

Original Article**Study Survey of Efficiency Agricultural Weast in Removal of Acid Orang 7(AO7) Dyes from Aqueous Solution: Kinetic and Equilibrium Study**Ramazan Ali Diyanati Tilaki¹ *Davoud Balarak² Mehdi Ghasemi²

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Abstract

Background and purpose: dye is widely used in industries such as cosmetic, leather, paper and textile and release to the environment via their effluents. The purpose of this study was to compare the efficiency of low-cost adsorbents in acid orang 7 dyes removal from water.

Materials and Methods: The Rice Stem biomass was sun dried, crushed and sieved to particle sizes in range of 1-2 mm. Then treated with 2.0 mol/L nitric acid for a period of 1 h followed by washing with distilled water and finally washed Stem was dried at 105° in oven. The residues concentration of acid orang 7 dyes was measured by spectrophotometer in λ_{max} of 452 nm. The effect of pH, contact time and initial AO7 dye concentration, kinetic and isotherm models were studied. Then data interpreted and analyzed by Excel 16 software.

Results: The pH value of 3, contact time of 75 min, adsorbent dosage of 8 g/L and dye concentration were 10 mg/l determined as optimum conditions for adsorbents. The most acid orang 7 dyes removal efficiency of 98% was obtained for modified Rice Stem in optimum conditions. The equilibrium data is best fitted on Langmuir isotherm and the adsorption kinetic model follows pseudo-second model.

Conclusion: Based on data obtained in this study, it can be concluded that adsorption by modified Rice Stem is an efficient and reliable adsorbent for acid orang 7 dyes removal from liquid solutions.

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Key words: Adsorption, Acid Orang 7, Kinetics, Rice Stem

1. Introduction

Since the Textile dyes can form toxic component by decomposition, therefore they can create great problems for the environment (1, 2). A large amount of fresh water is used in the dye industry and it contaminated during the process and it is discharged as wastewater which contains lot of pollutants like dyes etc(3, 4). The dyes are stable and hard biodegradable due to the complex molecular in their structure (5). Therefore, dye industry contributes in water pollution by discharging large volume of coloured and toxic effluent(6). The produced amount of dye is estimated between 7×10^5 - 10^6 which is used in various industries such as production of cosmetic, leather, paper and textile(7). The textile industries are largest dye consumer and they can generate high volume wastewater with dye concentration in range of 10- 500 mg/l (8). The dyes used in the textile industries include several structural varieties such as acidic, reactive, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes(9, 10). Many dyes and color effluents are toxic and their carcinogenic and mutagenic properties can make adverse effect on environment and human(11). The Color removal from textile industries wastewaters has been considered as big problem because the conventional methods can not successfully treat such wastewaters (12). The effluents of the manufacturing and textile industries which are discharged into rivers and lakes can change their biological life(13). Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electro dialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents (14). Although the

mentioned methods have been widely used, however they have many limitations to use such as high cost, formation of hazardous byproducts and intensive energy requirements(15,16). Among the mentioned techniques, the adsorption is one of the most effective and low-cost method for the dyes removal from aqueous solutions(17, 18). One of the problems in using of the activated carbon is the its high cost; therefore, many studies have tried to search for alternative materials, which are relatively inexpensive, and at the same time with reasonable adsorptive efficiency (19, 20) . Many studies have been made on use of different adsorbents like activated carbon, peat, coir pith, chitin, silica, fly ash, and many others like hardwood sawdust, bagasse pith, paddy straw, slag, lemna minor, Azolla, various blends of these (21-24). However search for cost-effective, efficient adsorbent is continuing(25). Agricultural weas Such as Rice Stem can prove to be better alternative for sorption process because it is freely available in countries like Iran (Particularly In the area North Iran) where agriculture is among the major businesses. It is cheap and shows good sorption capacities when properly treated. In many countries of world, it is used as high efficiency and inexpensive adsorbent to remove organics such as dyes and heavy metals with regarding to its adsorbing properties(11,26-28). Because there was no study on acid orang 7 (AO7) removal by Rice Stem, Therefore aim of the present work is to explore the possibility of utilizing Rice Stem for the removal of acid orang 7 from aqueous solution. The effect of such factors as pH, adsorbent dose (m), contact time (t), initial concentration (C_0) were investigated.

