Synthesis and Application of Iron Oxide/Silica Gel Nanocomposite for Removal of Sulfur Dyes from Aqueous Solutions

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A-B-S-T-R-A-C-T

Background & Aims of the Study: water pollution by synthetic organic dyes is mainly regarded as environmental and ecological critical issues worldwide. In this research, magnetite iron oxide/silica gel nanocomposite (termed as Fe_3O_4/SG) was synthesized chemically and then used as an effective adsorbent for removal of sulfur dyes from aqueous solution.

Materials and Methods: The various parameters such as pH, sorbent dosage, initial dye concentration, contact time and dye solution temperature were investigated in a batch system. The equilibrium data were analyzed by Langmuir and Freundlich isotherm models.

Results: The experimental data fit well with pseudo-second-order kinetic model ($R^2 \geq 0.998$) and conformed better to Langmuir isotherm model ($R^2 \geq 0.997$). The maximum adsorption capacity for Fe_3O_4/SG obtained from the Langmuir model was 11.1mg/g. Evaluation of thermodynamic parameters proved that the adsorption process was normally feasible, spontaneous and exothermic.

Conclusion: It can be concluded that the Fe_3O_4/SG can be considered as a cost-effective and an environmental friendly adsorbent for efficient removal of sulfur dyes from aqueous solutions.
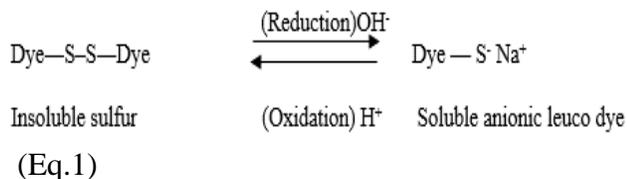
Background

Water is crucial to survive all living organisms on the earth, and access to safe drinking-water is important as health and development issue at a national, regional and local levels (1). One of today's environmental challenges is the excessive use of dyes for industrial and domestic activities which it contaminates the ground and surface water; therefore, it is important to remove these dangerous organic compounds from water and wastewater prior to discharge into the environment (2-5). Water pollution by synthetic organic dyes used in textile, cosmetics, pulp and paper industries etc., is mainly regarded as environmental and ecological critical issues worldwide (4-7). These industries produce considerable unfixed dyes that in turn impart strong color, expelling of these dyes into water bodies, produce a large quantity of dyeing wastewater which needs to treatment before being discharged into waterways.

Due to the aromatic structures, synthetic dyes have chemical stability; thus, they are difficult to biodegrade, oxidizing and photo degradation, giving water undesirable color, diminish light penetration and oxygen gas solubility, so, photosynthetic reactions of aquatic plants, will be decreased, having toxic effects on human health (8,9).

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Sulfur dyes are synthetic organic ones, manufactured by the thionation or sulphurisation of organic compounds containing nitro or amino group, and is mainly used for dyeing cellulose fibers in terms of volume. They are extremely colored, water insoluble and have to be converted to water soluble (leuco form) before application to textile material (Eq.1).

$$Dye—S—S—Dye \quad \xrightleftharpoons[\text{(Oxidation) H}^+]{\text{(Reduction)OH}^-} \quad Dye — S^- \ Na^+$$

Insoluble sulfur   (Oxidation) H$^+$ Soluble anionic leuco dye

(Eq.1)

Due to their good wet- light fastness, low-cost and rapid processing, consumption of these kinds of dyes remains high. An approximate production of these dyes was more than105 tons in the world annually. Averagely 25% of sulfur dyes are remained in waste streams, so it is important environmentally and ecologically, to remove these pollutants from waste water before discharging into hydrosphere (10,11).

There are two major remediation methods for color removal, including physico-chemical and biological treatments. As mentioned above, due to stability of dye molecule, biological treatment is not effective for removal of all dyes. Among physico-chemical methods, adsorption is one of the most effective, promising and superior to the others. Some characteristics such as easy operation, flexibility, economically feasible etc, make that this method has been used for good removal of wide variety of dyes in wastewater streams (10-12). Moreover dye chromospheres will be changed or collapsed by adsorption; this process can remove the whole dying molecules and their fragments and also control the bio-chemical oxygen demand in the effluent (10-13). Silica gel as an inert and non-toxic material with high specific surface area (~800 m^2/g), porosity and high efficiency for functionalization with various ligands allocated

to a wide range of biomedical and treatment applications.

