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Single-stage solution combustion preparation of $ZnFe_2O_4$ -ZnS nanoparticles as dye adsorbent: Effect of fuel to oxidant and Zn to Fe molar ratios

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ZnFe₂O₄-ZnS

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HIGHLIGHTS

powders

synthesized by single stage solution

• Fuel / oxidant and Zn/Fe molar

ratios as synthesizing parameters

· The kinetics of methyl orange

• The methyl orange removal (dye)

by ZnFe₂O₄-ZnS is highly pH-

• The removal of dye by ZnFe₂O₄-

ZnS follows a pseudo second-order

using

adsorbent was investigated.

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GRAPHICAL ABSTRACT



ABSTRACT

ZnFe₂O₄-ZnS adsorbent was synthesized by the single-stage solution combustion procedure applying the thiourea at different fuel to oxidant ratios ($\phi = 1, 1.2, 1.4$, and 1.6), and different Zn to Fe molar ratios (Zn : Fe = 0.5, 0.6, 0.7, and 0.8). The efficiency of the removal of methyl orange dye by synthesized powders in various conditions was investigated. The best sample, in terms of dye removal, was the synthesized powder at Zn : Fe = 0.6 and $\phi = 1.4$. Dye removal was discovered to be extremely pH-dependent. The highest dye removal was observed to be about 94% of methyl orange, which disappears after 20 min in a dark environment. Kinetics investigations were carried out to discover the mechanism of methyl orange elimination and its adsorption rate kinetics. It was found that the elimination of methyl orange by ZnFe₂O₄-ZnS powders follows a pseudo second-order adsorption kinetics model.

1. Introduction

Increasing population, expanding industries, and the introduction of harmful wastewater have exacerbated the risk of scarce drinking water resources [1-3]. So, removing pollutants from water, especially on a large scale, has become a necessity for human societies. Azo dyes are one of the worse pollutants in industrial wastewater [1,4]. The methyl orange contaminant is an azo compound whose molecular structure has a chromophoric group (-N=N-) [1,5]. Azo compounds are released as colored effluents in water and are easily identifiable but not easily destroyed [6]. Various approaches such as instance ultrafiltration, ion exchange, reverse osmosis, and adsorption have been used to eliminate this toxic contaminant [1,3-7]. The use of nanomaterials as adsorbents is one of the most popular and effective new-fashioned ways to remove pollutants [8,9]. It is imperative to determine the proper adsorbent to remove the dyes and contaminants to the desired level.

Different types of nanomaterials have been evaluated for the elimination of organic pollution. Spinel compounds with the general formula AB₂O₄, such as ZnFe₂O₄, have been studied in recent years to remove different types of contamination from water [10-12]. In addition to acceptable performance, spinels are easily collected from the environment due to their magnetic properties [13,14]. ZnS is well-known as a suitable candidate for environmental applications [15]. Recently, Yoo et al. have shown that a composite of spinel $(ZnFe_2O_4)$ and ZnS compounds exhibited enhanced effectiveness in dye removal as compared with only spinel or ZnS compounds and have easy magnetic separation [16]. Two-stage synthesis methods composed of hydrothermal and co-precipitation [16] and solution combustion [17] have been reported for the preparation of ZnFe₂O₄-ZnS composite. Among these methods, solution combustion synthesis is a rapid, economical, and single-step method [18]. In the past, combustion synthesis of ZnAl₂O₄ and ZnO nanostructure particles for wastewater treatment [19], as well as ZnO and ZnS nanoparticles and their composite [20,21], have been successfully synthesized.

The focus of the present study was the preparation of $ZnFe_2O_4$ -ZnS powders via a one-step solution combustion route. The effect of synthesizing parameters, including Zn to Fe(Zn:Fe) molar ratios and fuel to oxidant

