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Applications of response surface methodology for optimization of γ-alumina nanoparticles synthesis and acid dye adsorption

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Abstract

Gamma alumina (γ-alumina) nanoparticles were synthesized successfully by the calcination of aluminum hydroxide obtained from aluminum scrap using the control precipitation method. The effective parameters, including solution pH, temperature and time of aging, were optimized by response surface methodology (RSM) based on a central composite design to obtain γ-alumina nanoparticles with a high-surface area. The optimum conditions for γ-alumina synthesis were pH 6.5 with an aging temperature of 75 °C, an aging time of 8 h, and subsequent calcination at 550 °C. The synthetic material was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and the N_2 adsorption–desorption technique. The results showed that the γ-alumina nanoparticles had an average particle size of 21.18 nm, and a BET surface area of 283 m^2/g was obtained from inexpensive raw materials. The synthetic γ-alumina was examined for the adsorption of acid dye from aqueous solution and the isotherms were determined. RSM was also applied to evaluate the effect of experimental variables and their interaction in achieving the optimum conditions for acid dye removal. The adsorption behavior of acid yellow on γ-alumina nanoparticles was well explained by Langmuir isotherm model. The maximum adsorption capacity for the removal of acid yellow was found to be 125 mg/g.

Keywords**:** *adsorption, aluminum scrap, γ-alumina nanoparticles, precipitation, response surface methodology*

1. Introduction

Aluminum is mainly produced from bauxite mines and is most widely used as nonferrous metal in a variety of industrial applications due to its physical and mechanical properties, resulting in a large amount of aluminum scrap. A major portion of aluminum scrap is recovered by recycling to preserve the limited resources. This process requires less energy than the extraction of aluminum. Additionally, aluminum scrap is also used to synthesize alumina powders. In particular, γ-phase alumina is very important and is widely used as an adsorbent for the removal of metals or dyes from wastewater due to its large surface area (Asencios & Sun-Kou, 2012; Khosla, Kaur, & Dave, 2013; Siahpoosh, Salahi, Hessari, & Mobasherpour, 2016). Furthermore, it is used as catalytic support in many chemical reactions (Ahmedzeki, Hussein, & Abdulnabi, 2017; Chotisuwan, Sririrak, Har-Wae, & Wittayakun, 2012).

There are several methods for transforming aluminum scrap into γ-alumina, such as hydrothermal synthesis, the sol-gel method, and the control precipitation method. Many of these techniques produce alumina nanoparticles that are either gamma or alpha-phase (Zykova, Livanova, Kosova, Godymchuk, & Mamontov, 2015; Chotisuwan et al., 2012; Siahpoosh et al., 2016; Parida, Pradhan, Das, & Sahu 2009). The hydrothermal synthesis process of alumina nanopowder used as catalytic support is influenced by thermal treatment on the structure and specific surface area (Zykova et al., 2015), but the limitation of this method is the lack of high purity alumina powder (Siahpoosh et al., 2016). Chotisuwan et al. (2012) investigated the mesoporous alumina prepared from waste aluminum cans and showed that the surface area of the mesoporous γ-alumina obtained from aluminum isopropoxide using the sol-gel method was higher than that synthesized from aluminum hydroxide using the precipitation method. However, the use of the sol-gel method to prepare the γ-alumina is complicated and the starting materials are expensive (Chotisuwan et al., 2012;

Masouleh, Taghizadeh, & Yaripour, 2014; Siahpoosh et al., 2016), while γ-alumina nanoparticles can be synthesized from aluminum scrap by acid or alkali precipitation under mild conditions (Adans et al., 2016; Ahmedzeki et al., 2017; Asencios & Sun-Kou, 2012).

A considerable number of studies have focused on the control precipitation method due to its use of inexpensive raw materials. Nanosized porous γ-alumina can be prepared by the control precipitation method using aluminum salts as the precursors and different precipitating agents. The synthesis conditions, including the pH of the solution, the aging time, the aging temperature, and the calcination temperature strongly affect the surface area and particle sizes of the alumina. Aluminum hydroxides have been synthesized from sodium aluminate and precipitated by various types of acids, such as hydrochloric acid, sulfuric acid, and nitric acid. But during the preparation procedures, sulfur oxides or nitrogen oxides can be formed as by-products, causing environmental damage (Parida et al., 2009; Khosla et al., 2013; Osman et al., 2017). Therefore, the use of hydrochloric acid as a precipitating agent is an appropriate alternative for alumina synthesis in order to avoid environmental impacts. In addition, the study of Ahmedzeki et al. (2017) reported that the surface area of synthetic materials decreased by increasing calcination temperature from 550 to 650 ^{o}C. The reaction is accelerated at higher calcination temperatures, resulting in smaller crystallites will be coalesced and form into crystallite with larger sizes. This step will decrease pore volume and surface area of synthetic materials by crystallite sintering. Therefore, the calcination temperature of 550 ^{o}C was chosen for the synthesis of γ-alumina in this work.

Since, there are various parameters that affect the synthesis of γ-alumina, studying the effects of variables simultaneously may require a large number of experiments. Therefore, the response surface methodology (RSM) based on the central composite design (CCD) has been applied to find the optimal values of various parameters for γ-alumina synthesis from aluminum scrap using the precipitation method to achieve the maximum performance of fluoride ion adsorption. The fluoride adsorption capacity on the γ-alumina prepared under the optimum conditions has been associated with an optimal surface area of adsorbent material containing pores with an available volume. RSM is a collection of mathematical and statistical techniques useful for developing, improving, and optimizing processes. This methodology can be used to define the relationships between the response and the independent parameters with a minimum number of experiments. After application of the experimental design, linear regression can be used to obtain the results with a mathematical equation or a second-order (quadratic) model that explains the relationships between various parameters affecting the response (Chatterjee, Kumar, Basu, & Dutta, 2012; De Sales, Magriotis, Rossi, Resende & Nunes, 2013).

