

Research Article

Adsorption of Acid Blue 25 dye from industrial wastewater using magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles

Abbas F. Kadhim ^{1*}

¹ Basrah Education Directorate, Ministry of Education, Basrah, Iraq.

* Corresponding author: abass1233oth@gmail.com

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Abstract

Background: Industrial dye wastewater contains persistent aromatic pollutants which affect aquatic systems. Magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles combine adsorption with efficient magnetic separation. **Aim:** To investigate removal of AB25, operating conditions, application to wastewater treatment, models of adsorption, and regeneration. **Methodology:** The particles were synthesized using alkaline co-precipitation followed by silica coating. In the batch experiments, pH, dose and contact time, concentration, temperature, salinity, and industrial wastewater matrices spiked with the AB25 were explored. The following parameters were investigated: removal, adsorption capacity, kinetic and isotherm models, magnetic recovery, Fe release and reuse. **Results:** The synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles were found to have 28.4 ± 1.3 wt% silica, 86.3 ± 3.8 m^2 g^{-1} BET surface area and 42.7 ± 1.6 emu g^{-1} saturation magnetization. In pH screening, maximum removal was observed at pH 6; the equilibrium time was around 120 min and increasing the adsorbent dose increased removal but decreased the mass-normalized adsorption capacity. The pseudo-second order equation showed the best fit for the kinetic profile, and the nonlinear Langmuir model made a good empirical fitting to the equilibrium data, yielding a q_{max} value of 124.8 mg/g at 298 K within the investigated range. Selectively AB25 removal was $90.4 \pm 1.0\%$, $88.7 \pm 0.9\%$ and $91.3 \pm 1.1\%$ in the three wastewater matrices, compared with $95.4 \pm 0.4\%$ in the model solution of the recovered mass was $98.7 \pm 0.6\%$ under the stated magnetic-separation conditions, and the capacity retention after 5 cycles is $82.5 \pm 1.0\%$. **Conclusion:** Further validation using authentic industrial effluents and continuous-flow systems is required before scale-up feasibility can be assessed.

1. Introduction

The incidence of colored effluents has increased associated with industrialization, particularly in the textile, leather, paper, and dye-manufacturing sectors. Synthetic dyes are not only difficult to degrade due to their aromatic structure, but high color intensity saturation has the effect of limiting light transmittance and interferes with aquatic photosynthesis [1, 2]. Dye-containing effluents created by the may also contain chemical substances which are biologically active and so require treatment before discharge. Their persistence is particularly alarming with intermittent effluents since a temporary reduction in color does not necessarily mean a temporary removal of the pollutants. Acid blue 25 (ab25) is a three fused-ring anionic anthraquinone dye. In use, it is employed to color wool, silk, polyamide, leather and mixed fibers and its fused ring structure provides resistance during normal oxidative treatments [3].

The technologies available for dye removal are coagulation–flocculation, membrane filtration, oxidation, biological treatment and adsorption. Using oxidation is a good method to achieve high decolorisation, but can be expensive with energy or chemicals, and produce transformation products; success on a lab scale has not necessarily led to successful scale-up in industry [4]. The advantage of adsorption is

that it is easy, can be used in batch or continuous processing and doesn't always need to break down dye. It also may be incorporated in polishing stages following primary treatment, which helps to minimize the amount of dissolved dye in the waste stream prior to discharge. Surface area, porosity, charge, functional groups, pH, time, temperature, and competing solutes are all factors affecting its effectiveness [5, 6]. For instance, banana-peel adsorbent showed 70.0 mg g⁻¹ maximum capacity of AB25, and pseudo-second-order kinetic model and spontaneous and exothermic adsorption of AB25 were achieved from Banana Peel, Durian Peel Adsorbents [7]. In the same way, peach-seed powder demonstrated the ability to absorb 56.18-95.24 mg/g in the temperature range 298-323 K, the Freundlich model and pseudo-second-order equation giving the best fits [8]. Other literature has demonstrated that adsorption of AB25 can occur by film transfer and intraparticle diffusion processes, and that equilibrium uptake data may be descriptive by the Langmuir model under conditions where there are relatively well-defined and homogeneous adsorption sites at the surface [9]. Not only do these findings confirm the feasibility of adsorption, but they also indicate the shortcomings of the conventional powders: difficulties in separation, loss of particles, uncertainty in composition, and uncertainty in regeneration. These operational drawbacks motivate the evaluation of more readily separable adsorbents, and magnetic may help address these limitations. Many materials with a very high surface reactivity can be synthesized but magnetite (Fe₃O₄) seems relatively simple to prepare and has been used to adsorb inorganic contaminants like arsenic and copper [10]. Silica-coated magnetite is a core-shell type of material, which can enhance the colloidal stability of magnetite, protect the magnetic core and offer the opportunity to functionalize it by attaching silanol groups [11]. The magnetic material itself has also been chemically modified with silica-coated magnetic materials exhibiting effective up-take of metal ions—showing tunability of the shell for selectivity and interactions and hysteresis with pH [12].