ratios (ϕ), on the efficiency of the removal of methyl orange contaminants were investigated. However, the ultimate goal was to investigate the kinetics of methyl orange removal using the optimized sample. Various materials have been used to investigate the adsorption kinetics and isotherms for the removal of methyl orange from wastewater. Darwish et al. investigated the removal of methyl Orange by applying NiO and CuO nanoparticles to pseudo first-order, second-order, and intra-particle diffusion models [22]. They indicated that their kinetics data was only explained by the secondorder model. Ali et al. showed the mesoporous carbon nanostructured demonstrated high-speed adsorption of methyl orange dyes in 10 min [23]. Their kinetic data were fitted to various mathematical models, whereas the isotherm data were adjusted to isotherms types. They found that methyl orange adsorption was limited by chemical interactions and mixed diffusion, and methyl orange adsorption mostly occurred through ion exchange and electrostatic interactions. Simonescu et al. reported methyl orange removal by adsorption onto CoFe₂O₄ synthesized by a co-precipitation method and found CoFe₂O₄ particles exhibited a superparamagnetic behavior that enabled their efficient magnetic separation after the adsorption process [24]. Their research indicated that methyl orange adsorption onto an adsorbent takes place as a monolayer onto a homogeneous surface. Their kinetics study results revealed that pseudo-first-order and pseudo-second-order kinetics models represent the adsorption process of methyl orange on CoFe₂O₄. To the best of our knowledge, these studies are the first to be conducted on ZnFe₂O₄-ZnS powders.

2. Experimental

2.1. Chemicals and instruments

Zinc nitrate hexahydrate, iron nitrate nonahydrate, thiourea, potassium chloride, nitric acid, and methyl orange chemicals were obtained from the Merck Chemical Company. Twice distilled aqua was prepared in the laboratory.

X-ray diffraction analysis with a Cu- $K\alpha$ radiation tube (XRD, Bruker, Advance D8, Germany), scanning and transmission electron microscopy (SEM, KYKY EM3900M, China, and TEM, Philips EM208S, Netherlands), vibration sample magnetometer (VSM, Meghnatis Daghigh Kavir Co., Kashan, Iran), and nitrogen adsorption-desorption (Belspor-mini II, Japan) were used for the characterization of synthetic powders. Also, UV-visible spectroscopy (JASCO V-570, Japan) was used to evaluate dye removal.

2.2. Synthesis procedure

100 ml of distilled water was provided and adjusted to pH= 4 by adding nitric acid. The required amounts of iron and zinc nitrate (Fe(NO₃)₃.9H₂O and Zn(NO₃)₂.6H₂O), potassium chloride (KCl), and thiourea $(SC(NH_2)_2)$ were dissolved in the water. After the mixture was homogeneous, it was warmed till it transformed into a gel. By continuing to steadily heat the gel, the combustion process was established in the eruption mode. To initiate a self-sustained combustion reaction, the solution prepared from the reaction agents was heated to a temperature of about 250 °C. The obtained powders were washed with hot water to remove any KCl solvable salt. The KCl, as an inert inorganic material, prevents the hard agglomeration of nanocrystallites. Also, melting the KCl during the combustion reaction helps to increase the crystallinity of the powders [17].

The thiourea was used as the fuel/sulfidizing agent at four fuel to oxidant ratios ($\phi = 1, 1.2, 1.4, 1.6$). The oxidants were zinc and iron nitrates used at four zinc to iron ratios (Zn:Fe= 0.5, 0.6, 0.7, 0.8). The reason for choosing these ratios was to increase the amount of ZnS formation in the composite by increasing the amount of thiourea (ϕ) as a sulfur source on the one hand and increasing the Zn:Fe ratio by increasing the zinc source on the other hand. The ratio of KCl to total oxidants was considered a constant value of 2/3 in all experiments according to [25,26]. Therefore, 16 experiments were performed, as shown in Table 1.

For instance, the combustion reaction for the stoichiometric state reaction can be presented as Eq. (1).

$$Zn(NO_{3})_{2}.6H_{2}O + 2Fe(NO_{3})_{3}.9H_{2}O + 5SC(NH_{2})_{2} \rightarrow Zn_{1-x}Fe_{2}O_{4} + Zn_{x}S + 5CO_{2} + 34H_{2}O + 18N_{2}$$
(1)

It was not feasible to determine the temperature of the reaction due to the lack of measurement facilities. Nevertheless, assuming the reaction is performed in adiabatic conditions, the highest achievable temperature would have been about 1263 K as estimated in [17] for the stoichiometric state of the combustion reaction.