2. Objectives

In this research, the inexpensive process of synthesizing γ-alumina nanoparticles from the acid precipitation of aluminum hydroxide gel obtained from aluminum scrap under mild conditions was studied. The main purpose of this work was to investigate the relationship between the effective parameters (pH of the solution, temperature, and time of aging) and the γ-alumina nanoparticles with a high adsorption performance. The synthesis process was optimized by using response surface methodology based on a central composite design. Finally, the adsorption performance of synthetic alumina was tested by the removal of acid dye from an aqueous solution. RSM was also applied to evaluate the effect of experimental variables and their interaction in achieving the optimum conditions for acid dye removal by using synthetic alumina adsorbent. The equilibrium study was investigated to determine the maximum adsorption capacity of synthetic alumina.

3. Materials and methods

3.1 Materials

Aluminum scrap was collected from aluminum packaging, washed, and cut into small pieces. The chemical composition of the aluminum scrap, as analyzed by X-ray fluorescence spectrometry, consisted of 99.9% Al and traces of other components. The chemicals used in this work were all of analytical grade. These included sodium hydroxide (NaOH) and hydrochloric acid (HCl) 35.4% w/w (Ajax Finechem Pty Ltd), sodium fluoride (NaF) (Merck), and acid dye: Metanil yellow (type: anionic dye, chemical formula: $C_{18}H_{14}N_3NaO_3S$, color index: acid yellow

36, MW: 375.38 g/mol, λ_{max}: 414 nm) (Ajax Finechem Pty Ltd).

3.2 Optimization of γ-alumina synthesis from aluminum scrap

3.2.1 Preparation of γ-alumina from aluminum scrap

In this work, the process of γ-alumina synthesis from aluminum scrap was developed to investigate the effects of the main operating parameters (Asencios & Sun-Kou, 2012; Ahmedzeki et al., 2017). For each experiment, the values of the parameters (pH of the solution, temperature and time of aging) were defined according to the experimental design in Section 3.2.3. A total of 100 g of small piece aluminum scrap was dissolved in a stoichiometric amount of 3 M NaOH solution at room temperature to produce sodium aluminate solution ($NaAl(OH)_4$), as shown in Equation (1). This hot mixture was filtered to remove any impurities. After that, the sodium aluminate solution was diluted with deionized water, and 3 M HCl solution was added dropwise under gentle stirring at room temperature to reach the desired pH, resulting in the precipitation of an aluminum hydroxide gel ($Al(OH_3)$), as shown in Equation (2). The mixture in the glass reactor was immersed in a water bath to maintain the desired aging temperature and aging time. The optimization of γ-alumina synthesis using RSM based on CCD was applied to investigate how these parameters affected the process. After completion of the aging time, the aluminum hydroxide gel was filtered and washed many times with deionized water and dried at 80 °C for 6 h. The dry product was calcined in a muffle furnace at 550 °C for 3 h in air to form porous alumina. The reactions are shown in Equations (3) and (4):

$$2Al\,(s) + 2NaOH\,(aq) + 6H_2O\,(l) \rightarrow 2NaAl(OH)_4\,(aq) + 3H_2\,(g) \quad (1)$$

$$NaAl(OH)_4\,(aq) + HCl\,(aq) \rightarrow Al(OH)_3\,(s) + NaCl\,(aq) + H_2O\,(l) \quad (2)$$

$$Al(OH)_3\,(s) \rightarrow AlOOH\,(s) + H_2O\,(g) \quad (3)$$

$$2AlOOH\,(s) \rightarrow \gamma\text{-}Al_2O_3\,(s) + H_2O\,(g) \quad (4)$$

3.2.2 Fluoride adsorption experiments

To determine the optimum conditions for the synthesis of alumina as an adsorbent, the adsorption of fluoride ions onto the alumina samples was tested by placing 100 mL of the 50 mg/L fluoride concentration into the flask. The pH was adjusted to 6.0 with 0.1 M HCl, and 0.2 g of the alumina sample was added. The mixture was agitated at 200 rpm by the shaker at room temperature for 3 h. Then, the mixture was centrifuged to separate out the adsorbent. The remaining fluoride concentration was analyzed by ion chromatography. The fluoride adsorption capacity was calculated using Equation (5) as follows:

$$q = \frac{(C_o - C)\,V}{m} \quad (5)$$

where q is the amount of fluoride adsorbed per mass of adsorbent or (mg/g); C_o and C are the initial and final fluoride concentrations (mg/L); V is the volume of the solution sample (L); and m is the mass of the adsorbent (g).

3.2.3 Experimental design for γ-alumina synthesis

Response surface methodology is a statistical technique that uses experimental data obtained from a specified experimental design to determine the regression model and optimize the process conditions. The statistical analysis of variance (ANOVA) is useful for testing whether the process parameters are of statistical significance. The response factor is correlated to the parameters using a quadratic model as per Equation (6)

$$Y = \beta_o + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i=1}^{2}\sum_{j=i+1}^{2}\beta_{ij} X_i X_j \quad (6)$$

where Y is the predicted response; X_i, X_j are the uncoded independent parameters; and β_o, β_i, β_{ii}, and β_{ij} are the model coefficients (Chatterjee et al., 2012; De Sales et al., 2013).

In this work, the synthesis of alumina from aluminum scrap was investigated using statistically designed experiments to study the effects of three independent parameters: the pH of the solution, the temperature, and the aging time, and the adsorption capacity of fluoride on the synthesized alumina were used as the response. The choice of parameters and their levels was based on the previous studies of γ-alumina synthesis (Ahmedzeki et al., 2017; Asencios & Sun-Kou, 2012, Chotisuwan et al. 2012). The experiments were conducted according to a 5-level-3-parameter CCD, and the total number of

experiments was 20. The independent parameters and their levels are shown in Table 1. The response surface methodology statistical technique was used to analyze the experimental data by SigmaPlot to optimize the process conditions. The synthetic material obtained from the optimum condition was called γ-alumina, and it was used as an adsorbent for the removal of acid dye in further studies.

Table 1 Operating parameters and levels used for alumina synthesis

Operating parameters	Symbols (uncoded)	Code levels				
		–1.682	–1	0	+1	+1.682
pH of the solution	P	5.8	6.5	7.5	8.5	9.2
Aging temperature, °C	T	35	45	60	75	85
Aging time, h	H	2.5	8	16	24	29.5

3.2.4. Characterization of synthesized γ-alumina

Phase identification of the alumina sample was characterized by a Bruker D5005 X-ray diffractometer (XRD) using Cu-Kα radiation (λ = 1.5418 Å). The surface morphology was evaluated by scanning electron microscopy (SEM, model: FEI Quanta 250) at an acceleration voltage of 20 kV, and the elemental compositions were determined by energy dispersive X-ray spectroscopy (EDS) in an apparatus coupled to the electron microscope. The purity of the synthetic alumina was confirmed by X-ray fluorescence spectrometry (XRF). The specific surface area of the alumina sample was determined through the nitrogen adsorption–desorption isotherms using the Brunauer–Emmett–Teller method. The pore size distributions and diameters were calculated by the Barrett–Joyner–Halenda (BJH) method.