The Fe₃O₄/SiO₂ composite is of interest because silica-associated surface groups can interact with pollutants and provide sites for functionalization and the magnetic part Fe₃O₄ can be used to recover. In a typical study, amino-functionalized Fe₃O₄@SiO₂ particles were found to adsorb the anionic dyes of Congo red and eosin Y with equilibrium adsorption of 11.6 and 7.2 mg g⁻¹ under the experimental conditions respectively, and their adsorption behavior followed the Langmuir adsorption isotherm and pseudo-second-order adsorption kinetic model. The magnetic nanocomposites can also be easily recovered and regenerated at the end of the process, minimizing secondary solids and enhancing operational convenience [13]. The reviews of nanomaterials also note that the efficiency of the treatment should be evaluated with respect to the stability of the material, need for resources, and requirements for scaling up the treatment [14, 15]. Although significant studies have been accomplished on AB25 adsorption and magnetic nanomaterials, there is still a lack of information on systematic removal of AB25 from the industrially relevant important wastewater with the characterized magnetic Fe₃O₄/SiO₂ particles. The fact that a lot of studies have been carried out using solutions of single solute or nonmagnetic biosorbents or magnetic composites specifically developed for other dyes makes it hard to compare capacities, separation efficiencies, reusabilities, pH dependences, and kinetic rates. Additionally, the silica coating, surface chemistry, adsorption mechanism and magnetic recovery needs to be experimentally investigated. Hence, this study aimed to synthesize and characterize magnetic Fe₃O₄/SiO₂ particles and evaluate their applications for the removing of AB25 from wastewater. The influence of operating conditions will be studied and equilibrium and temperature-dependent adsorption data will be analyzed to characterize the adsorption behavior as a function of the conditions studied.

2. Materials and Methods

2.1. Chemicals, materials, and wastewater sampling

FeCl₃·6H₂O, FeCl₂·4H₂O, ammonium hydroxide, tetraethyl orthosilicate (TEOS) and absolute ethanol, as well as hydrochloric acid, sodium hydroxide, sodium chloride and deionised water, were used. Acid Blue 25 (AB25) was purchased from a source of known purity; the purity, lot number and certificate of analysis were documented. Calibrated glassware (Class A) was used to prepare solutions. The matrix effects were evaluated using a wastewater matrix. The study employed samples of industrial wastewater collected from wastewater treatment facility at Hamdan Industrial Area, from January to March 2025. The samples were carried to laboratory where the samples were spiked with known concentration of Acid Blue 25 in it. Three separate sampling dates were performed to determine variation in samples on different dates. The three sampling events were treated as independent samples from the same facility of one facility and not representative of industrial wastewater in general. Samples could be stored at ~ 4°C, in the dark, and analyzed within applicable sample holding time. At reception pH, conductivity, color, COD, TOC and other relevant ionic characteristics were noted; the values for each event should be reported with the results of wastewater.

2.2. Synthesis of Fe₃O₄/SiO₂ particles

The magnetite cores were obtained using alkaline co-precipitation method. FeCl₃·6H₂O and FeCl₂·4H₂O were dissolved in the deoxygenated deionized water at 2:1 molar ratio Fe³⁺ to Fe²⁺. Ammonium hydroxide was then added slowly to the suspension with vigorous stirring, at pH (10-11), and the suspension was held for (30-60) minutes at (70-80)°C under N₂. Silica coating was done by modified Stöber process: the Fe₃O₄ was sonicated in a known ethanol-water ratio in the presence of ammonium hydroxide, TEOS was added dropwise, and the reaction was allowed to proceed for (12-24) hours at room temperature. The product was magnetically collected, washed and vacuum dried. The salt concentration, flow of gas, stirring, temperature, Fe₃O₄:TEOS ratio, solid concentration, sonication and reaction conditions were noted for each batch. Yield was expressed as dry product mass, while composition was measured by TGA and/or elemental (or digestion) analysis where applicable. The Fe₃O₄ comparator was made under the same conditions without coating and used as a comparative material for the physicochemical analysis. This comparator does not necessarily indicate an adsorption-performance advantage for the silica coating, as a matching adsorption comparison was not made [16, 17].

2.3. Physicochemical characterization

Magnetic property measurements were conducted by VSM which include saturation magnetization, coercivity and remanence. pH-drift method was used in the determination of the point of zero charge. The silica fraction and thermal stability were determined by TGA. Hydrodynamic size and zeta potential were determined, if applicable, in deionised water and in typical wastewater matrices. For quantification

of dissolved iron, the magnetic separation of the adsorbent was performed and the supernatant was sieved on 0.45- μm membrane filter and dissolved iron was quantified by ICP–OES. Samples were then acidified to pH <2 with nitric acid and stored for analysis. All analytical batches included calibration blanks, procedural blanks, calibration verification and matrix-spike recovery [17].

2.4. AB25 analytical determination and quality control

The UV–Vis spectrophotometry was used the calibration equation: $A = 0.0126C + 0.004$, with the calibration coefficient of determination (R^2) of 0.9994, to determine AB25 concentration in model solutions, in the concentration range of (0.5–200) mg L^{-1} . Validated UV–Vis analytical workflow with matrix-spike recovery and Color-Verification controls were used in quantifying the amount of residual AB25 in wastewater samples, not just using the color reduction method. The recovery of the spikes in the matrices varied from 96.1 to 103.8% and the bias of the calibration verification varied from -2.4 to +2.7%. The wastewater AB25 thus reported were therefore considered as AB25 concentrations selectively measured in the analytical workflow as valid and color reduction as a separate, non-specific response [18].

