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Removal of Reactive Brown 9 by Adsorption with Electrochemical Regeneration using Nyex 1000 as Adsorbent.

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Abstract

Textile industries are producing a huge amount of wastewater that contains harmful pollutants. The main pollutants in textile wastewater are dyes. In this work, adsorption and electrochemical regeneration of adsorbent Nyex 1000 have been studied using Reactive Brown 9 dye as adsorbate. Nyex 1000 successfully removed the dye from water, and then the adsorbent was regenerated electrochemically. The Regenerated adsorbent was retreated several times to check the change in regeneration efficiency. Regeneration efficiency remained more than 90% each time. To find more effective method of finding adsorbent capacity, kinetics were studied. It was found that Pseudo first order kinetic was more effective than pseudo second order kinetic.

Keywords: Adsorbent, Brown 9, Electrochemical

1. Introduction:

Water after processing in textile industries is wasted into canals, rivers and oceans. The upper 200 meters (656 feet) of the ocean is called the euphotic, or "sunlight," zone [1]. Aquatic life needs light inside the ocean up to a certain depth for their survival. Photosynthetic activity decreases when the wastewater from the textile industry is mixed with canal, river or ocean water the dye in wastewater increases the darkness in water making sunlight difficult to pass through [2]. Textile industries must remove dyes from wastewater to save aquatic life. Water transparency could be easily affected by a very small amount of dye (10-20 mg L^{-1}) [3]. Before discharge, the removal of dyes from wastewater is an essential effluent treatment. Dyes could not be removed by conventional methods as dyes are not easily biodegradable and resistant to breakdown on exposure to water, soap and sunlight. Biological, physical, and chemical methods could be used to remove dyes [4]. In biological treatment, color could be removed by adsorption onto microorganisms (dead and/or alive) [5]. In industrial effluents, bacteria, yeasts, fungi, and algae could also be used to degrade pollutants. If all the three techniques are compared, biological is more favorable and economical as compared to physical and chemical; but limitations of biological process are that it do not remove color up to a satisfactory level and it require large area [4]. In physical methods, adsorption is a very effective technique for the removal of dyes from wastewater. A wide range of organic pollutants could be removed from water by using Activated Carbon as an adsorbent. Activated carbon could be regenerated effectively with

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minimum adsorbent loss and high regeneration efficiency [6]. On the other hand, the operating cost of regeneration of activated carbon is high because of high regeneration time due to highly porous structure and low electrical conductivity [6]. Graphite-based intercalation adsorbents rapidly remove dissolved organic compounds from water with 100% regeneration efficiency [7]. By using Nyex 1000 as an adsorbent for the removal of Reactive Brown 9, 90% of the dye was removed within five minutes. Thus, the method of adsorption with their electrochemical regeneration was found to be economically feasible for the removal of dye Reactive Brown 9 is a synthetic dye [8, 9]. When heated, it emits very toxic fumes. It is used in leather products, fabrics and textile. Serious eye irritation and allergy or asthma may be caused if inhaled. To the best of authors knowledge, limited work has been done on adsorption with electrochemical regeneration of Reactive Brown 9 as adsorbate and Nyex 1000 as adsorbent. This work aims to investigate the process of adsorption with electrochemical regeneration of Nyex 1000 adsorbent with Reactive Brown 9 as adsorbate in a simple divided batch electrochemical cell.

2. Materials & Methods:

2.1.Materials:

The dye Reactive Brown 9, adsorbent and distilled water were used in this research. Reactive Brown 9 ($C_{28}H_{20}ClN_7Na_2O_{12}S_3$) dye in traditional form is palm black powder with a molecular weight of 824.13. It was received from Crystal Chemicals Lahore, Pakistan. Reactive Brown 9 has been extensively being used in textile industries. The adsorbent used was a GIC (graphite intercalation compound) based adsorbent named Nyex 1000 [10] received from Arvia Technology Limited UK.

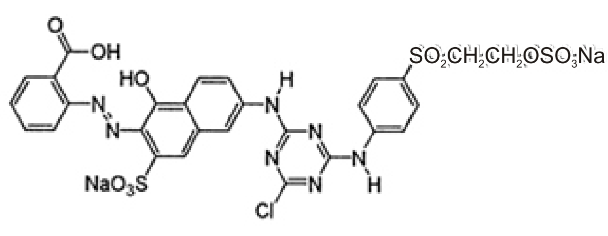

Figure 1: Structure of Reactive Brown 9 dye.