3.3 Optimization of acid dye adsorption onto γ-alumina

3.3.1 Acid dye adsorption experiments

Stock solutions of 1000 mg/L (1000 ppm) acid yellow 36 (AY36) were prepared by dissolving the appropriate amount of acid dye in distilled water to obtain the required concentration of solution in each experiment before being stored in a dark bottle.

The batch experiments were carried out by placing 100 mL of the 100 mg/L dye solution in 10 stoppered conical flasks at room temperature, adding an adsorbent dosage of 0.2 g (0.2% w/v), and adjusting the pH of the solution to 3. To determine the contact time in which the AY36 dye adsorption reached equilibrium, the mixtures were agitated at 200 rpm by the shaker at room temperature in time intervals between 30 to 300 min, respectively. The concentration of the residual AY36 solution in each flask was analyzed using a UV-visible spectrophotometer at 414 nm. All experiments were carried out in duplicate and the average values were used for analysis. The amount of AY36 adsorbed by the synthetic alumina was calculated using Equation (7) as follows:

$$\%Adsorption = \frac{C_o - C_t}{C_o} \times 100 \quad (7)$$

where C_o is the initial dye concentration (mg/L) and C_t is the dye concentration (mg/L) at time t (min).

3.3.2 Experimental design for acid dye adsorption

The adsorption of the AY36 dye was performed in batch experiments. A 5-level-3-parameter CCD was applied and a total of 20 experiments were conducted to study the effects of the initial dye concentration, adsorbent dosage, and pH of the dye solution on the removal of AY36 using synthetic alumina. The independent parameters and their levels are shown in Table 2, and the responses were obtained from the adsorption of AY36 on synthetic alumina which was analyzed by a UV-visible spectrophotometer at 414 nm. Response surface methodology statistics were used for the experimental data analysis by SigmaPlot to optimize the process conditions.

3.3.3 Adsorption isotherms

The adsorption isotherms were studied in the range of AY36 dye concentrations between 100 and 500 mg/L under the optimum conditions. The amount of dye adsorbed per mass of adsorbent at equilibrium was calculated using Equation (8):

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$$q_e = \frac{(C_o - C_e)\,V}{m} \quad (8)$$

where q_e is the amount of dye adsorbed per mass of adsorbent at equilibrium; C_o and C_e are the initial and equilibrium dye concentrations (mg/L); V is the volume of the solution sample (L); and m is the mass of the adsorbent (g).

Table 2 Operating parameters and levels used for AY36 adsorption

Operating parameters	Symbols (uncoded)	Code levels				
		–1.682	–1	0	+1	+1.682
pH of the solution	P	2.6	4	6	8	9.4
Mass of adsorbent, g	M	0.06	0.2	0.4	0.6	0.74
Initial concentration, mg/L	C	16	50	100	150	184

4. Results and discussion

4.1 Statistical analysis for γ-alumina synthesis

Response surface methodology was applied to study the relationships among the fluoride adsorption capacity of synthetic γ-alumina from each condition (response, Y) and three operating parameters: the pH of the solution (P), the temperature (T), and the aging time (H). Twenty experiments were carried out according to the CCD, and the parameters and experimental responses are presented in Table 3. A regression model was performed using analysis of variance (ANOVA). The significance of each parameter was analyzed in terms of its probability value (*p*-value), as shown in Table 4. The response factor was correlated to the parameters using a quadratic regression model, as shown in Equation (9). At the 95% confidence level, the coefficient of determination (R^2) for this process was 0.9104, which indicated that the model is quite appropriate for the relationships examined in the current study.

$$Y = -47.847 + 21.175P + 0.690T + 0.123H - 1.466P^2 - 0.001T^2 - 0.008H^2 - 0.064PT + 0.113PH - 0.009TH \quad (9)$$

The ANOVA results showed that the pH of the solution (P) had the lowest *p*-value (0.0049) among the parameters and the square term of pH (P^2) was also significant ($p < 0.05$). These results indicate that the pH of the solution was the most important parameter in the γ-alumina synthesis process. During the aluminum hydroxide precipitation step, the pH had a significant effect on the degree of aggregation and dissolution of aluminum hydroxide gel grains, resulting in the formation of the surface area of alumina. This result is in agreement with the research studies by Ahmedzeki et al. (2017) and Asencios and Sun-Kou (2012). In addition, the linear term aging temperature (T) was shown to have a significant effect ($p = 0.05$), while the aging time (H) was not significant ($p > 0.05$). The quadratic terms T^2 and H^2 also had less significant effects. However, the interaction effects of the parameters PT, PH, and TH were significant, showing that the aging temperature and time (TH) are correlated in the synthesis of alumina. Increasing the aging temperature can reduce the aging time; therefore, the determination of the optimum conditions for γ-alumina synthesis requires consideration of the interaction effects of pH with the other two parameters.

4.2 The effects of operating parameters on adsorption capacity

The response surface plots and contour plots of the fluoride adsorption capacity using the synthetic alumina from each condition, obtained by Equation (9) at the center point of CCD are displayed in Figure 1. Figure 1a shows the effects of the aging temperature and pH of the solution on the adsorption capacity of the synthesized alumina with a constant aging time at 16 h. It was found that at low aging temperatures, the adsorption capacity slightly increased when the pH was near its medium value and then decreased sharply. At a high aging temperature and low pH, the adsorption capacity was at its highest. The pH of the solution during precipitation strongly affects the surface area of synthetic alumina due to the level of aggregation and precipitation of aluminum hydroxide gel, resulting in a high surface area of alumina. Figure 1b shows the effects of aging time

and pH of the solution on the adsorption capacity of the synthesized alumina with a constant aging temperature (60 °C). At low pH values, the adsorption capacity increased as the aging time increased. Figure 1c shows the effects of aging time and temperature on the adsorption capacity of the synthesized alumina with a constant pH of 7.5. It was found that at low-aging temperatures, the adsorption capacity increased as the aging time increased. The significance of the interaction parameters between the aging time and temperature was the lowest among all interactions. This means that alumina synthesis will take less aging time at high aging temperatures.