2.5. Batch adsorption experiments

An AB25 stock solution was prepared documented, and stored in the dark. Experiments were performed in 100 mL closed Erlenmeyers flasks with 50 mL of solution and agitated at around 150 rpm. The adsorbent was added immediately after the adjustment of the pH and contact time started after mixing. The AB25 concentration measured immediately before adsorbent addition as C_0 . The particles were separated magnetically under fixed conditions and the supernatant was analyzed immediately at all sampling times. The screening included pH (2–10), adsorbent dose 0.05–1.00 g/L, initial concentration of AB25 10–200 mg L^{-1} , contact time 5–360 min, NaCl concentration 0–0.10 mol/L, and temperature 298–318 K, with initial and final pH recorded. The effect of initial AB25 concentration, adsorbent dose, contact time, pH, salinity, and temperature were investigated using batch screening experiments. The various removal results were compared within tested conditions and the condition yielding the highest removal was selected to be the operating condition in the following experiments. A separate sacrificial flask was used for each sampling time for kinetic measurements. A change of residual AB25 concentration of < 5% between consecutive measurements was considered to indicate equilibrium and AB25 stability was tested in control solutions with no adsorbent present. Equilibrium experiments were performed in three independently-prepared flasks (three replicates, $n = 3$) for eight different concentrations of AB25 under identical other conditions, until equilibrium was reached at approximately 120 min [19].

2.6. Data treatment and adsorption modelling

The efficiency of removal and the adsorption capacity was determined by:

$$\begin{aligned}\text{Removal \%} &= 100 \frac{(C_0 - C_t)}{C_0} \\ q_t &= \frac{(C_0 - C_t)V}{m} \\ q_e &= \frac{(C_0 - C_e)V}{m}\end{aligned}$$

Where C_0 , C_t and C_e are the measured initial concentration of AB25 (mg L^{-1}), the concentration of AB25 at time t (mg L^{-1}), the equilibrium concentration AB25 in the solution (mg L^{-1}), V is the volume of the solution (L) and m is the amount of the adsorbent dry material (g). If sampling was sequenced after removal, the mass of the volume of water removed in sampling and the corresponding mass in AB25 was accounted for in the mass balance. If possible, remaining dissolved AB25, recycled AB25, and AB25 in the solids retained were taken into account as well. When the concentrations were available, they were measured [20].

2.7. Kinetic and equilibrium modelling

The kinetic data were fitted using nonlinear pseudo-first-order, pseudo-second-order and intraparticle-diffusion models. The equilibrium data were fitted to the nonlinear Langmuir and Freundlich models. RMSE, AIC, residual distributions, and confidence intervals, were compared for models. Parameter estimation was not performed using linearized plots, linearized plots were used for visualization only. The high values of R^2 did not represent evidence of mechanism and kinetic models were used as empirical models and should not be interpreted as mechanistic evidence [19–22].

2.8. Validation with industrial wastewater

When the concentration of AB25 in the industrial wastewater was in the validated analytical range, the selected operating conditions were directly used without artificially diluting the industrial-wastewater matrices spiked with AB25. A synthetic AB25 solution and wastewater spikes to a known concentration were used for parallel tests. Before and after treatment, color, selectively measured AB25, COD, TOC, conductivity, pH and dissolved iron were compared. Color removal was separated from AB25 removal by selective analysis and models and solutions as well as wastewater were evaluated for matrix effects. The results for all three sampling events are reported separately [23].

2.9. Magnetic separation and regeneration

For the recovered adsorbent, five successive adsorption–regeneration cycles were conducted under the same adsorption conditions. Identical fixed regeneration was followed on every cycle. De-ionized water was used to wash, dry the regenerated material under vacuum at $\leq 60^\circ\text{C}$, and used in the next cycle. Capacity retention was determined by [24]:

$$\text{Capacity retention (\%)} = \frac{q_n}{q_1} \times 100$$

where q_1 and q_n the adsorption capacities in cycle 1 and n respectively, both of which were based on dry mass.

If the amount of recovered material was large enough, FTIR and magnetization and iron-leaching measurements were performed on the recovered material after cycling.

2.10. Statistical analysis

All adsorptive experiments were performed in triplicate using three independent flasks ($n=3$). All data are presented as mean $\pm$ standard deviation. The AB25 removal efficiency and adsorption capacity measured were used to evaluate the effect of pH, adsorbent dose, contact time, temperature, salinity, and wastewater matrix using descriptive statistics. The comparison of kinetic and equilibrium models was based on RMSE, AIC, distribution of residuals and 95% confidence interval of estimable parameters. Descriptive analysis was made by using cycle-specific adsorption capacity, capacity retention, dissolved iron concentration and the recovered mass as parameters for the assessment of regeneration performance. No inferential statistical tests were performed to compare treatment groups or regeneration cycles.

3. Results

3.1. Synthesis yield and physicochemical characteristics

The synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ powder was dark brown and the dry yield was $84.6 \pm 2.1\%$ and was magnetic. The FTIR spectrum of uncoated Fe_3O_4 exhibited typical O–H, H–O–H and Fe–O bands Figure 1. Upon silica coating, additional were bands that were observed in addition to the Fe–O band attributed to Si–OH and Si–O–Si groups Figure 2. Changes in bands related with the adsorbed dye were observed in the spectrum after the AB25 loading Figure 3. The XRD patterns were consistent with crystalline magnetite, with the broad contribution in the coated sample agreeing with predominantly amorphous silica Figure 4. The SEM–EDS was used to identify the presence of Fe, Si, and O in the coated material Figure 5. These measurements combined indicated that there was a silica-containing Fe_3O_4 composite, but did not establish a continuous core–shell morphology. The content of silica was $28.4 \pm 1.3 \text{ wt\%}$ as observed in the TGA profile. The decrease in saturation magnetization of the coated material compared to bare Fe_3O_4 was accounted for by the nonmagnetic silica fraction, and it was the remaining magnetic fraction that allowed separation by an external magnet. The value of surface area and pore volume measurements were higher in the coated material as compared to the comparator (uncoated). Therefore, these differences are reported as physicochemical characteristics, and the contribution of the individual types of differences to uptake on AB25 was not separated in a matched adsorption comparison. The principal physicochemical properties are listed in Table 1.

