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كفاءة إدمصاص اصباغ نسيج على ألومينا منشطة ومثبتة

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الملخص:

تصف هذه الدراسة تحضير ألومينا منشطة معدلة ومثبتة (MIAA) واستعمالها في ازالة اصباغ نسيج في وسط مائي. تم اجراء التثبيت باستعمال طريقة هلام سول، بينما جرت التعديلات اثناء عملية التحضير بإضافة مسحوق الألومينا المنشطة. وتم اجراء التجربة على شكل دفعات عند درجة حرارة 1 ± 20 درجة مئوية وذلك لدراسة تأثير المعامل المختلفة مثل زمن الاتصال، معدل التحريك، التركيز الأولي لمحلول الصبغة والجرعة من (MIAA). لقد كانت النسبة المئوية لكفاءة ازالة صبغة سيباكرون الصفراء المنشطة بتركيز أولي 400 مج/ليتر أكثر من 90% في زمن اتصال دقيقة. وعند تطبيق معامل إدمصاص كل من لانجموير او فرويندش الايزوثيرمي وجد أنها تتطابق مع البيانات المتحصلة بمعامل ارتباط يساوي 0.99. وقد وجد بأن أعلى سعة إدمصاص للصبغة على (MIAA) تصل إلى 25 مج/جرام عند تركيز أولي يساوي 400 مج/ليتر. ولقد وجد بأن ألومينا (MIAA) عند إعادة استعمالها بعد إخضاعها لأربع عمليات إعادة تجديد حرارية أو كيميائية متتالية قد احتفظت بكفاءة إدمصاص تصل إلى 85%. وكانت عملية التجديد الحراري قد تمت باستعمال فرن دثاري عند حرارة 450 درجة مئوية، بينما تمت عملية التجديد الكيميائي عن طريق غمر الألومينا (MIAA) في محلول هيدروكسيد الصوديوم المولاري (0.1 مولاري) لمدة ساعتين. كما وجد بأن ألومينا (MIAA) ذو كفاءة إدمصاص للصبغة في الماء الراجع لعينات نسيج حقيقية معطيا كفاءة ازالة تصل إلى 75%.



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ORIGINAL ARTICLE

Adsorption of textile dye onto modified immobilized activated alumina



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Abstract The study describes the synthesis of modified immobilized activated alumina (MIAA) and its application for the removal of textile dye from aqueous media. Immobilization was carried out by using the sol–gel method while modifications were made during the synthesis by adding powder activated alumina. Batch adsorption experiments were carried out at 20 ± 1 °C to see the effect of different parameters like contact time, stirring rate, initial concentration of the dye and dose of MIAA. The removal efficiency of Cibacron reactive yellow dye with an initial concentration of 400 mg/L was greater than 90% for 90 min contact time. Langmuir and Freundlich adsorption isotherms were applied which fitted the data with an R^2 value of 0.99. The maximum adsorption capacity of MIAA was 25 mg/g at the initial dye concentration of 400 mg/L. MIAA can be regenerated thermally and chemically with the dye removal efficiency remained above 85% during the first 4 regeneration cycles. Thermal regeneration was achieved in a muffle furnace at 450 °C while chemical regeneration was done by immersing MIAA in 0.1 M NaOH solution for 2 h. MIAA also proved effective for the adsorption of dyes from actual textile wastewater giving a removal efficiency of 75%.

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1. Introduction

Textile wastewater is an amalgam of pollutants but mainly it is characterized by high levels of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), dissolved solids and colors (Naik et al., 2013; Ghaly et al., 2014). During the dyeing operation a significant amount of dyes remain unfixed on the fabric and they are directly discharged into the water

bodies in South Asian countries. Most of the textile dyes are resistant to photodegradation, oxidizing agents and biodegradation (Ventura and Marin, 2013). If the textile wastewater is not treated properly they tend to pose serious threats to the environment (Ratna and Padhi, 2012). Colored water is esthetically unbearable and the dyes prevent the sunlight to penetrate through the water which inhibits the photosynthetic activity affecting the aquatic life (Ghaly et al., 2014).