Mean particle diameter of Nyex 1000 was 484 mm (range 50–850 mm). Distilled water was obtained from Institute of Chemical Engineering & Technology Department, University of the Punjab, Lahore, Pakistan.

2.2. Methods:

2.2.1. SBR (Sequential Batch Reactor):

A Sequential Batch Reactor was used in this research for adsorption and electrochemical regeneration. The Sequential batch reactor has been discussed in details elsewhere [11, 12]. For proper mixing of adsorbent with water, the air was introduced at the bottom of the reactor during adsorption. To keep conditions similar in each step, the flow rate of air was maintained at 10-12 $Lmin^{-1}$. A microporous Daramic 350 polyethylene separator was used to separate electrode compartments. A 5 mm thick graphite plate was used as anode. Two plates of stainless steel 1mm and 3 mm thickness were used as cathode.

2.2.2. Batch Adsorption and Electrochemical Regeneration:

A solution of Reactive Brown 9 and distilled water was prepared. The solution was added to the adsorption & electrochemical regeneration column. First of all, the initial sample was taken as a reference. Then, 120 g of adsorbent was added to one liter of solution. Air was introduced at the bottom of the apparatus to initiate adsorption. Sample was taken after every five miunte to observe the results. The time required by Nyex 1000 to adsorb the maximum quantity of dye was calculated in this way. Fig.2. represents two zones apparatus used in this process (adsorption zone and regeneration zone). After calculating contact time for Nyex 1000, seven continuous cycles of adsorption and regeneration were studied. First of all, a solution of water and Reactive Brown 9 was prepared. One liter of the solution with 120 g of adsorbent was added in SBR. The process of adsorption was started with a supply of air. When the adsorption is completed, 2 min were given as settling time. Then, the sample was taken and studied by spectrophotometer. After adsorption, the regeneration step was started by DC electric source of 1 amp and 4 volts. The electrolyte chamber was filled with NaCl solution with pH 1.7. To maintain the pH of the solution HCl and NaOH were used. The catholyte solution prepared by mixing tap water with 3% w/v sodium chloride (NaCl) was added to the cathode compartment. The catholyte solution was found to be best for electrochemical regeneration. The results after absorption and regeneration were compared, and it was found that, absorbance is less after adsorption and more after regeneration. This was due to regeneration of the adsorbent. After first cycle of adsorption is complete, the sample was replaced with second one and adsorbent remained in the apparatus. Perkin Elmer Ultra Violet spectrometer Lamda 10 at 589 nm was used to determine the concentration of Reactive Brown 9 in an aqueous solution. The wavelength with maximum absorbance was found by scanning a sample of 120 mgL^{-1} Reactive Brown 9 solution. It was 589 nm in the visible spectral range (400–700 nm).

2.2.3 Regeneration Efficiency:

Regeneration efficiency was calculated using the formula:

$$R.E = \frac{q_r}{q_f} X100 \tag{1}$$

Where, q_r is adsorptive capacity regenerated and q_f is adsorptive capacity of fresh Nyex 1000 under the same adsorption conditions.

2.2.4. Pseudo First Order Kinetics

Equation for pseudo first order [13]:

$$\ln(q_e - q_t) = lnq_e - K_1 t \tag{2}$$

where

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3}$$

Here, the units of pseudo 1st order rate constant (K_1) are min^{-1}, the units of mass of adsorbate at equilibrium (q_e) are mg.g^{-1}, the units of mass of adsorbate (q_t) are mg g^{-1}.