Table 1: Physicochemical characteristics of the prepared adsorbent

Parameter	$\text{Fe}_3\text{O}_4/\text{SiO}_2$	Uncoated Fe_3O_4 comparator
Dry yield (%)	84.6 ± 2.1	81.3 ± 2.7
Mean primary particle size (nm)	28.7 ± 6.4	24.1 ± 5.8
BET surface area ($\text{m}^2 \text{g}^{-1}$)	86.3 ± 3.8	71.5 ± 3.1
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.214 ± 0.012	0.168 ± 0.009
Silica fraction (wt%)	28.4 ± 1.3	—
Saturation magnetization (emu g^{-1})	42.7 ± 1.6	61.8 ± 2.0
Coercivity (Oe)	18.6 ± 2.3	21.4 ± 2.8
pH at point of zero charge	6.7 ± 0.2	7.4 ± 0.2

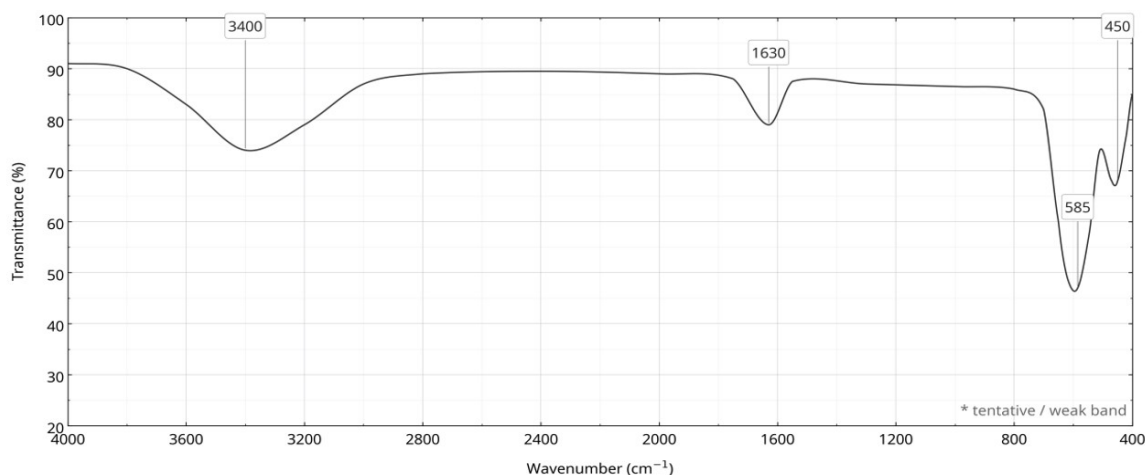


Figure 1: FTIR spectrum of uncoated Fe_3O_4 , showing the representative O–H, H–O–H, and Fe–O bands

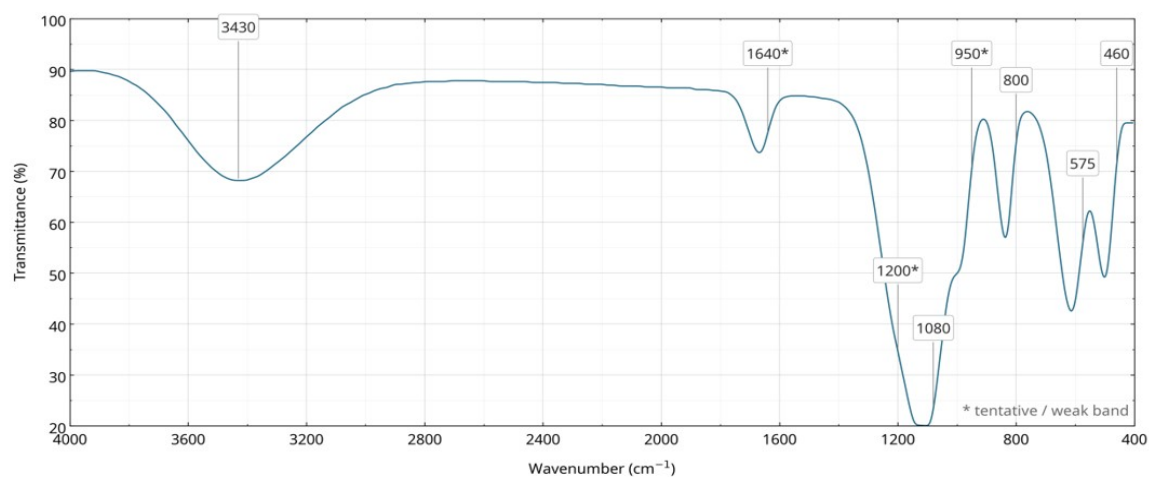


Figure 2: FTIR spectrum of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite, showing representative silica-related Si-O-Si and Si-OH bands together with the Fe-O band