A number of conventional methods are present for textile wastewater treatment generally classified as biological, chemical and physical treatments (Naveed et al., 2006). The current study focuses on the adsorption technique as it is an effective

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and inexpensive treatment option. The adsorption process can be carried out by using various inexpensive and renewable adsorbents making the treatment even more inexpensive (Kumar and Sivanesan, 2007). The most perfect adsorbent used for color removal is an activated carbon (Gupta et al., 2011) but it is expensive and its regeneration is time consuming. Additionally powdered activated carbon requires filtration and centrifugation for its separation after use (Issa and Degs, 2009). Therefore, the researchers have focused their attentions to find out low-cost adsorbents for the removal of dyes from water. In this regard, agricultural waste materials like sugarcane bagasse (Sadaf et al., 2014; Noreen and Bhatti, 2014), peanut hulls (Nawaz et al., 2014), peanut husk Sadaf and Bhatti (2014), bottom ash and de oiled soya (Mittal et al., 2008), and corn stalk (Fathi et al., 2015) have been tried successfully. Similarly, the researchers have also synthesized adsorbents and tested for the removal of dyes (El-Bindary et al., 2014; Fu et al., 2015). Although, the adsorbents used in these studies exhibited excellent adsorption potential the procedures involved time consuming steps.

Powdered activated alumina is another efficient adsorbent but it too requires laborious separation processes after adsorption in water. In a study, powdered activated alumina has effectively been used for the removal of Alizarin Red (textile dyes from the water sample (Rehman et al., 2011).

The present study was designed to immobilize activated alumina adsorbent in order to facilitate its separation after use. The aim of the research was to prepare an immobilized adsorbent in the form of granules that could easily be separated from water without undergoing filtration and centrifugation processes. The sol-gel method has been adopted (Buelna and Lin, 1999) to prepare immobilized activated alumina granules in order to meet the objectives.

The adsorption efficiency of the modified immobilized activated alumina (MIAA) was tested by undertaking a set of experiments using Cibacron reactive yellow (a textile dye) as an adsorbate. Fig. 1 shows the structure of the dye. Reactive dyes are applied on cotton fabric and they form covalent bond upon fixation. The dyes require a high pH for fixation and still remain partially unfixed (Kolonko, 2005). These dyes have complex structures and are difficult to degrade (Chakraborty et al., 2003) hence cause problems to the environment. MIAA was tested for the treatment of actual textile wastewater collected from a local industry.

2. Materials and methods

2.1. Reagents

Chemicals used in the present study include aluminum tri-sec butoxide (Merck, Germany), paraffin oil (MP Biomedicals,

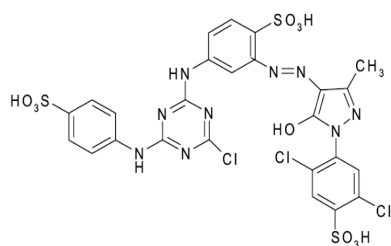


Figure 1 Cibacron reactive yellow dye.

LLC Germany), ammonia solution (Burdick and Jackson, Germany), nitric acid (Panreac, Spain), and activated alumina powder (Merck, Germany). Cibacron reactive yellow dye was obtained from a local textile industry.

Main equipments used in the study include muffle furnace (NEY M-525, USA), orbital shaker (Stuart SSL1, UK), and UV-visible spectrophotometer (Spectronic Genesys 5, USA).

2.2. Synthesis of immobilized adsorbent

Sol-gel method (Deng et al., 2006) was employed with some modifications in order to synthesize immobilized activated alumina. Boehmite sol was prepared by dissolving drop wise 25 mL of aluminum tri sec butoxide in 100 mL of distilled water and adding 1 g of powdered activated alumina at 75 °C with constant stirring. After dissolution, the solution was heated at 90 °C for one hour and 3.5 mL 1 M HNO₃ was added in the sol. The sol was refluxed in closed vials at 90 °C for 1 h. The sol formed (boehmite sol) was dropped into ammonia solution under paraffin oil layer with the help of a syringe. The droplets remained immersed in the ammonia solution for 45 min in order to form firm granules. After that the granules were washed thoroughly by distilled water and ethyl alcohol, dried and calcined at 450 °C for three hours to obtain new adsorbent named as modified immobilized activated alumina (MIAA). Fresh MIAA granules were synthesized for each batch experiment. The same procedure was applied to synthesize pure immobilized activated alumina that excluded the addition of powdered activated alumina.

Surface morphology of MIAA was examined by a scanning electron microscope (JEOL JSM-6460, Japan).