2. Materials and Methods

2.1. Preparation of adsorbent

Rice stem was collected from rice paddy in Sari city; Then It was dried in the sunlight, and was crushed and sieved to particle sizes in the range of 1–2 mm. The biomass was treated with 2.0 mol/L nitric acid for a period of 1 h and it was washed with distilled water and finally washed Stem was dried at 105° in oven(15). The resultant biomass was subsequently used in sorption experiments.

2.2. Instruments used for characterization

The specific surface area of dried Rice Stem before use was determined by the BET-N2 method using an ASAP 2000 apparatus based nitrogen adsorption–desorption isotherms at 77K. The FTIR spectra(Nicolet 5700 instrument, Thermo Corp, USA) were recorded in the range of 400– 4000 cm⁻¹ to find out the information regarding the bending vibrations and the stretching of the functional groups which are responsible for the adsorption process. The surface images of dried Rice Stem before and after adsorption process were captured by scanning electron microscopy (SEM). The SEM used was a Philips XL30.

2.3. Preparation of dye solution

Acid orange7(AO7) was obtained from Sigma–Aldrich Corporation, The properties

and chemical structure the dye used are shown in table 1 and Fig. 1. Stock solution of 1000 mg/L of the dye was prepared and suitably diluted to required initial concentrations. pH was adjusted by adding either HCL or NaOH as required.

2.4. Batch adsorption

The adsorption experiments were carried out in a batch process. The literature review indicated that the most important effective variables on adsorption is including pH, adsorbent dose, contact time and pollutants concentrations. Therefore, the initial acid orang 7 concentration was selected (10-500 mg/l). The effect of absorbent dosage (0.1-1g), contact time (10- 180 min) and pH (3-11) were studied. The experiments in batch system were carried out in a 100 ml Erlenmeyer flask Meyer. In every experiment, a certain concentration of AO7 and specific dose of absorbent spilled into the Flask and completely mixed with shaker at 120 rpm for 180 minutes. Then the sample was centrifuged at 3600 rpm for 10 minutes. Finally, the residual concentrations were measured using Spectrophotometer (DR2800) in λ_{max} of 452 nm(19, 29). The amount of adsorbed TCP was calculated according to the following Eq 1(30).

$$q_e = (C_o - C_e) V/m \quad (1)$$

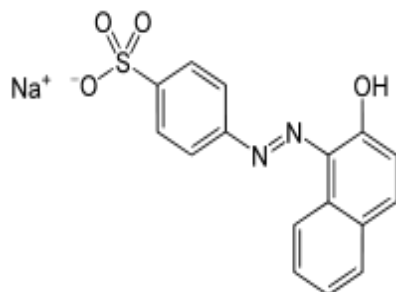


Fig 1. The chemical structures Acid orange 7

Table1. The characteristics of Acid orange 7(31)

C.I. name	Molecular weight	λ_{\max} (nm)	Molecular formula
Acid orange 7	350.32 g/mol	452	C ₁₆ H ₁₁ N ₂ NaO ₄ S

2.5. Adsorption isotherms

The equilibrium adsorption isotherm is importance in the design of adsorption systems. Although several isotherm equations are

available, but four important isotherms including Langmuir, Freundlich, Tekmin and BET isotherms were selected. The Isotherm equations are presented the Table 2.

