centers. SEM studies indicated that the morphology of composite has a porous structure with a size in the range of 2–50 μm, resulting in good adsorption capacity with different sizes. In addition, the saturation magnetization of the Fe_3O_4/PVA/APSCGs sorbent was 21.5 emu/g, which is lower than the synthesized magnetite powder 73.6 emu/g but enough to separate sorbents after adsorption process. Using this technique, we were able to remove up to 95% of the sorbents from the solution [13, 14].

In this study, we used two important physicochemical aspects for the evaluation of adsorption mechanism as unit operations that are the adsorption kinetics and the adsorption thermodynamics. In addition, kinetic modeling using well - known models and adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants at various temperatures. All studies were carried out trying to understand the involved mechanisms (physical and/or chemical) between sorbates molecules and on the sorbent surface.

Adsorption kinetics. To study the adsorption kinetics of sorbates on the surface of Fe_3O_4/PVA/APSCGs sorbent, the kinetic curves were analyzed using models of external and internal diffusion, intraparticle diffusion and chemical kinetics [13].

Analysis of kinetic curves was performed with the diffusion models[13]. Dependence has been constructed:

External diffusion: $-\ln(1-F) = f(t)$ (2)

Internal diffusion: $F = f(t^{1/2})$ (3)

where $F = q_t/q_e$ is the degree of completion of the adsorption process, in which q_t and q_e are the adsorption capacity of sorbates onto the composite at the time t (hours (h)) and at equilibrium, respectively.

It is known that if the correlation coefficient (R^2) is closely related to dependencies, then the diffusional kinetics predominates over the limiting stage of those sorption process [14]. The results of the experimental data showed in Table 1. It can be seen that the correlation coefficient (R^2) for both models are quite satisfactory. This suggests that the adsorption process of MB, CR, and TA onto magnetic composite sorbent were controlled by a mixed-diffusion model.

To clarify the mechanisms that control the adsorption rate of multistage process we used the intraparticle diffusion model [15], which can be formulated as follows:

$$q_t = k_{id}t^{1/2} + C \qquad (4)$$

where q_t (mmol/g) is the adsorption capacity, k_{id} (mmol.g^{-1}.h$^{-1/2}$) is the rate constant of intraparticle diffusion and C (mmol/g) is the intercept.

From Figure 1 can be seen that three continuous adsorption stages of MB, CR and TA could occur.

The first stage characterized for the diffusion of MB, CR, and TA from the solution phase through the diffusion layer outside to the surface of the magnetic composite (external diffusion) [15]. The second stage refers to the diffusion of the MB, CR, and TA from surface of the magnetic composite to the adsorption centers (internal diffusion). The third stage was indicated to process of the formation bonds between the sorbates and the functional groups of the Fe_3O_4/PVA/APSCGs sorbent [16].

Table 1. Parameters Of Diffusion Models For Adsorption Of mb, cr and ta Onto Fe_3O_4/pva/apscgs Sorbent

Sorbate	C_o (mmol/l)	Internal diffusion		External diffusion
		K_{id} (mmol g^{-1}h$^{1/2}$)	R^2	R^2
MB	0,15	0,419	0,983	0,990
	0,30	0,435	0,972	0,969
CR	0,07	0,305	0,978	0,981
	0,14	0,320	0,987	0,996
TA	0,03	0,262	0,992	0,993
	0,06	0,274	0,985	0,970

To study the adsorption kinetics for MB, CR, and TA from aqueous solutions on the surface of magnetic composite sorbent we used the pseudo-first order model and pseudo-second order model and written as follow [17]:

The pseudo-first order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

The pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where q_e (mmol/g) is the amount of adsorbed sorbates at equilibrium, q_t (mmol/g) is the amount of adsorbed sorbates at time t, k_1 (h^{-1}) and k_2 (g.mmol^{-1}h^{-1}) are the rate constants for the first order model and second order model, respectively.