2.3. Adsorption study

Cibacron reactive dye adsorption experiments were conducted in order to determine the efficiency of MIAA adsorbent and the effect of controlling parameters like dose, contact time and stirring rate. The stock solution of 400 mg/L of dye was prepared by dissolving its 0.4 g in 1000 mL distilled water. All adsorption experiments were carried out in a 250 mL conical flask with 100 mL dye solution at 20 ± 1 °C using an orbital shaker at pH 7. Batch experiments were performed in triplicate for precision. The concentration of the dye in solution after adsorption was determined with the help of a calibration curve. The calibration curve was constructed by running standards of the dye on UV-Visible spectrophotometer at λ_{max} = 396 nm.

The effect of increase in the adsorbent dose on the dye removal was studied by varying the MIAA dose from 0.2 to 25 g/L in dye solutions with an initial concentration of 400 mg/L. In order to determine the optimum contact time, the flasks containing dye test solutions (with optimum MIAA dose) were agitated on the shaker for 5 to 105 min. Similarly, optimum stirring rate was determined by changing the rpm from 10 to 350.

The concentration of the dye was also varied from 5 to 700 mg/L in order to study its effect on adsorption. The specified amount of dye adsorbed q_e (mg/g) was calculated by Eq. (1).

$$q_e = \frac{C_i - C_s V}{m} \quad (1)$$

where C_i (mg/L) is the initial dye concentration, C_s (mg/L) final dye concentration at equilibrium, m (g) is the mass of adsorbent and V (L) is the volume of the solution (Noreen et al., 2013).

2.4. Isotherm study

An adsorption isotherm is developed when an equilibrium condition is developed between the adsorbent and the adsorbate during the adsorption process. There are various models to explain adsorption isotherms but the current study was focused on Langmuir and Freundlich isotherm models. Langmuir isotherm equation for monolayer adsorption is as follows:

$$\frac{C_s}{q_e} = \frac{C_s}{V_m} + \frac{1}{KV_m} \quad (2)$$

where q_e is the amount of dye adsorbed per unit mass of the adsorbent, C_s equilibrium concentration of dye, V_m is the adsorption capacity and K is Langmuir constant. The values of the constants were obtained from the intercept and the slope of the linear plot between q_e and C_s .

Freundlich isotherm equation given below:

$$\log q_e = \frac{1}{n} \log C_s + \log K_f \quad (3)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent, C_s equilibrium concentration, n is adsorption intensity and K_f is adsorption capacity. The value of the constant was obtained from the intercept and the slope of the linear plot between $\log q_e$ and $\log C_s$.

2.5. MIAA regeneration and actual textile wastewater treatment

The MIAA was regenerated both thermally and chemically. Thermally, the MIAA granules were heated at 450 °C for 30 min while chemically beads were shaken in 0.1 M sodium hydroxide solution for two hours. After the specified time, the chemically treated adsorbent was washed with distilled water until the washed water pH become neutral. Adsorption experiments using the regenerated MIAA were carried out as per the procedure mentioned above.

MIAA was also employed on actual textile wastewater collected from a local industry. The sample was light yellowish green in color and had relatively low amount of particulate matter. 500 mL of the sample was shaken well and then allowed to stand for 30 min. 100 mL of the supernatant was transferred to a 250 mL Erlenmeyer flask and the pH was adjusted to 7.0 by adding small amount of diluted HCl solution. The dye removal experiment was run under optimized adsorption conditions at 20 ± 1 °C using an orbital shaker. The absorbance scan spectrum (in the range 380–630 nm) revealed that the sample absorbance was maximum at 462 nm. Absorbances of both the original and treated samples were recorded at 462 nm in order to determine the % decrease in absorbance after the adsorption.

3. Results and discussion

The surface morphology of the MIAA granules before and after the adsorption of Cibacron dye is shown in Figs. 2A & 2B respectively. The SEM images exhibited that there was a

considerable change in the surface after adsorption of dye molecules which were supposed to adhere on the MIAA surface. Fig. 2C shows the appearance of the MIAA granules, the size of the white and hard granules varied from 3 to 6 mm. The MIAA morphology resembled the morphology of immobilized activated alumina granules prepared in one of our previous studies tackling the removal of fluoride from drinking water (Rafique et al., 2012).

Various experiments were conducted in order to find the appropriate adsorption conditions such as adsorbent dose, concentration of dye, contact time and stirring rate for the adsorption of dye on MIAA.

3.1. Effect of adsorbent dose

The study was carried out to examine the effect of MIAA dose on the Cibacron dye removal (adsorption) at 20 ± 1 °C. Fig. 3 exhibits that the percentage removal of dye increased with an increase in the MIAA dose (0.2–25 g/L). The increase in the dye removal with increasing MIAA dose was due to the increase in surface area as more active sites were available for adsorption. But after a specified adsorbent dose (15 g/L) the percentage of the dye removal did not increase considerably and that dose was considered as an optimum dose. The dye removal efficiency was 90% at the optimum MIAA dose.