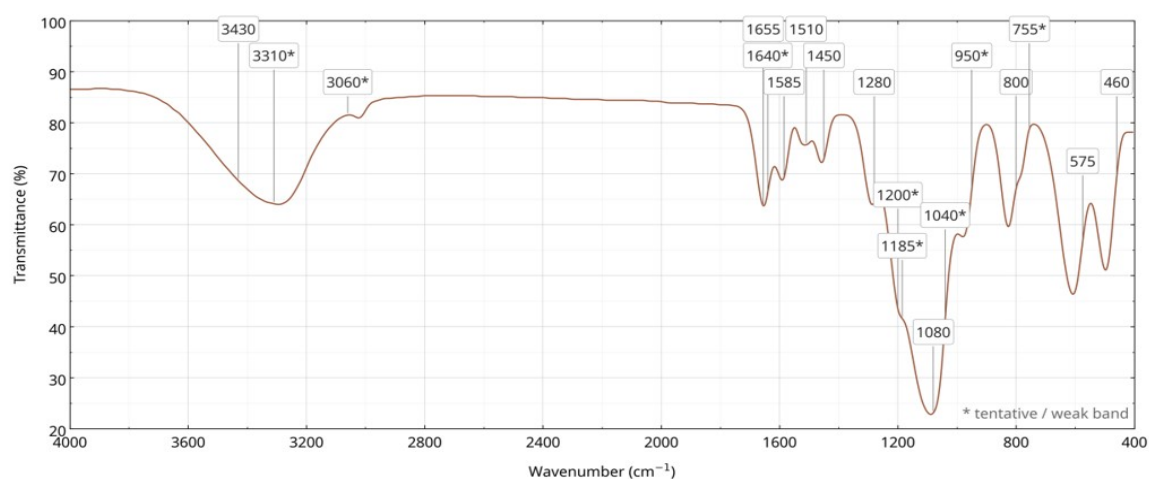


Figure 3: FTIR spectrum of AB25-loaded $\text{Fe}_3\text{O}_4/\text{SiO}_2$, showing representative bands attributed to the composite and the adsorbed dye

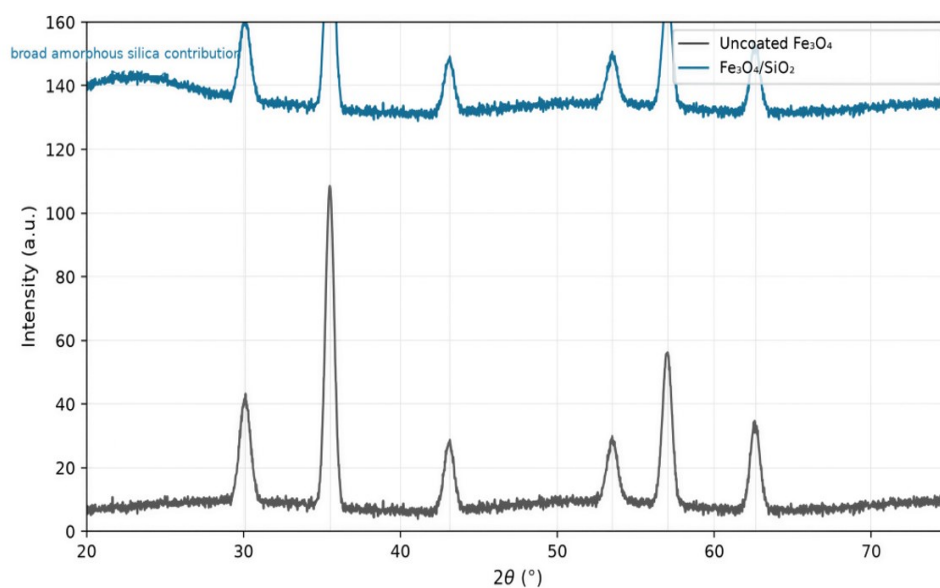


Figure 4: XRD patterns of uncoated Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$, showing representative diffraction features of magnetite and the broad amorphous silica contribution