Table 2. The equations of isotherms(30, 32)

Model	Equation
Langmuir	$\frac{ce}{qe} = \frac{1}{qm KL} + \frac{ce}{qm}$
Freundlich	$\text{Log } \frac{x}{m} = \frac{1}{n} \text{ log } Ce + \text{ log } K_F$
Tekmin	$q_e = B_1 \ln(k_t) + B_1 \ln(c_e)$
BET	$\frac{ce}{(c_s - c_e)q} = \left(\frac{1}{qm Kb} \right) + \left(\frac{Kb-1}{qm Kb} \right) \frac{ce}{c_s}$

2.6. Adsorption kinetics

The study of kinetic models was performed in contact time between 15-180 min with dye concentration of 50mg/l and optimum amount of pH and adsorbent dose. To evaluate the differences in the biosorption

rates and uptakes, the kinetic data were described with Elovich, Intra particle diffusion, pseudo first, pseudo second order models. The linearized form of model is shown in Table 3.

Table 3. The equations of kinetics(29, 33)

Model	Equation
pseudo first order	$\log(q_e - q) = \log q_e - k_1 t / 2.3$
pseudo second order	$t / q = 1/k_2 q_e^2 + 1/q_e t$
Elovich	$q_e = \left(\frac{1}{\beta} \right) \ln(\alpha\beta) + \left(\frac{1}{\beta} \right) \ln t$
Intra particle diffusion	$q_t = k_{dif} t^{0.5} + c$

3. Results

The specific surface areas of modified Rice Stem were determined in size of 82 m²/gr which it indicated that the modified Rice Stem have relatively good ability to remove the pollutants. Scanning electron microscopy (SEM) images were used to analyze the surface structure of Rice Stem (Fig. 2). It was found that the adsorbent has Heterogeneous surface structure with deep

pores. To understand the interaction between function groups on the surface of modified Rice Stem and dye, both dried Rice Stem before and after use were examined using FT-IR spectroscopy. As shown in Fig.3, dried Rice Stem before and after use showed a similar pattern and the same number of observed peaks in the FT-IR spectra.