3.2. Effect of contact time

Contact between the adsorbent and adsorbate increases the probability of the adsorption and it increases with longer contact time. The effect of contact time on dye adsorption is shown in Fig. 4. As the contact time increased, the adsorption capacity (q_e mg/g) of adsorbent also increased. The increase in the adsorption capacity in the first 45 min was very rapid. This might be due to the diffusion of dye molecules into the surface pores of the MIAA granules. After 45 min, the increase was less rapid probably due to the migration of dye molecules from upper adsorbent surface to inner pores. After 90 min there is no significant change with the increase in time because all the active sites have been occupied while reaching this time. Therefore, 90 min is considered as the optimum contact time for the adsorption.

3.3. Effect of stirring rate (rpm)

The rate of stirring (rpm) enhances the chance of adsorbate contact with the adsorbent. The influence of varying stirring rate on the dye removal efficiency of MIAA is depicted in Fig. 5. It was observed that at lower rpm, the removal capacity was low but as the rpm increased, the dye removal also increased. This might be due to the better contact between the adsorbent and the adsorbate at higher rpm. In this study the optimum stirring rate was considered as 250 rpm.

3.4. Effect of dye concentration

The effect of increasing dye concentration on adsorption capacity of MIAA is shown in Fig. 6. The adsorption capacity increased to a specified level then attained equilibrium. The maximum adsorption capacity of MIAA was 30 mg/g, when the initial dye concentration (C_i) was 600 mg/L.

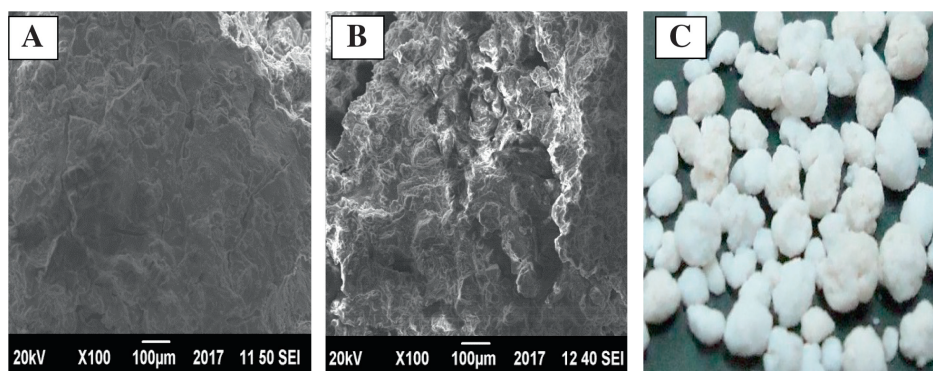


Figure 2 (A) SEM image of MIAA before adsorption, (B) SEM image of MIAA after adsorption MIAA and (C) MIAA granules.

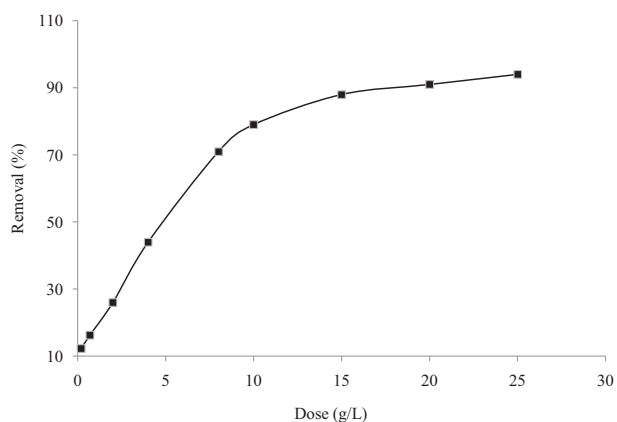


Figure 3 Effect of MIAA dose on removal of Cibacron reactive dye $20 \pm 1^\circ\text{C}$.