Table 3 Central composite design arrangements and experimental results in fluoride adsorption capacity using synthetic alumina from each condition

Run No.	P (pH)	T (^oC)	H (h)	Fluoride adsorption capacity (mg/g)	Run No.	P (pH)	T (^oC)	H (h)	Fluoride adsorption capacity (mg/g)
1	6.5	45	8	43.53	11	7.5	35	16	42.12
2	8.5	45	8	35.88	12	7.5	85	16	44.34
3	6.5	75	8	44.64	13	7.5	60	2.5	39.92
4	8.5	75	8	36.18	14	7.5	60	29.5	44.44
5	6.5	45	24	45.18	15	7.5	60	16	41.71
6	8.5	45	24	44.16	16	7.5	60	16	42.86
7	6.5	75	24	45.00	17	7.5	60	16	44.40
8	8.5	75	24	37.11	18	7.5	60	16	44.44
9	5.8	60	16	43.65	19	7.5	60	16	44.72
10	9.2	60	16	35.30	20	7.5	60	16	43.42

Table 4 Summary output from data analysis in alumina synthesis step

ANOVA	Significance F	p-value
Regression	0.00038	
Intercept		0.1143
Linear ; P		0.0049
T		0.0561
H		0.8287
Square; P*P		0.0024
T*T		0.7054
H*H		0.1923
Interaction; P*T		0.0774
P*H		0.0951
T*H		0.0514

4.3 Optimization of γ-alumina synthesis from aluminum scrap

The optimal conditions to achieve maximum fluoride adsorption capacity on γ-alumina nanoparticles were a pH of 6.0, an aging temperature of 75 °C, and an aging time of 8 h, followed by calcination at 550 °C for 3 h. The predicted fluoride adsorption capacity was evaluated as 46.28 mg/g.

To check the validity of the quadratic model in Equation (9), a sample was synthesized under the predicted optimum conditions and efficiently used for fluoride removal. The fluoride adsorption capacity was found to be 45.95 mg/g with 83% adsorption. This is very close to the predicted value, which indicates that the model has high accuracy. The fluoride adsorption capacity on the γ-alumina prepared under the optimum conditions was associated with an optimal surface area of adsorbent material containing pores with an available volume. According to the experimental results and predicted values, under acidic conditions at pH 6.5, the degree of aggregation of the aluminum hydroxide gel grains was probably favored, leading to the formation of aluminum oxides with small pores and a high surface area

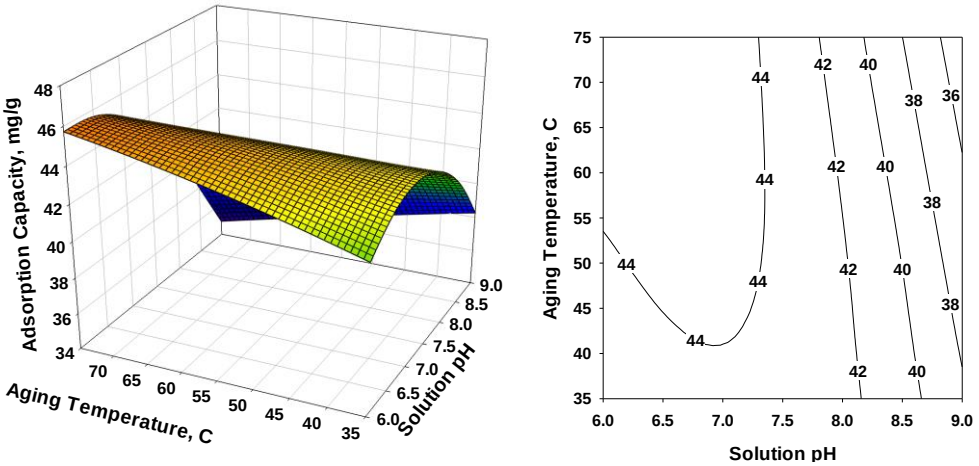
after calcination. This result is in agreement with the research undertaken by Hellgardt and Chadwick (1998). γ-alumina nanoparticles with a high fluoride adsorption capacity were acquired from this synthesis process. The decrease in surface area at higher pH values (7-9) corresponded to the increasing crystalline size of the alumina (Ahmedzeki et al., 2017), resulting in a low fluoride adsorption capacity. Since the dissolution of alumina gel grains is favored, this results in the formation of oxides with larger pores and lower surface area. The crystalline size of the formed alumina is dependent on the pH of the precipitation of the gel grains (Okada, Nagashima, Kameshima, Yasumori & Tsukada, 2002). In terms of the aging temperature, it was found that the sodium aluminate solution aged at high temperatures around 75 °C could form a high yield of aluminum hydroxide gel. This trend can be explained by the fact that high temperature aging leads to an acceleration of aluminum hydroxide gel formation and more orderly growth of the gel network. The adsorption performance of synthetic alumina was also tested by the removal of acid dyes from the aqueous solution in further studies.