2.3. Adsorption experiments

To investigate the adsorption process, a 15 ppm solution of methyl orange was prepared, and its initial absorbance was recorded by the UV-Vis apparatus. Then, 20 ml of methyl orange solution and a certain amount of adsorbent powder (0.03 g) were mixed in a glass beaker. The adsorbent-containing container was placed in a completely dark place for 10 min over a magnetic stirrer until the adsorption and desorption were balanced. Then, some of the solution was separated by centrifugation, and its absorbance was recorded by a UV-Vis apparatus in the band of 190-800 nm. Sample adsorption was recorded at specific times. After obtaining the concentration of the pollutant, the removal efficiency (R%) and adsorption capacity (q_a) were calculated with Eqs. (2) and (3), respectively, at different times. It is worth noting that since the aim of the present study is to investigate the adsorption kinetics, all experiments were accomplished in the dark to avoid the effect of photocatalytic activity. Photocatalytic activity may increase efficiency and adsorption capacity [3,27].

$$R\% = (C_0 - C_\tau) \times 100/C_0 \tag{2}$$

$$q_e = (C_0 - C_T) V/m \tag{3}$$

where C_0 is the primary pollutant concentration, and C_T is the pollutant concentration after removal at a certain period. q_e is the adsorption capacity (mg.g⁻¹), *m* is the mass of adsorbent (g), and V = 20 ml.

3. Results and discussion

3.1. Effect of synthesizing parameters on adsorption

Fig. 1(a) shows the effect of synthesis parameters, including Zn:Fe and oxidant ratios, on the amount of contaminant removal after 20 min as the highest achievable values. After 20 min, no notable increase in the removal efficiency was discerned. For better comparison, the data in Fig. 1(a) are shown as a contour plot and a 3D surface graph in Figs. 1(b) and 1(c), respectively. As can be observed, the highest dismissal efficiency of methyl orange corresponded to the synthetic powders with an oxidant ratio (ϕ) of 1.4 and Zn:Fe ratios in the 0.5 to 0.6 range. Samples 3 and 7 in Table 1 show the highest amount of contaminant

Test #	Molar ratio of raw materials		Actual v	Removal				
	Zn : Fe ratio	$\phi = ratio$	Zn(NO ₃) ₂ .6H ₂ O	Fe(NO ₃) ₃ .9H ₂ O	SC(NH ₂) ₂	KCl	efficiency (%)	
1	0.5	1	2.975	8.080	3.806	1.491	14	
2	0.5	1.2	2.975	8.080	4.567	1.491	30	
3	0.5	1.4	2.975	8.080	5.328	1.491	80	
4	0.5	1.6	2.975	8.080	6.090	1.491	58	
5	0.6	1	3.570	8.080	3.996	1.590	17	
6	0.6	1.2	3.570	8.080	4.796	1.590	20	
7	0.6	1.4	3.570	8.080	5.595	1.590	78	
8	0.6	1.6	3.570	8.080	6.394	1.590	46	
9	0.7	1	4.165	8.080	4.187	1.690	6	
10	0.7	1.2	4.165	8.080	5.024	1.690	34	
11	0.7	1.4	4.165	8.080	5.861	1.690	60	
12	0.7	1.6	4.165	8.080	6.699	1.690	46	
13	0.8	1	4.760	8.080	4.377	1.789	8	
14	0.8	1.2	4.760	8.080	5.252	1.789	28	
15	0.8	1.4	4.760	8.080	6.128	1.789	48	
16	0.8	1.6	4.760	8.080	7.003	1.789	66	

Table 1. Molar ratios and actual values of chemicals used for the synthesis of ZnFe₂O₄-ZnS.

removal with values of 80 and 78%, respectively.

XRD analysis of the synthesized powders showed that sample 7 (Zn : Fe = 0.6 and ϕ = 1.4) contained more ZnS than the other samples. Therefore, it can be claimed that higher amounts of ZnS in the ZnFe₂O₄-ZnS composite increases the efficiency of pollutant absorption. Fig. 2 shows the XRD pattern of several selected samples synthesized under different conditions. As can be observed, initially increasing the Zn:Fe ratio causes the proportion of the ZnS phase formation to increase. However, with further increases in the Zn:Fe ratio, the formation of the ZnS phase decreases sharply. As the Zn:Fe ratio increases, the amount of ZnS increases as more zinc becomes available. The heat released from $Zn(NO_3)_2.6H_2O(\Delta H^\circ = -2307 \text{ kJ.mol}^{-1})$ is less than that of Fe(NO₃)₃.9H₂O ($\Delta H^{\circ} = -3258 \text{ kJ.mol}^{-1}$) [17]. Therefore, by further increasing the Zn:Fe ratio, ZnS formation is prevented due to decreasing system temperature. As the fuel ratio (ϕ) increases, the system temperature rises again, and ZnS is formed. But at the same time, a higher amount of sulfur enters the system, which remains unreacted. Also, by increasing the Zn:Fe ratio, the crystallinity of powders is reduced due to the decrease of system temperature, and the removal of contaminants is decreased.