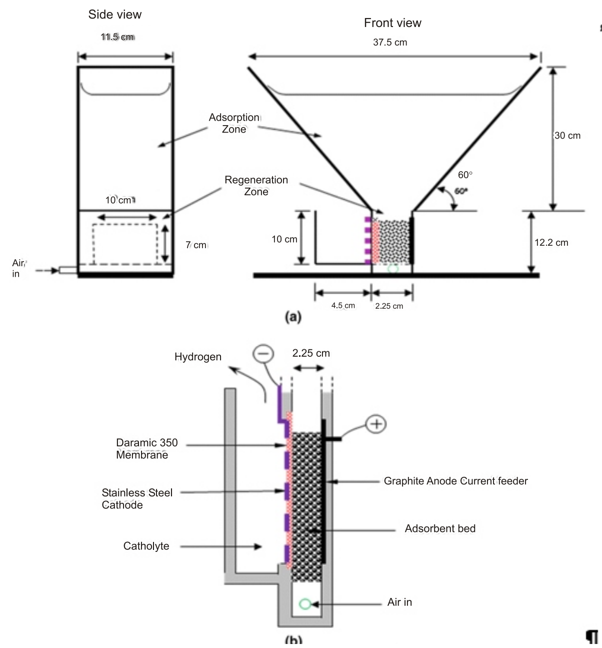

Figure 2: Apparatus used for the process was Sequential Batch Reactor. (a) front and side view and (b) electrochemical regeneration zone adapted from [14].

2.2.5 Pseudo Second Order Kinetics:

The equation for second order kinetics [15]:

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Here, the uni are g.mg^{-1}.min^{-1}, and units of the initial adsorption rate (h) are mg.g^{-1}.min^{-1}.

3. Results & Discussions:

3.1. Effect of contact time:

In SBR, 120g of adsorbent was added with 1 liter of 100ppm solution. The process of adsorption was started by the introduction of air at the bottom and samples were taken after every five minutes. Initially, the adsorption rate was high as there were more sites available on adsorbent to adsorb dye. But after 30 min, the curve becomes straight which means there is no more space left on the adsorbent to adsorb dye. From the results shown in Fig. 3, it could be determined that after 30 min, there is very low or no change in removal efficiency. So, contact time for further experiment was taken as 30 min.

3.2. Effect of Regeneration on Adsorption Efficiency:

The process of adsorption and electrochemical regeneration was repeated seven times. The solution was replaced with another solution of the same ppm and the same quantity. While the adsorbent remained in the reactor.

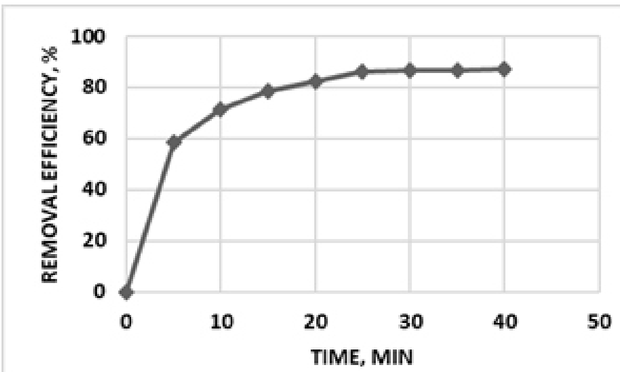

Figure 3: Effect of contact time of Nyex 1000 with the solution.

The efficiency of the adsorbent after each step was measured and shown in Fig. 4. From the results, it could be observed that regeneration efficiency of Nyex-1000 was different after each cycle.

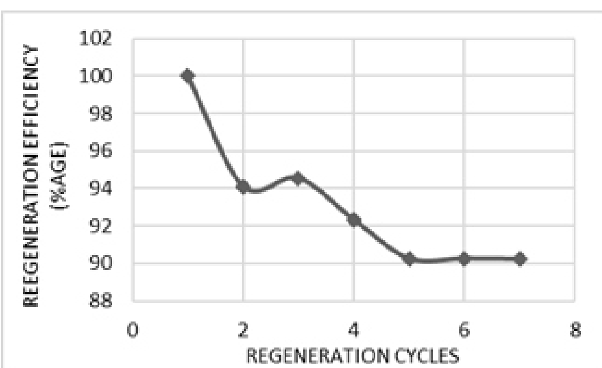

Figure 4: Regeneration Efficiency of Nyex 1000.

After 7 Cycles of adsorption and regeneration efficiency remained more than 90%. This Regeneration efficiency was observed at a density of 20 mA/cm^2, 3% sodium chloride concentration, but when the density of current was increased more than this, regeneration efficiency decreases because of the side reactions. Which were occurred due to high current density of current. Adsorption capacity was increased by rinsing the GIC adsorbent before re-adsorption [10]. From this experiment it was determined that using Nyex 1000 as adsorbent was very economical because it is easily regenerated and shows more than 90% regeneration efficiency.