4.4 Characterization of γ-alumina

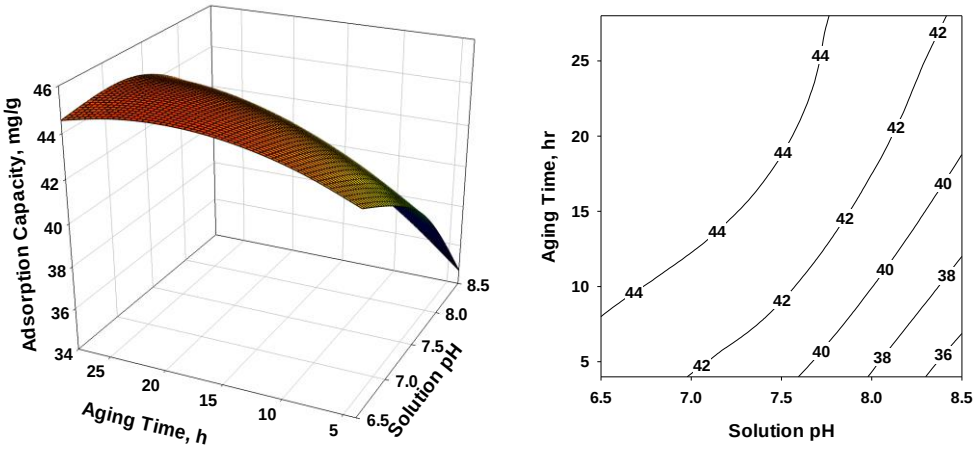
In this work, the aluminum hydroxide precipitated at optimum conditions (solution pH at 6.5, aging temperature of 75 ^{o}C and aging time of 8 h) had a high yield and was calcined at 550 °C for 3 h. The phase transformation of alumina synthesized from the above optimum condition was analyzed by XRD, and the resulting pattern is shown in Figure 2. The three dominant peaks of synthetic alumina were characterized by diffraction intensities at 2θ, 37.5°, 45.6°, and 66.8°, corresponding to the γ-alumina structure characterized at 2θ of 37.7°, 45.9°, and 66.9°, respectively. The obtained peaks were also found to be in agreement with standards database (JCPDS card 00-029-0063) (Huang, Bartholomew, Smith & Woodfield, 2013). These results are in agreement with the research study of Du, Wang, Su, and Li, (2009), who reported the effects of the pH value on the microstructure and phase transformation of aluminum hydroxide. The aluminum hydroxide precipitated at pH 7 was boehmite (AlOOH) which transformed to γ-alumina at 500–700 °C via the γ-AlOOH → γ-Al_2O_3 pathway. Moreover, the studies of Asencios and Sun-Kou (2012) and Matori, Wah, Hashim, Ismail, and Zaid, (2012) also reported that boehmite transforms to γ-alumina at a temperature range of 500-750 °C. The surface morphology was investigated using SEM and EDS. The SEM micrograph in Figure 3a shows the strong agglomeration of γ-alumina particles with various sizes in the nanoscale range. The EDS spectrum of synthesized γ-alumina in Figure 3b shows the major peaks of Al and O, which confirms the formation of alumina (Al_2O_3). The chemical composition of synthetic γ-alumina was confirmed by XRF analysis as containing 94.3% Al_2O_3, 0.152% SiO_2, 1.72% Na_2O, 3.50% Cl, and the balance of other components as traces.

An investigation of the nitrogen adsorption–desorption isotherms as shown in Figure 4. The isotherm shape is related to the type of adsorbent porosity. The pore size distribution of alumina synthesized at optimum conditions showed that the specific surface area and average pore diameter were calculated by the Brunauer–Emmett–Teller (BET) method, and the synthetic alumina was found to have a high surface area of 283.23 m^2/g, a bulk density of 1.000 g/$cm^3$and an average pore diameter of 5.03 nm. The pore volume was estimated by the Barret–Joyner–Halenda (BJH) method and was found to be 0.38 cm^3/g. The optimized γ-alumina with a high surface area and nanosized pores indicated its reasonably high adsorption capacity. In addition, the particle size can be estimated using the nitrogen adsorption techniques. The approximate diameter of alumina particles which assumed spherical shape was calculated from the BET method. It was shown that the synthetic material was γ-alumina nanoparticles with an average particle size of 21.18 nm.

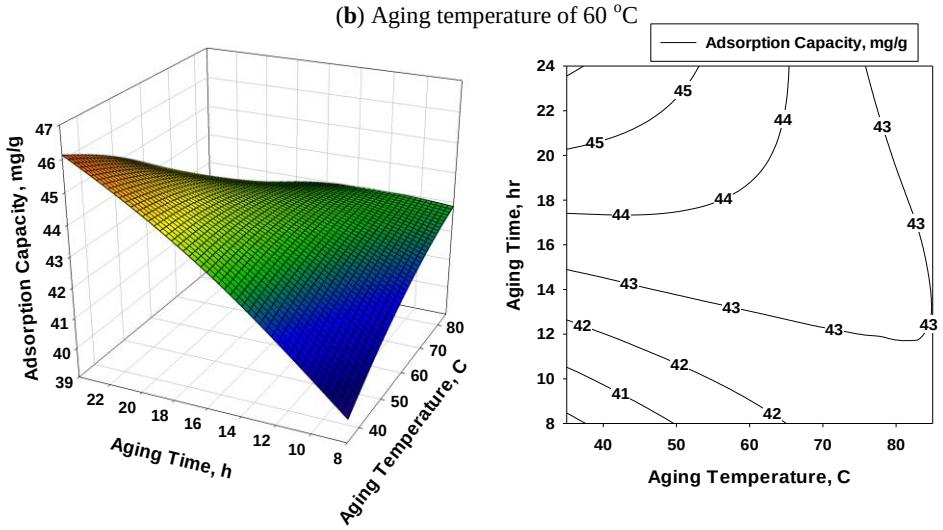
The results of the above analysis showed that the precipitation of aluminum hydroxides at a low pH value led to the formation of nanoparticles and aging at high temperatures led to the acceleration of aluminum hydroxide gel formation. This was related to the γ-alumina having a high surface area after calcination. The interaction effect between the aging time and aging temperature was the smallest, which means that the alumina synthesis will take less aging time at high aging temperature.