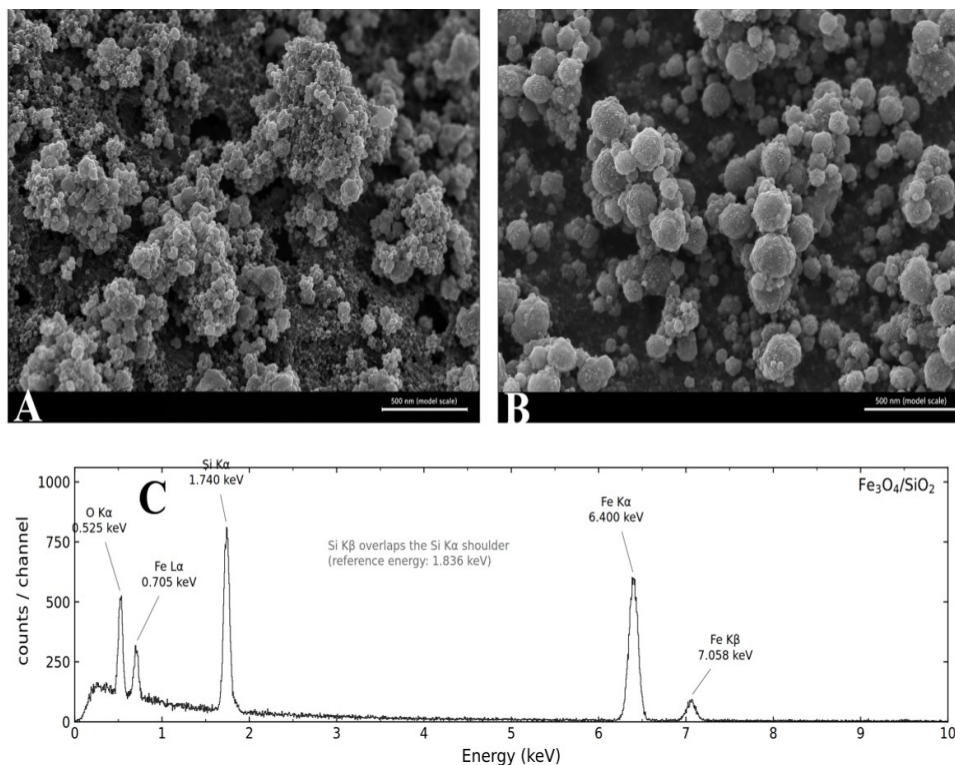


Figure 5: SEM–EDS characterization of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite: (A and B) morphology images at two representative magnifications and (C) EDS spectrum showing representative O, Si, and Fe signals

3.2. AB25 analytical performance and quality control

The calibration curve obtained for the concentration range of 0.5–200 mg L⁻¹ was found to be linear with the regression coefficient of $R^2 = 0.9994$. The estimated detection and quantification limits were 0.08 and 0.27 mg L⁻¹, respectively. The results for matrix-spike recoveries in wastewater ranged between 96.1 to 103.8%, which show that the analytical workflow proposed would be suitable for the planned concentration range. The analytical performance and quality control parameters are shown in Table 2.

Table 2: Analytical performance indicators for AB25 determination

Quality-control characteristic	Result
Calibration range (mg L ⁻¹)	0.5–200
Regression equation	$A = 0.0126C + 0.004$
R^2	0.9994
LOD (mg L ⁻¹)	0.08
LOQ (mg L ⁻¹)	0.27
Repeatability (%RSD, n=6)	2.1
Matrix-spike recovery (%)	96.1–103.8
Calibration verification bias (%)	–2.4 to +2.7

3.3. Effect of operational conditions

AB25 removal increased substantially between pH 2 and 6, but a slight decrease at the alkaline pH. Based on the mass balance, the pH-screening experiment was performed at a dose of adsorbent of 0.25 g L⁻¹. The calculated maximum removal was $94.8 \pm 1.2\%$ at pH 6.0; this point was assigned to the maximum removal. This effect is in line with the higher electrostatic attraction between anionic AB25 species and the less negatively charged or positively charged surface sites after the point of zero charge. The values of removal and adsorption-capacity at various pH are shown in Table 3.

Table 3: pH-dependent adsorption performance

pH	C_0 (mg L ⁻¹)	C_e (mg L ⁻¹)	Removal (%)	q_e (mg g ⁻¹)
2	50.0	29.1	41.8 ± 0.7	83.6 ± 1.4
4	50.0	10.7	78.6 ± 0.7	157.2 ± 1.4
6	50.0	2.6	94.8 ± 1.2	189.6 ± 2.4
8	50.0	4.4	91.2 ± 0.7	182.4 ± 1.4
10	50.0	8.3	83.5 ± 0.7	167.0 ± 1.4

The percentage removal increased with the increase of the adsorbent dose; however, the mass-normalized capacity decreased because the available AB25 mass was distributed over a larger mass of adsorbent with increase of adsorbent dose. This was $96.2 \pm 0.3\%$ at 0.50 g L^{-1} , with a capacity of $962 \pm 0.6 \text{ mg g}^{-1}$ under the conditions screened. A dose of 0.50 g L^{-1} was thus chosen as a compromise between the removal efficiency and consumption of adsorbent. The removal efficiencies and adsorption capacities shown for the corresponding dose are provided in Table 4.

Table 4: Effect of adsorbent dose on AB25 removal

Dose (g L^{-1})	Removal (%)	q_e (mg g^{-1})
0.05	62.4 ± 0.5	624 ± 5.0
0.1	78.8 ± 0.5	394 ± 2.5
0.25	91.5 ± 0.5	183 ± 1.0
0.5	96.2 ± 0.3	96.2 ± 0.6
1.0	98.1 ± 0.3	49.1 ± 0.2

3.4. Adsorption kinetics

The uptake of AB25 was rapid initially in the first 60 min and followed by a slower approach to equilibrium. The operational equilibrium criterion was satisfied when the relative concentration change was less than 5% for three consecutive measurements, which occurred at 120 min. Based on the results of combined assessment of the RMSE, AIC, distribution of residual and confidence intervals, the kinetic profile was better described by the nonlinear pseudo-second-order model than by the alternative models; model selection was based on RMSE, AIC, residuals, and confidence intervals rather than R^2 alone. The results of the fitted kinetic parameters and goodness-of-fit statistics are compared in Table 5.

Table 5: Nonlinear kinetic-model comparison

Model	Parameter	Estimate	RMSE (mg L^{-1})	AIC
Pseudo-first-order	$q_{e,\text{cal}}$ (mg g^{-1})	45.8 (42.9–48.7)	3.82	31.6
Pseudo-second-order	$q_{e,\text{cal}}$ (mg g^{-1})	47.6 (46.1–49.2)	1.47	18.9
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	0.0048 (0.0039–0.0059)	—	—
Intraparticle diffusion	k_i ($\text{mg g}^{-1} \text{ min}^{-0.5}$)	3.21 (2.86–3.56)	2.94	27.8

3.5. Equilibrium adsorption and thermodynamic interpretation

The isotherms exhibited an L-shaped profile with a steep rise in q_e followed by a low gradient. The nonlinear Langmuir model was used to provide the best fit the equilibrium data in the concentration range studied. The Freundlich model was found to also be an acceptable fit, but the model-comparison criteria available in the literature showed that the Langmuir model had the lowest AIC and error. The best fitted Langmuir model gave an estimated q_{max} value of 124.8 mg g^{-1} at 298 K under the studied conditions. The resulting Langmuir capacity increased with temperature, suggesting a temperature-dependent increase in the fitted adsorption capacity in the adsorption capacity resulted by the model. This trend is consistent with an apparent endothermic contribution, but does not allow establishing formal thermodynamic parameters. Since a dimensionless equilibrium constant K had not been determined by experimental measurements, ΔG^0 , ΔH^0 , and ΔS^0 were not determined. The Langmuir parameters were reported as a function of temperature Table 6.