The hydroxyl (OH) groups on the surface of silica can be functionalized to improve specialty silica gels with unique stationary phase characteristics. These properties make silica as a convenient material for iron oxide shielding and functionalization (14,15). Magnetic modification of low-cost adsorbent could result in materials which is useful for biotechnology and environmental applications (16). Adsorption process by magnetic separation technology combined with inexpensive adsorbents has been widely used in environmental purification.

Aims of the study:

In the current investigation, iron oxide/silica gel nanocomposite (Fe$_3$O$_4$/SG)) was synthesized, then used as a low-cost, cost-effective, and environmentally friendly to the treatment of sulfur dye. With their large surface areas, these particles can readily adsorb sulfur dye from aqueous solutions.

Materials & Methods

All chemicals which used in the study were from analytical grade and obtained from Merck Co. The reagents were used as received without further purification.

The stock solution was prepared by adding of 0.10 M Na$_2$S solution and 0.50 g of the sulfur blue 15 (C.I. 53540, CAS 1327-69-1, dye content 95%) in 1.0 L of distilled water under constant stirring, and the temperature was slowly increased to 90 ^{o}C, which was maintained at this state for 30 min. Finally, we were obtained practical solutions of varying concentrations for further experiments.

Iron oxide magnetic coated silica was prepared by co-precipitation method as described before after some modifications (17): 20 g of silica powder (in spherical sizes of 0.50 to 1.0 mm diameters), 1.48 g FeCl$_2$.4H$_2$O and 4.0 g FeCl$_3$. 6H$_2$O, were loaded into a 250 mL flask containing 60 mL of de-ionized water, at determined temperature, under refluxing

condition in N_2 atmosphere and adding 25% ammonia solution with continuous stirring. Final particles were then rinsed with de-ionized water and separated by low speed centrifugation from un-reacted magnetite. The resulting particles then dried at temperature about 60 ^{o}C for 4 h in an oven and were stored in a glass vial for further use.

The sulfur dye in aqueous media was determined spectrophotometrically by a single beam Perkin-Elmer UV-VIS spectrophotometer in λ_{max}=520 nm at pH 10.0 and quantified using a calibration graph which was obtained from the standard solutions prepared from the standard sulfur dye solution in distilled water in the concentration range of 1.0–100.0 mg L^{-1}.

The calibration curve shows that the Beer's law is obeyed in this concentration range. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for pH measurements. Dilute NaOH and HCl solutions were used for pH adjustment.

All experiments were done in the batch system to study the effects of solution pH, initial concentration, adsorbent dosage and temperature on the adsorption of sulfur dye on Fe_3O_4/SG composite.
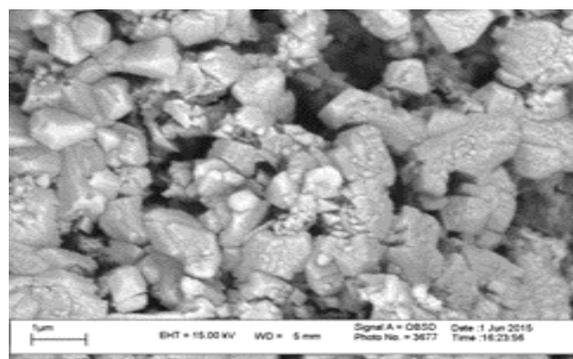
Results

Morphological structure

The Scanning Electron Microscopy technique (SEM) has been known as a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. Fig.1 (a) and (b) shows the SEM images of the Fe_3O_4/SiO_2 composite adsorbent before and after the dye treatment.
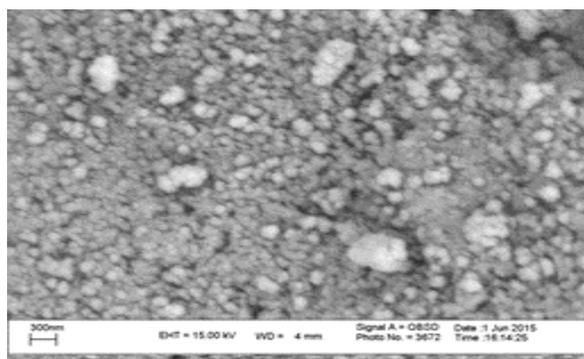
(a)   (b)

Figure 1) a: SEM micrographs of the Fe_3O_4/SiO_2 (before dye treatment), b: SEM Micrographs of the Fe_3O_4/ SiO_2 (after dye treatment).