(**a**) Aging time of 16 h



(**b**) Aging temperature of 60 ^{o}C



(**c**) Solution at pH 7.5

Figure 1 Response surface plots and contour plots of fluoride adsorption capacity using synthetic γ-alumina versus three operating parameters for the γ-alumina synthesis process at the center point of CCD

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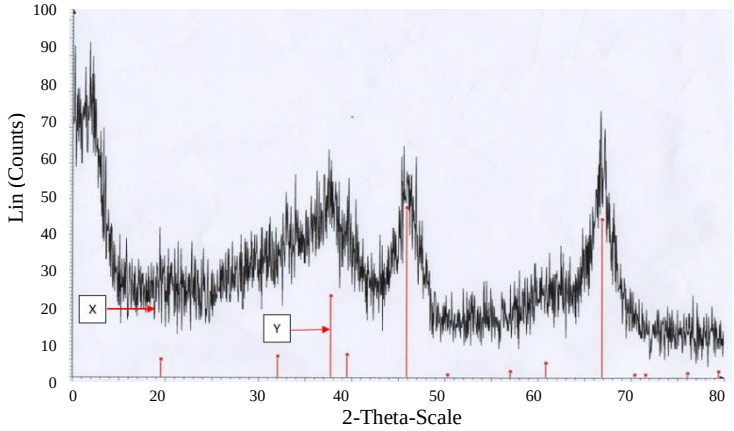
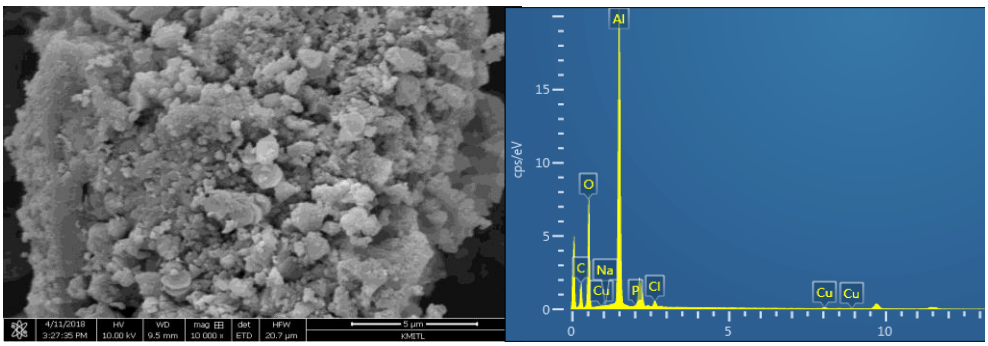


Figure 2 XRD pattern of the alumina synthesized from aluminum scrap under optimum conditions in this work (x) and pure γ-aluminum oxide (y, red line)



(a) (b)

Figure 3 (**a**) SEM image and (**b**) EDS spectrum of the γ-alumina synthesized from alumina scrap

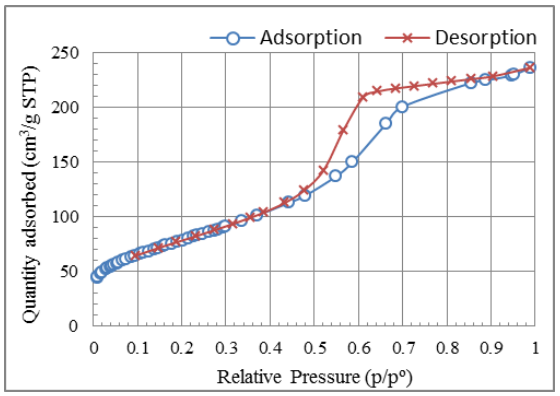


Figure 4 Isotherm linear plots for nitrogen on γ-alumina synthesized from alumina scrap

4.5 Optimization of acid dye adsorption on synthetic γ-alumina

The adsorption of large dye molecules using synthetic γ-alumina as an adsorbent was carried out to evaluate the adsorption capacity. The relationship between the adsorption of AY36 on synthetic γ-alumina as the response (Z) and three independent parameters, the pH of the dye

solution (P), the mass of the adsorbent (M), and the initial dye concentration (C) were studied and the results were analyzed using RSM, as shown in Table 5. The response factor was correlated to the parameters using a quadratic regression model, as shown in Equation (10). At the 95% confidence level, the coefficient of determination (R^2) for this process was 0.9455. This indicates that the model was appropriate to determine the relations between the parameters and the response.

$$Z = 86.850 - 2.642P + 183.010M - 0.410C - 0.125P^2 - 294.172M^2 - 0.001C^2 + 4.487PM + 0.007PC + 1.026MC \quad (10)$$

The significance of each parameter, as determined by ANOVA, was analyzed by its probability value (*p*-value) as shown in Table 6, where the mass of the adsorbent (M) had the lowest *p*-value (0.0063) among all parameters and the square term of M was also significant ($p < 0.05$). These results indicate that the mass of γ-alumina had a significant effect on the adsorptive removal of AY36. The interaction between the mass of the adsorbent and the initial concentration (MC) was also found to be significant. The surface plots and contour plots of the AY36 adsorption percentage on γ-alumina obtained by Equation (10) at the center point of CCD are displayed in Figure 5.

Table 5 Central composite design arrangement and experimental results in AY36 adsorption using synthetic γ-alumina from optimum conditions

Run No.	P (pH)	M (g)	C (mg/L)	AY36 adsorption percentage (%)	Run No.	P (pH)	M (g)	C (mg/L)	AY36 adsorption percentage (%)
1	4	0.2	50	98.74	11	6	0.064	100	27.69
2	8	0.2	50	86.76	12	6	0.74	100	98.96
3	4	0.6	50	97.80	13	6	0.4	16	98.37
4	8	0.6	50	92.16	14	6	0.4	184	81.52
5	4	0.2	150	59.71	15	6	0.4	100	98.58
6	8	0.2	150	49.88	16	6	0.4	100	98.74
7	4	0.6	150	98.97	17	6	0.4	100	98.54
8	8	0.6	150	97.15	18	6	0.4	100	98.49
9	2.6	0.4	100	99.53	19	6	0.4	100	98.58
10	9.4	0.4	100	90.87	20	6	0.4	100	98.49

Table 6 Summary output from data analysis in AY36 adsorption step

ANOVA	Significance F	p-value
Regression	0.000035	
Intercept		0.0114
Linear ; P		0.6691
M		0.0063
C		0.0829
Square; P*P		0.7706
M*M		0.0000
C*C		0.1888
Interaction; P*M		0.4427
P*C		0.7466
M*C		0.0010

Figure 5a shows the effects of the pH and adsorbent mass on the percentages of adsorption with a constant initial AY36 concentration of 100 mg/L. The adsorption percentage increased when the mass of the adsorbent increased in aqueous solution with a low pH. This is in agreement with the research studies of Banerjee, Dubey, Gautam, Chattopadhyaya, and Sharma (2017) and Parida et