The results of the analysis parameters of the experimental data models are presented in Table 2. It is obvious that the pseudo-second order model described better the sorbates adsorption process onto magnetic composite sorbent because of its correlation coefficient (R^2) higher than the pseudo-first order model, and in all initial concentrations of sorbates, the calculated values q_e of the pseudo-second order model have a better similar with the experimental values ($q_{e, exp}$).

From the data above it can be concluded that the adsorption process of sorbates MB, CR and TA onto Fe_3O_4/PVA/APSCGs sorbent not only involves pore diffusion processes but also includes the formation of the interactions of sorbates with the functional groups of the sorbents.

Adsorption thermodynamics. Adsorption thermodynamic parameters were calculated using Langmuir constant (K_L) from constructing the adsorption isotherms at different temperatures 298-318 K. The linear Langmuir adsorption isotherms are described by the following equations [18]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (7)$$

where C_e (mmol/L) is the equilibrium concentration of sorbates; q_e (mmol/g) is amount of adsorbed sorbates onto the magnetic composite at equilibrium; q_m (mmol/g) is the maximum adsorption capacity, K_L (L/mmol) is Langmuir constant.

Results (Table 4) showed that the adsorption isotherms of studied sorbates onto Fe_3O_4/PVA/APSCGs sorbent have a high adsorption capacity and increase with growth temperatures [19]. Comparison with many other common sorbents can be seen that Fe_3O_4/PVA/APSCGs sorbent have relatively high

adsorption capacity among these adsorbents (Table 3). More importantly, the utilization of Fe_3O_4/PVA/APSCGs sorbent has a huge advantage of low cost due to the abundant resource of spent coffee grounds and sorbent after adsorption process can be easy for separating and regenerating from aqueous solution using an external magnet.

The thermodynamic parameters such as enthalpy change (ΔH, kJ.mol^{-1}) and entropy change (ΔS, J.K^{-1}.mol^{-1}) for the studied various temperatures were calculated using the Van't Hoff equation (8) and Gibbs free energy change (ΔG, kJ.mol^{-1}) by the equation (9) [20]:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

$$\Delta G = -RT \ln K \qquad (9)$$

where K is the equilibrium constant, K was calculated as dimensionless by multiplying it by 55.5 (number of moles of water per liter of solution), then $K = K_L \times 55.5 \times 10^3$ (10), R is the universal gas constant (8.314 J.mol^{-1}K^{-1}); T is the temperature (K).

Thermodynamic parameters obtained are shown in Table 5. From the data presented in Table 5, it was evident that adsorption of all studied sorbates was endothermic since the value of ΔH is positive. Similar results for endothermic adsorption were also observed on adsorption on chitosan [21], bentonite [12], alkaline pretreated spent coffee grounds [22]. The positive value of ΔS corresponding to the randomness rising at the solid–solution interface during the adsorption process [22]. In this study, the negative ΔG values indicated that adsorption sorbates onto the magnetic composite sorbent was spontaneous and adsorption capacity increased at higher temperatures.
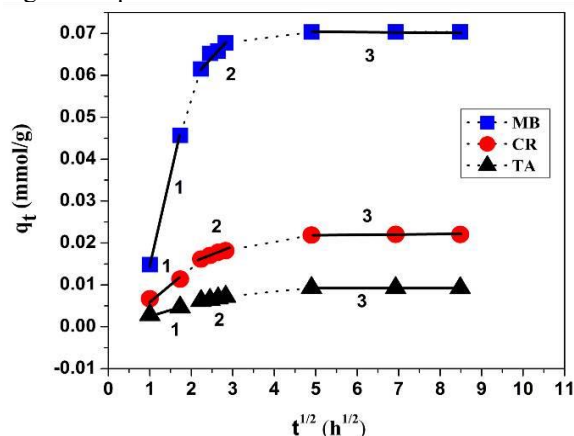

Fig. 1. Multistage process of q_t at $t^{1/2}$ for MB (0.15 mmol/l), CR (0.07 mmol/l) and TA (0.03 mmol/l) adsorption at 298 K onto Fe_3O_4/PVA/APSCGs sorbent

Thus, according to the results of adsorption kinetic and thermodynamic studies, one might conclude that the mechanism for removal of the studied sorbates by adsorption onto magnetic composite sorbent Fe_3O_4/PVA/APSCGs may be assumed both physisorption (electrostatic interaction, internal and external pore diffusion and chemisorption (involve charge sharing or transfer from the organic molecules to the functional groups of sorbent surface to form a coordinate type of chemical bond.