3.3. Adsorption Kinetics Study:

Pseudo first order and second order kinetic model was applied on adsorption data to find the optimum conditions, mechanism of sorption and possible rate controlling step [16]. From the results, it could be determined that with the increase in time interval the amount of dye adsorbed increases; however, the adsorption rate was very high at the start of the reaction and decreases gradually with time. It happened because, initially there were plenty of active sites available on the surface of adsorbent, so, adsorption rate was high at start, but with the passage of time these sites got occupied, so magnitude of adsorption decreases gradually [17].

3.4. Pseudo First Order:

For pseudo first order kinetic model, $\ln(q_e\text{-}q_t)$ was plotted against time interval. The value of k_1 and q_e were obtained from the slope line and intercept respectively

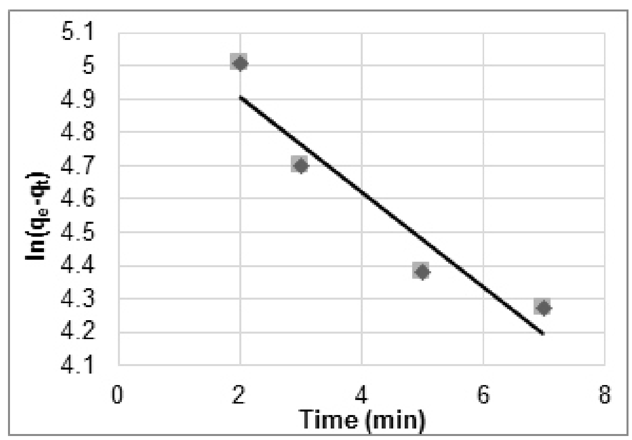

Figure 5: Pseudo first order kinetics.

The equation obtained by graph is:

$y = 0.2754x - 1.5535$, Slope $K_1 = 0.2754$,

y-intercept $\ln qe = 1.4438$,
Regression Factor $R^2 = 0.9763$.

Good correlation was found with higher value of regression factor (0.9763). So, the results indicate adsorption of Reactive Brown 9 dye onto Nyex 1000 adsorbent best fits pseudo first order kinetic model.

3.5. Pseudo Second Order:

For pseudo second order kinetic model, t/q_t was plotted against time interval. $1 / (k_2\ q_e^2)$ was obtained by intercept.

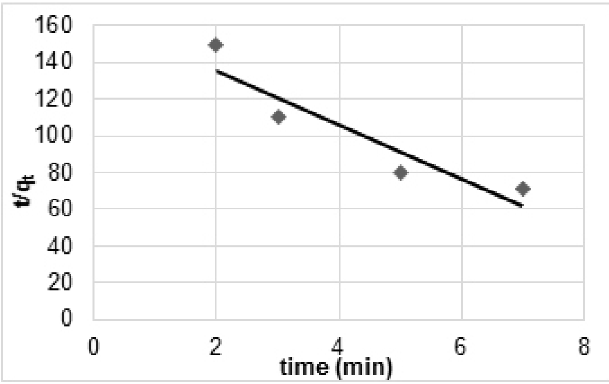

Figure 6: Pseudo second order kinetics.

Equation obtained from the graph:

$y = -14.691x + 165.03$, slope = -14.691,

y-intercept $1 / (k_2\ q_e^2) = 238.65$,

Regression factor $R^2 = 0.8558$.

Poor correlation was found with lower value of regression factor. So, the results indicate that adsorption of Reactive brown 9 dye on Nyex 1000 adsorbent did not best fits the model.

Table 1. Comparison between the results obtained from pseudo first and second order kinetics.

1st Order Kinetics			2nd Order Kinetics		
q_e	k_1	R^2	q_e	k_2	R^2
($mg.g^{-1}$)	(min)		($mg \cdot g^{-1}$)	($g \cdot mg^{-1} \cdot min^{-1}$)	
4.2368	0.2754	0.9763	0.019	2.42	0.8558

4. Conclusions:

Adsorption with electrochemical regeneration using Nyex 1000 as adsorbent was found to be a feasible technique to remove Reactive Brown 9 dye from textile wastewater. During this process, upto 90% of the dye was removed within 30 min. Nyex 1000 (Graphite intercalation compounds) after removing dye could be regenerated electrochemically. It was observed by Pseudo first and second order kinetics study that pseudo first order kinetic better fits for this process due to higher regression factor.

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