Effect of solution pH

The dye solution pH, as one of the most important factors, effects on the surface charge of the adsorbent and the dissociation of functional groups on the active sites of the adsorbent (18). The percentage removal of sulfur dye at different pH values (2 to 8) is plotted in Fig. 2.
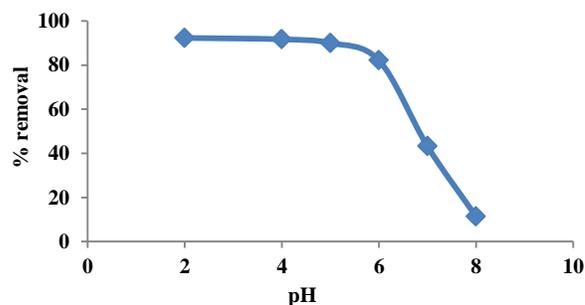

Figure 2) Effect of solution pH on dye removal (initial dye concentration=100 mg/L, adsorbent dosage=0.25 g, agitation speed=150 rpm, and temperature=298 K).

Effect of sorbent dosage

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Different weights of Fe₃O₄/SG (varied from 0.10 to 0.30 g) were exposed to the dye solution for 1 hour. The obtained results are illustrated in Fig. 3.
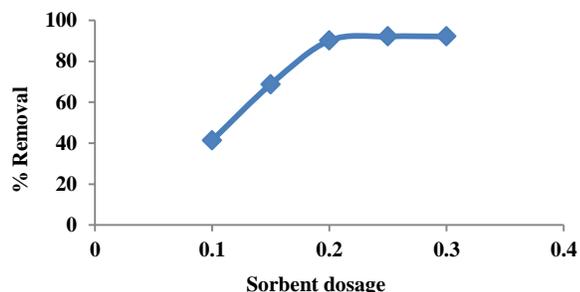

Figure 3) Effect of sorbent dosage on dye removal (initial sulfur dye concentration= 100 mg/L, pH=5, and temperature=298 K).

Effect of contact time

In this investigation, the effect of agitation time on dye removal at the various initial dye concentrations was studied. The obtained results are shown in Fig. 4.
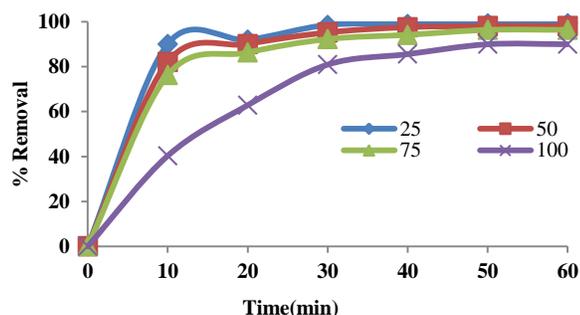

Figure 4) Effect of dye concentration on sorption of sulfur dye onto Fe3O4/SG (adsorbent dosage=0.20 g, pH=5, agitation speed=150 rpm, temperature=298 K).
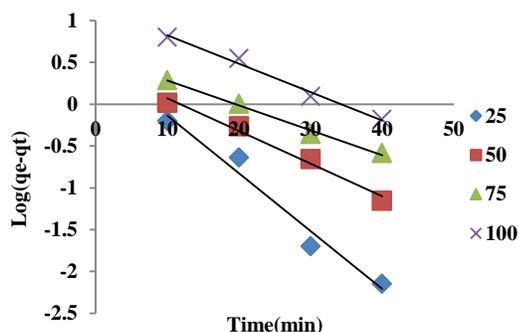
Adsorption isotherms