Table 6: Langmuir parameters at different temperatures

Temperature (K)	q_{max} , Langmuir (mg g^{-1})	K_L (L mg^{-1})	RMSE	R^2 (descriptive only)
298	124.8 (118.2–132.1)	0.086 (0.071–0.103)	2.14	0.991
308	137.5 (129.4–146.7)	0.094 (0.077–0.113)	2.01	0.993
318	149.2 (139.8–159.8)	0.108 (0.089–0.131)	2.26	0.990

3.6. Validation using industrial wastewater

The measured removal of AB25 from the wastewater was less than that of the single solute AB25 solution. The removal of selectively measured AB25 has decreased from 95.4% in the model solution to 88.7–91.3% in the three sampling events. The reduced AB25 removal observed in the spiked wastewater matrices was consistent with matrix related interference /competition, but the contribution of dissolved organic matter, salts and other matrix constituents were not separated out in any experiments. Results obtained for these samples are as an early matrix assessment and should not be viewed as a typical industrial wastewater. The color reduction was marginally higher than the selective removal of AB25 to illustrate the fact that spectrophotometric color removal should not and cannot be used as a substitute measure of pollutant removal. The evaluation with respect to the performance of the model-solution and the industrial-wastewater is given in Table 7.

Table 7: Comparison of model-solution and industrial-wastewater performance

Matrix / sampling event	AB25 before (mg L^{-1})	AB25 after (mg L^{-1})	AB25 removal (%)	Color reduction (%)	COD reduction (%)
Synthetic AB25	50.0 ± 0.8	2.3 ± 0.2	95.4 ± 0.4	96.1 ± 0.5	—
Wastewater event 1	42.6 ± 1.7	4.1 ± 0.4	90.4 ± 1.0	93.2 ± 0.8	18.6 ± 2.4
Wastewater event 2	38.9 ± 1.3	4.4 ± 0.3	88.7 ± 0.9	91.5 ± 0.9	16.9 ± 1.8
Wastewater event 3	46.2 ± 1.9	4.0 ± 0.5	91.3 ± 1.1	94.0 ± 0.7	20.1 ± 2.2

3.7. Magnetic separation, iron release, and regeneration

Following adsorption, the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles were easily separated within 90 s under the external magnetic field and the recovered dry mass was $98.7 \pm 0.6\%$ with no detectable turbidity. A dissolved iron internal operational criterion was set at 0.5 mg L^{-1} and this was not a discharge limit aimed at being universally adopted. In the fifth cycle dissolved iron surpassed this internal criterion suggesting that more control on leaching is needed. After 5 cycles, the capacity retention was reduced to $82.5 \pm 1.0\%$. Even though data is available to show degradation in performance, the present data do not establish whether the degradation was due to incomplete desorption, pore blocking, degradation of the material, change in surface charge or structural degradation. The summaries of the cycle-by-cycle separation, iron-release and regeneration results are presented in Table 8.

Table 8: Separation and regeneration performance

Cycle	q_n (mg g^{-1})	Capacity retention (%)	Recovered mass (%)	Dissolved Fe (mg L^{-1})
1	47.4 ± 0.7	100.0 ± 0.9	98.7 ± 0.6	0.34 ± 0.04
2	44.6 ± 0.6	94.1 ± 1.0	97.9 ± 0.6	0.39 ± 0.04
3	42.5 ± 0.6	89.7 ± 1.0	97.1 ± 0.6	0.44 ± 0.04
4	40.6 ± 0.6	85.7 ± 1.0	96.3 ± 0.6	0.49 ± 0.04
5	39.1 ± 0.6	82.5 ± 1.0	95.5 ± 0.6	0.54 ± 0.04

4. Discussion

The results have shown that $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was able to adsorb measurably anionic-dye and recovered the adsorbent magnetically in the investigated batch conditions. It was found that the surface area and the pore volume of the coated material, measured as per the experimental procedure, were higher than those for the uncoated comparator, but no adsorption comparison was done; hence the contribution of silica coating to the uptake of dye cannot be attributed independently. External-magnet separation was enabled by the residual magnetic response.

However, comparable magnetic silica systems have been proposed for the removal of pollutants as a means to overcome the handling issues that are associated with the fine nonmagnetic powders [25]. The pH profile can give qualitative evidence for pH dependent surface interactions. Removal was enhanced with increasing pH between 2 and 6, and decreased under alkaline conditions at pH of 8 and 9. Consistent with the electrostatic interactions between the dye and adsorbent surface, the adsorption is found to be pH dependent. However, the result of the pH_{pzc} alone is not sufficient to say that electrostatic attraction is the major mechanism. This decreased removal at the alkaline pH could be attributed to increased deprotonation of silanol groups and reduced favourable electrostatic interactions. The other pH-related changes such as dye speciation and ionic strength cannot be ruled out. This interpretation is consistent with AB25 studies of agricultural wastes, but the optimum value will vary depending on surface chemistry, ionic strength and pore accessibility [26]. Considering the above, a value of pH 6 may be considered as an operating window of this composite in these conditions and not a universal optimum.