The ZnS is formed through the reaction of ZnO and H_2S [28],

$$ZnO + H_2S \to ZnS + H_2O \tag{4}$$

and the FeS is formed through the reaction of Fe_2O_3 and H_2S .

$$0.5Fe_2O_3 + 1.5H_2S \to FeS + 0.5S + 1.5H_2O$$
(5)

The Gibbs free energy formation of ZnS is less than FeS at temperatures below 1800 K. Hence, the ZnS which is thermodynamically more stable than FeS, has formed [17].

Fig. 3 compares the magnetic behavior of samples 3 and 7. The magnetic hysteresis loops are very narrow in both samples due to the nanoparticle size of the synthetic powders [25]. The saturation magnetization of sample 7 is higher than sample 3. It is known that the magnetization in $ZnFe_2O_4$ is impressed by the cationic distribution in its lattice. The higher saturation magnetization of sample 7 is likely due to the repartition of Fe³⁺ ions among tetrahedral and octahedral sites when the Zn:Fe ratio is high enough [25]. Yoo *et al.* reported similar magnetic behavior for core-shell $ZnFe_2O_4$ -ZnS



Fig. 1. (a) Effect of Zn:Fe and ϕ ratios on dye removal after 20 min, (b) the contour plot, and (c) the 3D surface graph of a diagram.

powders synthesized by a two-stage hydrothermal and co-precipitation method [16]. Also, Shojaei *et al.* synthesized $ZnFe_2O_4$ -ZnS powders with magnetic behavior very close to the current work [29].

 $ZnFe_2O_4$ powders have high saturation magnetization [30]. By composing $ZnFe_2O_4$ with the diamagnetic ZnS, the saturation magnetization decreased because of the



Fig. 2. XRD patterns of the synthesized powders at (a) Zn:Fe = 0.5 and $\phi = 1$ (b) Zn:Fe = 0.6 and $\phi = 1.4$ (c), Zn:Fe = 0.8 and $\phi = 1.4$ and (d) Zn:Fe = 0.8 and $\phi = 1.6$.

presence of the ZnS between the $ZnFe_2O_4$ particles. However, the ZnFe₂O₄-ZnS powders still show the ferromagnetic behavior with admissible magnetization to be magnetically retrieved. The relatively weak saturation magnetization of ZnFe₂O₄-ZnS powders may be favorable because of the reduced aggregation between the magnetic particles. This behavior avoids the negative effect of aggregation on the adsorption efficiency due to the decreased surface area.

Sample 7 was selected as the optimal sample due to its high amount of dye adsorption and better magnetic



Fig. 3. Hysteresis curves of sample 3 (Zn:Fe = 0.5, ϕ = 1.4) and sample 7 (Zn:Fe = 0.6, ϕ = 1.4) at room temperature.

behavior. The morphology of sample 7 was determined by SEM (Fig. 4(a)) and TEM (Fig. 4(b)). The physical morphology of the samples was determined using the SEM instrument on carbon-coated copper grids with gold pre-coating samples. $ZnFe_2O_4$ -ZnS powders were simply dispersed onto TEM grids using solvents and air-dried before TEM imaging. These micrographs show that the $ZnFe_2O_4$ -ZnS powders formed from agglomerated nanoparticles. The particles size distribution is at the nanoscale range. The surface area of $ZnFe_2O_4$ -ZnS powders (sample 7) was calculated by a BET apparatus to be 3.3 m².g⁻¹.

It should be noted that the removal of dye, as reported in Fig. 1(a), was performed at neutral pH. The outcome of the primary pH of the solution on the behavior of methyl orange removal was then investigated. HCl and NaOH were exert to regulate the pH of methyl orange. The influence of pH on the elimination efficiency of the ZnFe₂O₄-ZnS composite is displayed in Fig. 5, which demonstrates that the removal efficiency of ZnFe₂O₄-ZnS is completely influenced by the pH of the solution.





Fig. 4. (a) SEM and (b) TEM micrographs from $ZnFe_2O_4$ -ZnS powder at Zn:Fe = 0.6, ϕ = 1.4.

The adsorption of methyl orange onto $ZnFe_2O_4$ -ZnS increases up to 94% when the pH decreases. The maximum adsorption capacity of $ZnFe_2O_4$ -ZnS (q_{max}) was 9.4 mg.g⁻¹ for methyl orange. The methyl orange ions are negatively charged. When the pH is decreasing, large amounts of H⁺ in solution make the surface of ZnFe_2O_4-ZnS more positively charged. Therefore, a strong electrostatic repulsion exists between the methyl orange and ZnFe_2O_4-ZnS, which facilitates the adsorption of methyl orange onto the ZnFe_2O_4-ZnS composite.