The plot $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ related to the adsorption of sulfur dye on the Fe₃O₄/SG composite adsorbent at room temperature is shown in Fig. 5.
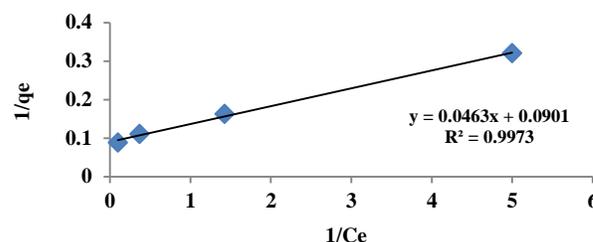

Figure 5) Langmuir isotherm obtained for sorption of sulfur dye at 298K (initial dye concentration=25-100 mg/L, sorbent dosage=0.20g and agitation speed=150 rpm).

Adsorption kinetics

Adsorption processes and suitability of an adsorbent for removal of a special adsorbate is usually described through graphs known as isotherm. For isotherm investigation, the initial concentration of adsorbate is varied then the amount of adsorbate on the adsorbent as a function if its pressure or concentration at constant temperature is plotted. From linear plot of log (q_e-q_t) versus t for the pseudo-first-order model (not shown), and t/q_t versus t for the pseudo-second-order (shown in Fig.6), the kinetic parameters in both models were calculated. Table 1 gives the values of the parameters for the pseudo-first-order and second-order kinetic models.

Figure 6) Pseudo-first-order kinetics plots for sulfur dye adsorption at different initial dye concentration (T=298 K).
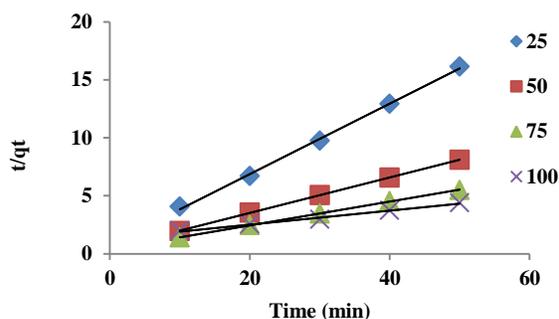
Table 1) Adsorption kinetic parameters of sulfur dye onto Fe$_3$O$_4$/SG at 298 K.

C$_o$	Pseudo- first-order kinetic model				Pseudo- second-order kinetic model		
	q$_{e,exp}$	q$_{e1,cal}$	k$_1$	R^2	q$_{e2,cal}$	k$_2$	R^2
25	3.10	3.59	0.159	0.969	3.30	0.119	0.998
50	6.16	2.88	0.089	0.985	6.53	0.052	0.999
75	9.03	3.81	0.066	0.990	9.80	0.026	0.999
100	11.20	14.52	0.075	0.988	16.66	0.002	0.990

Table 2) Thermodynamic parameters for adsorption of sulfur dye onto Fe3O4/SG

T (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o [kJ/(mol k)]	R^2
298				
308	- 5.44	-77.92	-0.24	0.991
318				

Adsorption thermodynamic

To study the effect of temperature on sulfur dye removal, adsorption experiments were performed at three different temperatures. The results are given in Table 2.

Discussion

The surface of composite was coarse-grained because of the presence of both Fe$_3$O$_4$ and SiO$_2$. The existence of high surfaces area reduces the mass transfer resistance and facilitates the diffusion of dye molecules, which may prove suitable for dye removal.

The sorption of dye was also affected by pH of solution. The removal percentage, was increased from 10 to 90% when pH was decreased from 8 to 5. With decreasing of solution pH, the number of positively charged active sites increased due to the protonation of the surface of the adsorbent. Consequently, the electrostatic interaction between the surface of the adsorbent and the sulfur dye anions increased, which resulted in increased adsorption. As the results show at highly acidic medium the removal percentage decreased. We suppose that the strongly acidic solution caused the destruction and dissolution of iron oxide; it is therefore recommended pH between 4 and 5. Moreover it was found that, with increase in pH the degree of color removal decrease and no significant color removal was occurred, this is because of the presence of excess hydroxide ions, which competed with the negatively charged sulfur dye for adsorption sites.

In the adsorbent dosage study, it was found that with increasing the dosage of sorbent, removal percentage of the dye is also increased gradually (Figure 3). This result is expectable, because with increasing the amount of sorbent, more adsorption sites will be available. 90% of the dye sorption was observed for 0.20 g of the adsorbent dosage. After that, the increase was little. Then, we applied this amount as optimal value in our further investigations in this research.