Table 2. Kinetic parameters for adsorption of mb, cr And ta Onto Fe₃o₄/pva/apscgs Sorbent

Sorbate	C_o (mmol/l)	qe exp (mmol/g)	Pseudo-first order model			External diffusion		
			k_1 (h^{-1})	q_e (mmol/g)	R^2	k_1 (gmmol^{-1}h^{-1})	Qe (mmol/g)	R^2
MB	0,15	0,070	0,44	0,086	0,990	10,39	0,072	0,998
	0,30	0,128	0,40	0,175	0,968	03,93	0,133	0,997
CR	0,07	0,022	0,22	0,018	0,980	20,46	0,023	0,999
	0,14	0,041	0,29	0,037	0,996	16,07	0,042	0,999
TA	0,03	0,009	0,16	0,007	0,993	38,88	0,009	0,999
	0,06	0,017	0,24	0,014	0,970	35,24	0,018	0,999

Table 3. Comparison Of q_m Value Of Different Sorbents For mb, cr, ta Adsorption

Sorbent	Sorbate	Adsorption conditions	q_m, (mmol/g)	References
Fe₃O₄/PVA/APSCGs	MB	pH 9, 25° C, 24 h	0,369	In present study
	CR	pH 4, 25° C, 24 h	0,088	
	TA	pH 5, 25° C, 24 h	0,066	
Spent coffee grounds	MB	pH 5, 25° C, 12 h	0,059	[21]
Magnetically modified coffee silverskin	MB	pH 6, 20° C, 6 h	1,738	[8]
Magnetically modified spent coffee grounds	CR	pH 4, 25° C, 3 h	0,014	[9]
Zeolite SMZ-CBC	TA	pH 5,5 25° C, 24 h	0,065	[22]
Nano sorbent Fe₃O₄@SiO₂-NH₂	TA	pH 6, 25° C, 24 h	0,08	[4]

Table 4. Langmuir Isotherm Parameters For mb, cr and ta Adsorption Onto fe₃o₄/pva/apscgs Sorbent

Sorbate	T(K)	Langmuir model		
		K_1 (L/mmol)	q_{max} (mmol/g)	R^2
MB	298	11,31	0,396	0,987
	308	20,29	0,613	0,995
	318	23,96	0,711	0,996
CR	298	13,97	0,088	0,985
	308	15,53	0,108	0,997
	318	25,55	0,112	0,993
TA	298	16,08	0,066	0,987
	308	19,32	0,082	0,993
	318	23,60	0,084	0,994

Table 5. Thermodynamic Parameters Adsorption mb, cr and ta Onto Fe₃o₄/pva/apscgs Sorbent

Sorbate	T(K)	ΔG	ΔH	ΔS
MB	298	-33,07	29,76	221.37
	308	-35,68		
	318	-37,28		
CR	298	-33,60	18,75	175,28
	308	-35,00		
	318	-37,12		
TA	298	-33,95	15,09	164,51

4 Conclusion

The composite sorbent obtained from alkaline pretreated spent coffee grounds and the synthetic magnetite has a high sorption capacity towards sorbates MB, CR, and TA. Adsorption of sorbates was controlled by a mixed diffusion model and pseudo-second order model.

Detailed analysis of q_e dependence on $t^{1/2}$ allowed to distinguish three separate stages of the process.

The results of determination of thermodynamic parameters ΔG, ΔH and ΔS showed that the process of adsorption of sorbates was shown to be an endothermic one and adsorption mechanism may be a combination of both physisorption and chemisorption.

Acknowledgment

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