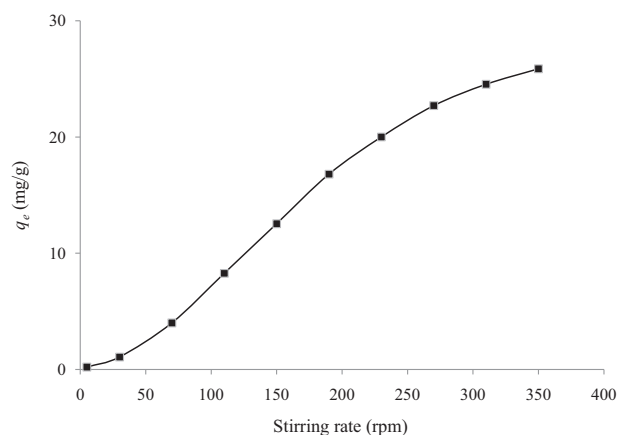


Figure 5 Effect of stirring rate on adsorption capacity of MIAA at $20 \pm 1^\circ\text{C}$.

3.5. Isotherm study

An adsorption isotherm defines the relation between the mass of the adsorbate that is retained on per unit mass of the adsorbent and the concentration of adsorbate at equilibrium (Lail, 2010). Freundlich and Langmuir isotherms provided a deep insight into the adsorption of dye on MIAA, refer to Figs. 7. The values of the adsorption constants, K_f , n , K and V_m are given in Table. 1.

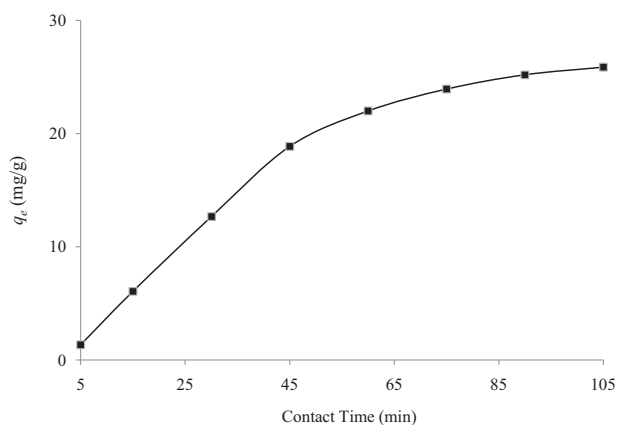


Figure 4 Effect of contact time on adsorption capacity of MIAA at $20 \pm 1^\circ\text{C}$.

The Freundlich model fitted well with the regression coefficient R^2 of 0.99. K_f is the Freundlich constant representing the relative adsorption affinity of the adsorbent toward the adsorbate molecules, and n is the adsorption intensity. If the adsorption intensity n is greater than unity it shows that the adsorption was favorable (Vijayaraghavan and Yun, 2008). In the present study the adsorption intensity was greater than unity (1.75).

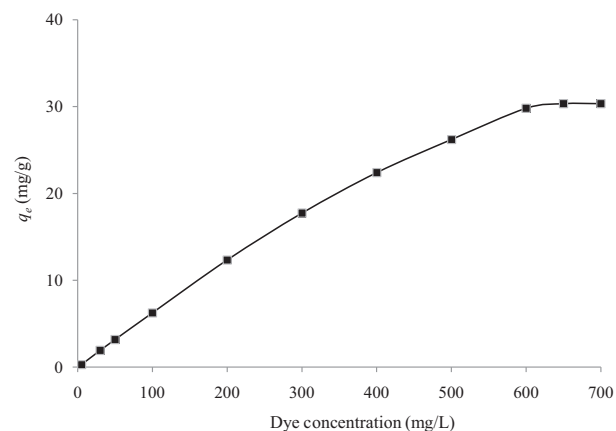


Figure 6 Effect of initial dye concentration on adsorption capacity of MIAA at $20 \pm 1^\circ\text{C}$.