3.2. Adsorption kinetics of methyl orange

An adsorption kinetics study is essential to identify the adsorption mechanism in the system [27]. Kinetic models are utilized to evaluate empirical data to investigate the adsorption mechanism and rate-controlling steps [3,31]. Also, kinetic information of methyl orange dye adsorption is needed to select the optimum conditions for large-scale dye removal processes. For the adsorption kinetics, there are several models that express the mechanism and rate in a different way. In this work, kinetics research of the adsorption process was investigated using pseudo firstorder, pseudo second-order, Elovich, and intramolecular diffusion kinetics models.

3.2.1. Pseudo first-order kinetics

According to the pseudo first-order kinetic model, the adsorption process is performed in two stages. In the first step, the adsorbed molecule travels from the solution to the adsorbent area. In the next step, the adsorbed molecule penetrates the adsorbent surface from its



Fig. 5. Outcome of primary pH on the adsorption of methyl orange by ZnFe₂O₄-ZnS, methyl orange concentration 15 mg.l⁻¹, ZnFe₂O₄-ZnS dosage 0.1 g, contact time 20 min.

surface. In this kinetics model, the second step is a slow process and determines the rate of the process [3,27,32-34]. Based on pseudo first-order kinetics, the adsorption reaction depends on the adsorbent value [32-34]. The pseudo first-order kinetics is commonly expressed as Eq. (6) [35].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$
(6)

In this relationship, q_e (mg.g⁻¹) is the ZnFe₂O₄-ZnS capacity at balance time, q_t (mg.g⁻¹) is the methyl orange adsorbed at time t, k_1 (min⁻¹) is the adsorption rate constant, and t (min) is time. If the pseudo first-order kinetics for the adsorption process is true, the diagram $log (q_e-q_t)$ against time must be linear. Fig. 6 shows the diagram of log (q_e-q_t) against time for the adsorption of methyl orange dye by ZnFe₂O₄-ZnS. The rate constant (k_1) and q_e were appraised from the tilte and intercept of the diagram presented in Table 2, along with the correlation coefficient (R^2) .

3.2.2. Pseudo second-order kinetics

The pseudo second-order kinetics is defined based on Eq. (7) [3,27,32].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

In this relationship, q_e (mg.g⁻¹) is the ZnFe₂O₄-ZnS capacity at balance time, q_t (mg.g⁻¹) is the methyl orange adsorbed at time t, k_2 (min⁻¹) is the adsorption rate constant, and t (min) is time.

If the pseudo second-order kinetics for the adsorption process is true, the diagram t/q_t against time must be linear.



Fig. 6. Pseudo first-order kinetics for the adsorption of methyl orange by $ZnFe_2O_4$ -ZnS powder.



Fig. 7. Pseudo second-order kinetics for the adsorption of methyl orange by $ZnFe_2O_4$ -ZnS powder.

Fig. 7 displays the chart of t/q_t versus t for the adsorption of methyl orange dye by $\text{ZnFe}_2\text{O}_4\text{-ZnS}$. The tilt and intercept of the linear chart of t/q_t against time yield the amounts of $1/q_e$ and $1/k_2 q_e^2$. The rate constant (k_2) and q_e were appraised from the tilt and intercept of the chat and are given in Table 2, along with the correlation coefficient (R^2) .

3.2.3. Elovich kinetics

The Elovich formula has been widely proposed to explain the adsorption kinetics and chemical adsorption of gases on solid adsorbents. This equation explains the adsorption kinetics of ion exchange. In other words, this is the best process kinetic expression when the adsorption mechanism is ion exchange. The Elovich equation is in the form of Eq. (8) [3,27].

$$q = \frac{1}{\beta} (\alpha \beta) + \frac{1}{\beta} \ln (t)$$
(8)

In the above equation, α (mg.g⁻¹.min⁻¹) is the primary adsorption rate constant, β (mg.g⁻¹) is a variable linked to the amount of area coating and activation energy for physical/chemical adsorption, and q_t (mg.g⁻¹) is the surface adsorption ability in time t (min). If the adsorption process follows the Elovich equation, the change curve of the q_t graph, in terms of ln(t), must be linear. In this relationship, the tilt is equal to $1/\beta$, and the width from the origin is equal to $1/\beta ln(\alpha\beta)$. Fig. 8 is a diagram drawn to match the testable data with the linear relationship of the Elovich correlation for methyl orange adsorption.