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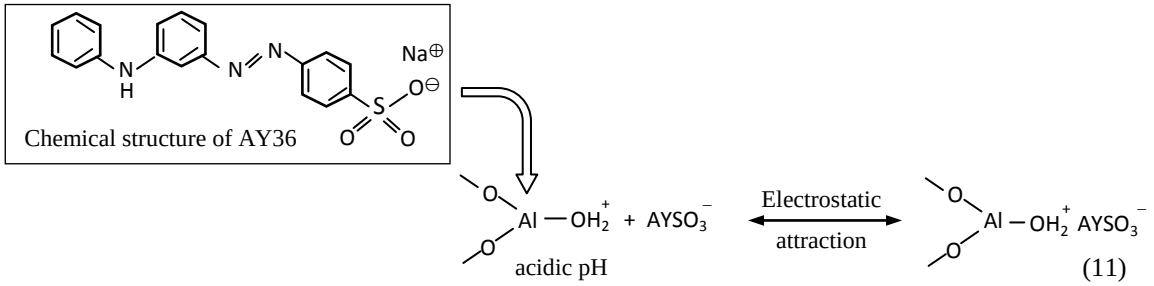
al. (2009). Acid dye adsorption depends on the pH of the solution and can be explained by the changes in the surface properties of the adsorbent in aqueous solution. At a high pH, negatively charged hydroxide ions were abundant and can compete with anions from acid dyes, which results in less acid dye adsorption. The surface properties of alumina nanoparticles are strongly governed by the aqueous pH condition. Thus, acid dyes are highly adsorbed at acidic pH values, the surface of adsorbent is charged positively and this electrostatically attracted the anionic dyes and leads to a higher adsorption of acid dyes as shown in Equation (11). A similar observation has been reported by Khosla et al. (2013) and Banerjee et al. (2017) for the adsorption of the anionic dyes, acid orange-7 and acid orange G respectively.

Figure 5b shows the effects of the initial concentration and mass of adsorbent on the adsorption percentage of AY36 with a constant pH of 6.0. When the mass of adsorbent was constant, the adsorption percentage decreased as the initial dye concentration increased, possibly due to saturation of the adsorbent surfaces. A large amount of adsorbent was used, resulting in increased dye adsorption capacity due to more active adsorption sites. The maximum adsorption percentage of AY36 was obtained when the initial dye concentrations were studied in the range of 50–150 mg/L. The appropriate amount of γ-alumina adsorbent was 0.5 g.

Figure 5c shows the effects of initial concentration and pH of the solution on the percentages of adsorption with the constant mass of adsorbent at 0.4 g. It was found that at any initial concentration, the percentage of adsorption increased as the pH of the solution decreased. The optimum conditions to achieve the maximum percentage of adsorption on synthetic γ-alumina were an initial concentration of 100 mg/L, pH 2.6, and an γ-alumina dosage of 0.5 g. The predicted AY36 adsorption was evaluated as 100%. To check the validity of the fitted model (Equation (10)), a sample was prepared under the optimum conditions. The adsorption percentage of AY36 onto synthetic γ-alumina was found to be 99.8%.



(11)

4.6 Adsorption isotherms

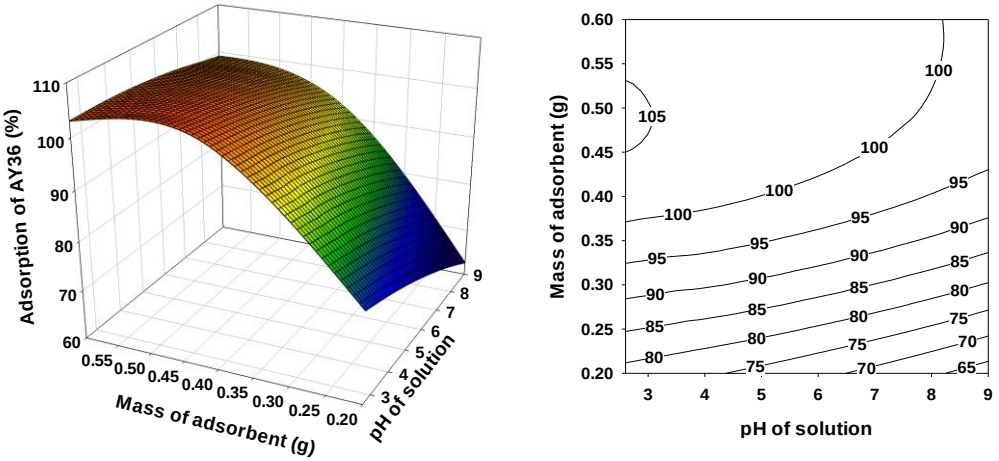
The adsorption isotherm, which describes the relation between the equilibrium concentration of AY36 in aqueous solution and the quantity of AY36 on the surface of γ-alumina at constant temperature, was investigated. The equilibrium data were studied by the various adsorption isotherm models with the following equations:

Langmuir isotherm, $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$ (12)

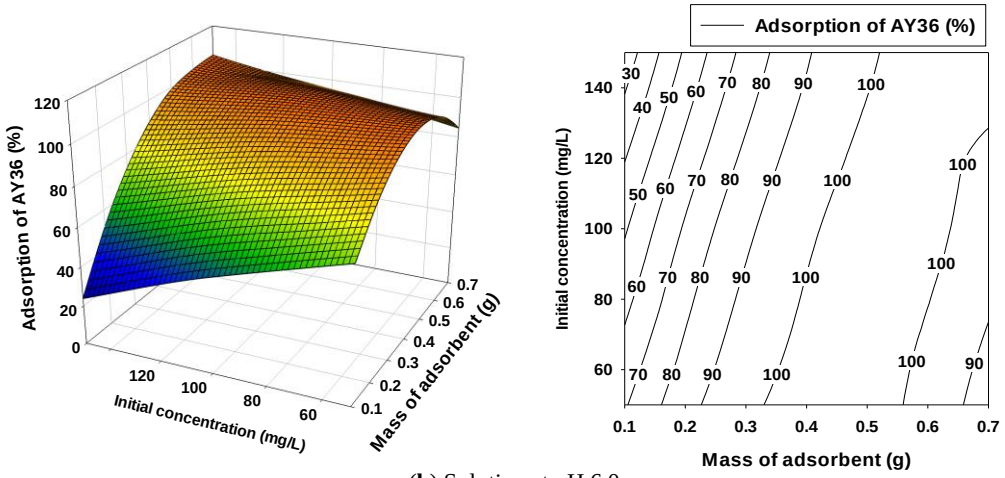
Freundlich isotherm, $q_e = K_F C_e^{1/n}$ (13)

where q_m indicates the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant, which indicates the adsorption distribution constant. K_F and n are the Freundlich constants. The value of K_F indicates the adsorption capacity in mg/g and the value of 1/n indicates the strength of the adsorbent material.