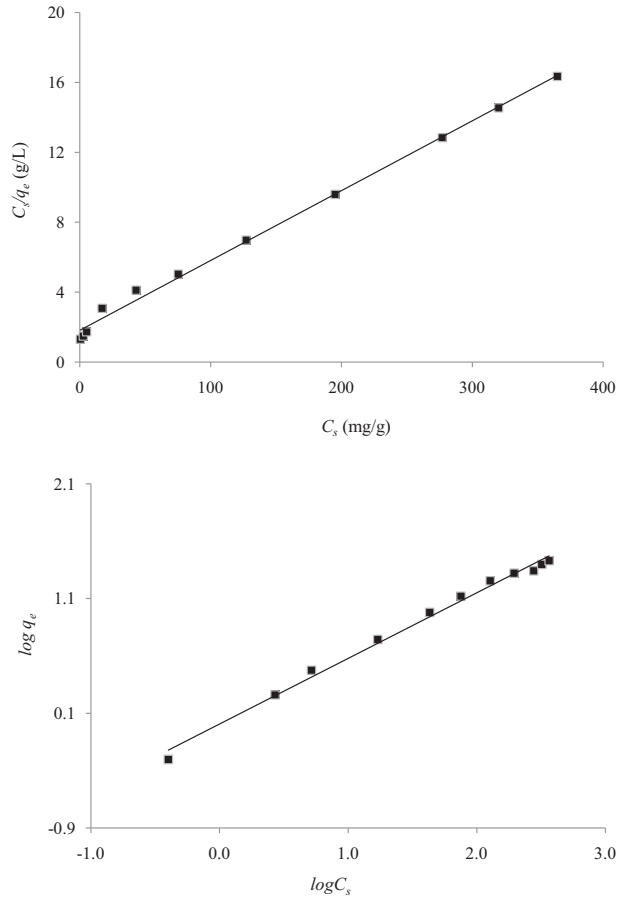


Figure 7 Langmuir (top) and Freundlich (bottom) isotherms for dye adsorption on MIAA at (20 ± 1 °C).

Table 1 Langmuir and Freundlich constant values.

Langmuir constant				Freundlich constant		
K (L/mg)	V_m (mg/g)	R^2	R_L	K_f (L/g)	n	R^2
0.02	25	0.9958	0.111	1.08	1.75	0.9924

The linear correlation coefficient R^2 value shows how well the data can be interpreted by Langmuir isotherm (Cheng et al., 2008). Langmuir adsorption isotherm also fitted very well for the dye adsorption on MIAA adsorbent with the regression coefficient R^2 of 0.99 as shown in Fig. 7. Values of the adsorption coefficient K and the monolayer capacity V_m calculated from Langmuir equation are given in Table 1. The adsorption capacity V_m (mg/g) shows strong electrostatic forces between the adsorbent and adsorbate. In the present study the value of V_m was significantly high i.e. 25 mg/g.

Langmuir constant K can help to estimate whether an adsorption system is favorable or not (Alagumuthu et al., 2011). In this regard, a dimensionless separation factor R_L is generally employed.

$$R_L = \frac{1}{1 + KC_i} \quad (4)$$

where, R_L = dimensionless separation factor, C_i = initial dye concentration, K = Langmuir constant (see Table 2).

Table 2 Value of R_L factor and type of isotherm.

R_L	Type of isotherm
Greater than 1	Unfavorable
1	Linear
Between 0 and 1	Favorable
0	Irreversible

Table 3 Chemical and thermal regeneration of MIAA and the corresponding % dye removal.

Regeneration cycles	Removal efficiency (%)				
	1	2	3	4	5
Thermal	95	95	85	85	80
Chemical	87	84	85	85	80

The parameter R_L indicates the isotherm shape accordingly:

In this work, R_L values were calculated against initial dye concentration, $C_i = 400$ mg/L is 0.111, which suggest favorable adsorption of the dye onto the MIAA at 20 ± 1 °C. This shows that Langmuir model describes the MIAA-dye adsorption phenomenon very well.

3.6. Regeneration and actual water sample treatment

Table 3 describes results of the MIAA regeneration study. The thermal treatment was efficient for the first two regeneration cycles where 95% removal efficiency was obtained. The efficiency reduced to 80% in the fifth cycle whereas in case of chemical regeneration the efficiency remained consistent during the first four cycles.

A real textile wastewater sample was also treated with MIAA under optimized adsorption conditions. 75% decrease in absorbance was observed by comparing the absorbance of the original and treated samples at 462 nm. Although the matrix of real sample was complex because of the presence of several competing contaminants, but still MIAA demonstrated considerable dye removal efficiency (75%). This is a worthy indication that the developed MIAA could effectively be used for the adsorption of textile wastewater.

4. Conclusions

The immobilization of activated alumina was achieved by using the modified sol-gel method. The modification involved addition of powder activated alumina during the synthesis process which resulted in the formation of firm immobilized granules. The adsorption of Cibacron reactive yellow dye was examined at different experimental conditions using modified immobilized activated alumina (MIAA). The research results corroborate that MIAA is an efficient adsorbent for Cibacron dye with a removal efficiency of 90%. Langmuir and Freundlich isotherm models fitted well the adsorption data with the regression coefficient R^2 of 0.99. The developed MIAA granules can easily be regenerated both thermally and chemically. MIAA also proved effective for the removal of dyes from actual textile wastewater.

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