In the investigation of the contact time, it was found that the removal of sulfur dye is occurred quickly and large amounts of the dye was removed within 40 min and then reach the equilibrium in 50 min. However a tiny decrease of the dye adsorption was occurred to the Fe$_3$O$_4$/SG after 20 min of contact time; this phenomenon maybe because of the dissolution of the sulfur dye adsorbed on the Fe$_3$O$_4$/SG, which could be an evidence to demonstrate the adsorption is also a physical process. Linear forms of Langmuir and Freundlich equations were used for isotherm studies (19):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m}\frac{1}{C_e}$$

(Eq. 2)

Where q_e is the amount of sulfur dye adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of sulfur dye in solution (mg/L), q_m (mg/g) and k_L(L/mg) are the maximum adsorption capacity and Langmuir adsorption constant respectively. The linearized form of Freundlich isotherm can be written as below:

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

(Eq.3)

Where, k_F [mg/g (L/g) $^{1/n}$] and n are Freundlich constants which are represent the adsorption capacity and intensity of adsorption, respectively.

Examining the equilibrium sorption data, using above mentioned adsorption models, the high value of the correlation coefficient R^2 derived for the adsorbent indicates that, this adsorption process was better described by Langmuir isotherm model (Figure 5). It was clear that, adsorption takes place at fixed and specific homogeneous sites within the adsorbent. Based on Langmuir adsorption isotherm, maximum adsorption capacity (monolayer coverage) was 11.1 mg/g.

In order to study the mechanism of adsorption, two kinetic models including pseudo-first-order and pseudo-second-order have been employed (20,21). The pseudo-first-order kinetic model can be shown by the following Lagergren kinetic equation:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

(Eq.4)

Where, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at contact time t (min) respectively, and k_1 is the pseudo-first-order kinetic constant (1/min). The linear form of this kinetic model is shown below:

$$\frac{t}{qt} = \frac{1}{K_2 qe2} + \frac{1}{q_e} t$$

(Eq.5)

Where, K^2 is the pseudo-second-order rate constant [g/(mg min)]. Table 1 shows that the correlation coefficient value obtained for pseudo-second-order kinetic model (R^2=0.998) was more than one which value obtained for pseudo-first-order model (R^2=0.969). Moreover the qe (exp) is closer to q_{e2} (calc) rather than q_{e1} (calc).

Therefore, the pseudo-second-order kinetic model validated this removal process more than the pseudo-first-order model. The thermodynamic parameters like the Gibbs free energy change ΔG^o (kJ/mol), the change in enthalpy ΔH^o (kJ/mol) and entropy change ΔS^o [kJ/(mol ^{o}k)] were also calculated by means of the following relations (22).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(Eq. 6)

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

(Eq. 7)

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

(Eq. 8)

Where, R is the gas constant (8.314 J/mol ^{o}K), T is the temperature of solution in Kelvin, K_c is the equilibrium constant, C_{Ad} is the amount of dye adsorbed on solid at equilibrium (mg/L) and C_e is equilibrium concentration of dye in solution (mg/L). ΔH^o and ΔS^o were calculated from the slope and intercept of a plot of ln K_c versus 1/T (Table 2). The negative ΔH^o value confirms the exothermic nature of adsorption. The negative ΔS^o value shows the decreased randomness at the solid/solution interface during the adsorption process. The negative values of ΔG^o for the adsorption on Fe_3O_4/SG composite are due to spontaneous nature of adsorption.

Conclusion

Fe_3O_4 was synthesized via simple co-precipitation method on the surface of silica gel particles (Fe_3O_4/SG) and applied for sulfur dye from aqueous solution effectively. Adsorption isotherm study indicated that sulfur dye sorption by the introduced adsorbent (Fe_3O_4/SG) obeys from Langmuir equation that implies chemisorption. Kinetics studies

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indicated that the investigated sorption process obeys from pseudo-second-order kinetic model which is also in consistent with chemisorption mechanism. Thermodynamic studies also confirmed that the investigated sorption process is exothermic and the spontaneity of dye removal controls by enthalpy.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

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