3.2.4. Intraparticle diffusion kinetics

The intraparticle diffusion kinetics model investigates

Table 2	. Kinetic	studies da	ata of methy	'l orange	adsorption	by	$ZnFe_2O_4$	-ZnS powders.	
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Kinetics models	Model linear form	R^2	Calculated parameters		
Decudo fuel orden	$\log(q_1, q_2) = \log(q_1)$ k_1	0.964	<i>k</i> ₁	q_{e}	
r seudo IIrst-order	$\log(q_e - q_t) = \log(q_e) - \frac{1}{2.303}t$	0.804	0.021	42.18	
Decude second ander	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	0.000	k_2	q_{e}	
r seudo second-order		0.999	3.36×10-5	12500	
Elevieh	$a = \frac{1}{2}(\alpha \theta) + \frac{1}{2}\ln(t)$	0.704	α	β	
Elovien	$q = \frac{1}{\beta}(\alpha\beta) + \frac{1}{\beta}in(t)$	0./94	7.86×10 ⁴	7.20×10 ⁻⁴	
Introporticle diffusion	$a = k + t^{0.5} + C$	0.878	С	k _{diff}	
	$q_t - \kappa_{diff} \cdot t + C$	0.070	6778	495.4	

the adsorption mechanism of the adsorbent on the porous adsorbent. Also, this model determines the step controlling the adsorption rate. The mathematical expression of this kinetics is in the form of Eq. (9) [27].

$$q_{t} = k_{diff} \cdot t^{0.5} + C \tag{9}$$

where q_t (mg.g⁻¹) is the amounts of methyl orange adsorbed at time t (min), k_{diff} (mg.g⁻¹.min^{0.5}) expresses the rate constant of intraparticle diffusion, and C (mg. g⁻¹) is linked to the boundary layer thickness. k_{diff} and Ccan be evaluated from the tilt and intercept of the linear chart of q_t against $t^{0.5}$, respectively. The diagram drawn to match the methyl orange dye adsorption data for the ZnFe₂O₄-ZnS adsorbent is demonstrated in Fig. 9.

If the linear regression of q_t versus $t^{0.5}$ moves via the zero origin of the diagram, intraparticle diffusion occurs only in the rate-limiting stage. However, as can be perceived from Fig. 8, the linear chart at each amount of ZnFe₂O₄-ZnS did not move via the origin of the diagram. Therefore, it can be claimed that the intraparticle diffusion was not alone rate-controlling stage.

For better comparison, Table 2 summarizes the



Fig. 8. Elovich kinetics for the adsorption of methyl orange by $ZnFe_2O_4$ -ZnS powder.

data obtained from kinetic studies for methyl orange adsorption by the ZnFe₂O₄-ZnS adsorbent. According to Table 2, the highest adsorption capacities, q_e , were computed in the pseudo second-order model. Also, q_e calculated in this model is in accordance with the experimental values. Moreover, the superior correlation coefficient (R^2) demonstrates that pseudo second-order kinetics is an answerable model for the methyl orange adsorption by ZnFe₂O₄-ZnS. The pseudo second-order kinetic model is based on the assumption that the ratelimiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on ZnFe₂O₄-ZnS capacity, not on the concentration of methyl orange.

4. Conclusion

1. It was found that the Zn to Fe molar ratio Zn:Fe = 0.6 and fuel to oxidant ratio ϕ = 1.4 are the optimal parameters for the synthesis of ZnFe₂O₄-ZnS powders by the solution combustion method.

2. Methyl orange removal by ZnFe₂O₄-ZnS is highly



Fig. 9. Adsorption of methyl orange by ZnFe₂O₄-ZnS powder via intraparticle diffusion kinetics

pH-dependent. It was found that acidic pH is suitable for methyl orange removal.

3. The amount of ZnS in the $ZnFe_2O_4$ -ZnS composite and the degree of crystallinity of the particles affect the dye absorption.

4. Synthesized powder under optimal parameters can degrade the methyl orange dye up to 94% in 20 min.

5. The maximum adsorption capacity of $ZnFe_2O_4$ -ZnS (q_{max}) was 9.4 mg.g⁻¹ for methyl orange.

6. It was found that the removal of methyl orange by $ZnFe_2O_4$ -ZnS powders follows a pseudo second-order degradation model. In this condition, the adsorption rate is dependent on $ZnFe_2O_4$ -ZnS capacity, not on the concentration of methyl orange.

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