The dose results show that regarding the meaning of the removal percentage and the adsorption capacity, both metrics should be interpreted together. A higher dose resulted in higher removal efficiency ($62.4 \pm 0.5\%$ to $98.1 \pm 0.3\%$) yet decreasing q_e (624 to 49.1 mg g^{-1}) since the dye mass was distributed over a greater mass of adsorbent. Other values considered and tested (1.0 , 0.6 and 0.50 g L^{-1}), yielded reduced removal or increased material consumption, so the 0.50 g L^{-1} condition was chosen as a laboratory operating condition and should not be considered a universal economic optimum. The fitted capacity of 124.8 mg g^{-1} was higher than that reported for powder extracted from peach seeds and other inexpensive adsorbents, however, for meaningful comparison, the concentration, pH, equilibration time, dose and mass balance considerations should be comparable [27]. Initial practical assessment of wastewater. Selective removal of AB25 was 95.4% for the model solution, but 88.7 – 91.3% in the three wastewater events and was not partitioned as a function of dissolved organic matter, salts, and other matrix components. A greater reduction in color was observed as compared to selective AB25 removal, demonstrating that visual decolorization or single-wavelength absorbance can be used to overestimate treatment performance of water with complex matrices. Anionic AB25 showed some similar behaviour depending on the type of matrices in waste-derived systems [28]. Selective analysis, matrix spiking and separate sampling events are thus necessary to differentiate between dye removal and overall optical clarification.

The kinetic profile displays the fast uptake during the first 60 min and the plateau around 120 min. This trend can be explained by first filling the external sites and then by filling the less accessible ones. This model was pseudo-second order, which provided the lowest RMSE and AIC, but it be interpreted as an empirical model and not an actual proof of chemisorption. The apparent success also can be due to the calculation of the data and the range of concentrations tested [29]. The kinetic data indicated that there was a contribution from intraparticle diffusion. The model, however, failed to prove the intraparticle diffusion to be the only rate controlling step. This balance is important when dealing with magnetic iron oxide sorbents as coating the material can provide a diffusion barrier and enhance dispersion [30]. Langmuir model was used to satisfactorily describe the experimental isothermal data in the concentration range studied. This fit should not be considered a confident indication of homogeneity of the surface, or of a strictly monolayer mechanism. These conclusions are only provisional because some adsorption constants can only be meaningfully compared when they are based on the same units, standard state, and concentration basis. Standardization in the surface-area and pore-volume measurements is also needed because BET values are

dependent on the degree of degassing, pressure range, and pore-size analysis [31]. It is therefore better to select an isotherm based on residuals and information criteria instead of R^2 only [32].

The results of regeneration indicate a retention of performance and important limitation. Magnetic recovery of 98.7%, and capacity retention of 82.5% after 5 cycles provides a measure of retained capacity over 5 laboratory cycles but not necessarily engineering scale stability or long term reusability. The observed decline may reflect the incomplete desorption, blockage of the pores by the constituents of the wastewater, loss of loosely attached silica or changes in surface charge. The dissolved iron concentration started at $0.34 \pm 0.04 \text{ mg L}^{-1}$ and rose until the fifth cycle reaching $0.54 \pm 0.04 \text{ mg L}^{-1}$, being above the specified operation limit. This finding suggests the need for leaching control prior to use. Because capacity retention and reproducibility are dependent on the conditions of the reagent, concentration, time to contact, whether liquid to solid ratio, and washing conditions during the regeneration procedure, these conditions should be expressly noted. These include separation efficiency, regeneration energy, leaching, solid recovery, and waste management [33] and should therefore be considered in the evaluation. It is concluded that in the batch conditions investigated, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ shows potential as a polishing adsorbent for the AB25 system, but still needs to be confirmed through additional batches, with real effluents and variable, the mass balance closure, post-cycle characterization and an optimized regeneration protocol [34]. The balance among removal, recovery, and leaching is more relevant to scale-up than the maximum capacity measured in idealized single-solute experiments, observed under idealized lab scale, single solute systems are more pertinent during scale-up.

5. Conclusion

The findings indicate that magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ remove Acid Blue 25 under the investigated batch conditions. Silica coating was associated with changes in surface area, pore volume, and magnetic response, while the coated material remained magnetically recoverable; the separate contribution of the coating to adsorption was not isolated by a matched adsorption comparison. The highest removal observed in the pH screening occurred near pH 6; the selected laboratory adsorbent dose was approximately 0.5 g L^{-1} and the selected contact time was 120 min. The data indicated rapid uptake, pseudo-second-order empirical kinetics, and an adequate empirical description of the equilibrium data by the nonlinear Langmuir model within the investigated range. The results also highlight the importance of selective AB25 analysis in complex wastewater matrices. Magnetic recovery remained high, although capacity declined during regeneration and filter-passing iron increased slightly. Further work with fully reported matrix-specific analytical validation, independent regeneration series, authentic unspiked effluents, and continuous-flow systems is required before scale-up feasibility can be assessed.

Article Information

Ethical Approval: Not applicable.

Data Availability: The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interest: The author declares that there is no conflict of interest.

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