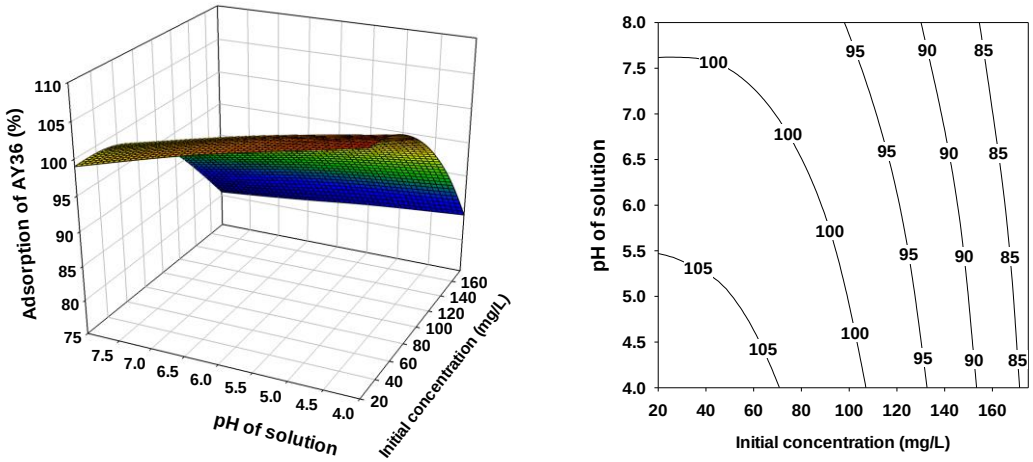
The adsorption isotherms were studied in the range of AY36 dye concentrations between 100 and 500 mg/L under the conditions of pH 2.6 and an γ-alumina adsorbent mass of 0.5 g. The contact time in which AY36 dye adsorption reached the equilibrium was 1 h. The equilibrium data fitted with different adsorption isotherms are shown in Figure 6. The constant coefficients obtained from various isotherm equations are given in Table 7. It was found that a value of R^2 (0.9909) was mostly satisfied in the Langmuir isotherm plot. Therefore, the equilibrium behavior was well described by the Langmuir isotherm model, and the corresponding monolayer maximum adsorption capacity was found to be 125 mg/g.



(**a**) Initial concentration of 100 mg/L



(**b**) Solution at pH 6.0

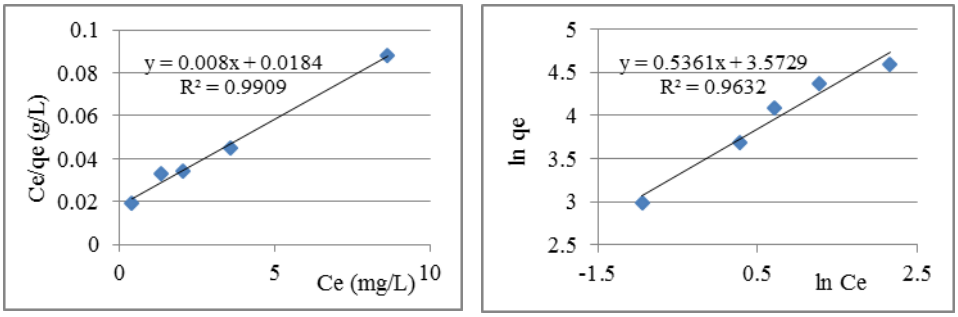


(**c**) Adsorbent mass of 0.4 g

Figure 5 Response surface plots and contour plots of the AY36 adsorption percentage on synthetic γ-alumina versus three operating parameters for dye adsorption at the center point of the CCD

Additionally, the important characteristics of the Langmuir isotherm can be explained by the separation factor R_L, which is calculated by Equation (14). In this experiment, the value of R_L was found in the range of 0.005–0.022, which lies between 0 and 1, indicating favorable adsorption, while the Freundlich constants calculated for the adsorption of AY36 on γ-alumina showed values of 1/n < 1 (0.5361). This indicates that when the concentration of dye under investigation increased, the adsorption capacity (K_F) decreased due to saturation of the adsorption sites.

$$R_L = \frac{1}{1+ K_L C_o} \quad (14)$$



(**a**) (**b**)

Figure 6 Isotherm plots for the AY36 adsorption on γ-alumina (a) Langmuir and (b) Freundlich

Table 7 Equilibrium isotherm coefficients obtained for AY36 adsorption on γ-alumina nanoparticles

Langmuir isotherm model			Freundlich isotherm model		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
125	0.435	0.9909	35.6	1.865	0.9632

5. Conclusion

Response surface methodology based on the central composite design was successfully applied to study the optimum conditions and the effects of the parameters on γ-alumina synthesis from aluminum scrap. The pH value during the aluminum hydroxide precipitation step had a significant effect on the degree of aggregation and dissolution of aluminum hydroxide gel grains, influencing the surface area formation of alumina. The optimum conditions for γ-alumina synthesis were pH 6.5, an aging temperature of 75 °C, an aging time of 8 h, and subsequent calcination at 550 °C. High-surface area γ-alumina nanoparticles of 283 m^2/g can be prepared from inexpensive raw materials by the control precipitation method. Moreover, the AY36 adsorption process on γ-alumina nanoparticles using RSM was successfully employed to study the effects of the parameters and the optimum conditions. The adsorption process with an initial dye concentration of 100 mg/L and synthetic γ-alumina adsorbent dosage of 0.5 g at pH 2.6 at room temperature was found to be optimum, and 99.8% AY36 removal was achieved. The phenomenon for the removal of AY36 on γ-alumina nanoparticles was well described by the Langmuir isotherm model. The γ-alumina synthesized in this work had a high adsorption capacity of acid yellow 36, showing that the γ-alumina nanoparticles was utilized as adsorbent for the removal of acid dyes.

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