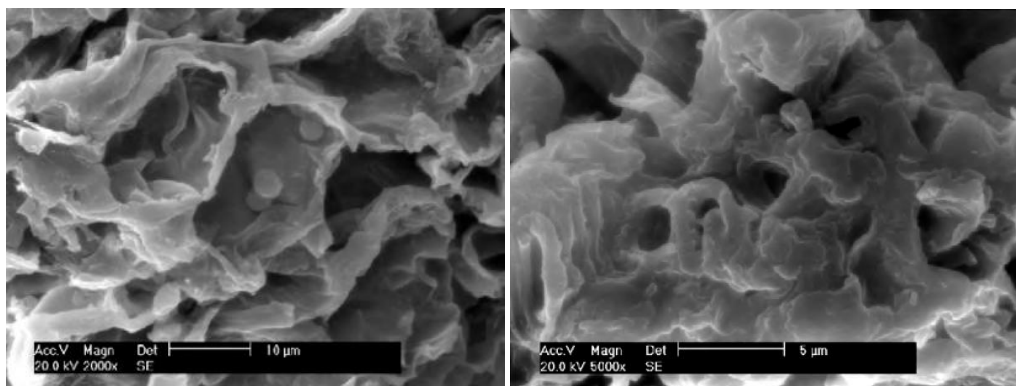


Fig2. The SEM image of modified Rice Stem before and after used

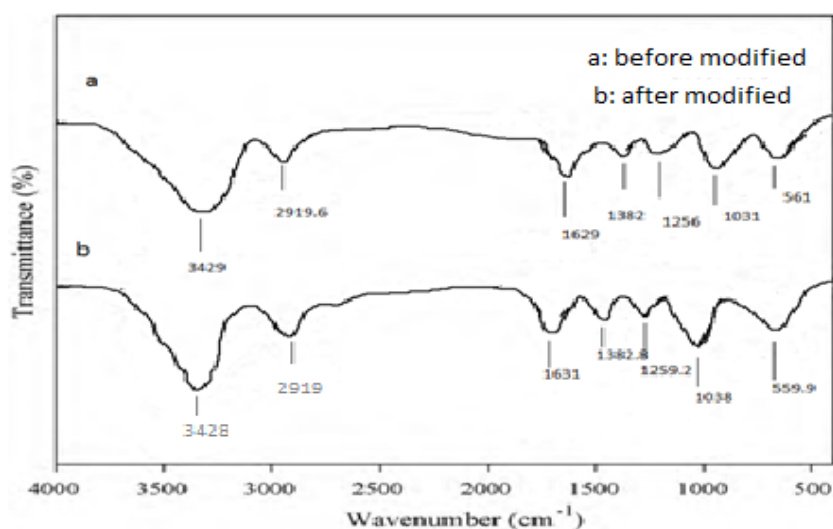


Fig3. The FT-IR spectra of modified Rice Stem before and after used

3.1. Effect of contact time and initial AO7 concentration:

Contact time is an important factors influencing adsorption of AO7 on dried Rice Stem. It is well known that the adsorption capacity and removal efficiency of dyes by biosorbents increases with increasing contact time. As shown in Fig. 4, biosorption of AO7 on dried Rice Stem increased rapidly within the first 60 min and then slowed from 60 min to 75min, reaching equilibrium after 1.5 h. The

influence of initial AO7 concentrations, ranging from 10 to 500 mg/L, on AO7 biosorption on dried Rice Stem was investigated. As shown in Fig. 5, biosorption increased significantly from 1.22 to 38.75 mg/g with increasing initial concentrations of AO7 from 10 to 500 mg/L, while the AO7 removal efficiency decreased from 98% to 62%.

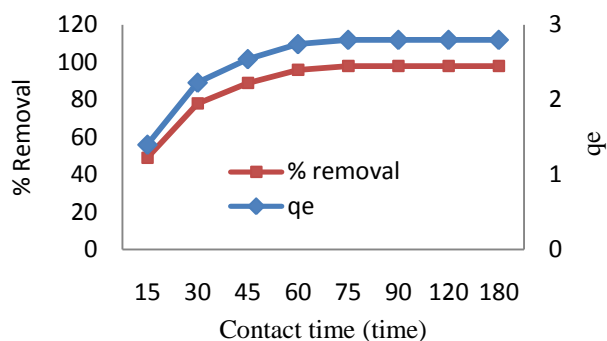


Fig4. Effect of contact time on removal efficiency of AO7 (pH = 3, dosage 10g/l, AO7 concentration: 10ppm)

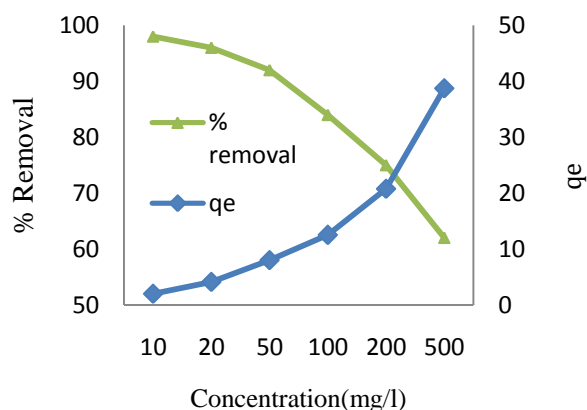


Fig 5. Effect of AO7 concentration on removal efficiency of AO7 (time = 90 min, dosage: 10g/l, pH = 3)

3.2. Effect of adsorbent dosage and pH:

The effect of biosorbent dosage on biosorption of AO7 on to dried Rice Stem was studied to determine an optimum biosorbent dosage. The tested biosorbent dosages varied from 1 to 10 g/L using an initial AO7 concentration of 10 mg/L and contact time of 90 min. As shown in Fig. 6, the biosorption capacity of AO7 on the biomass decreased from 7 to 1.96 mg/g, while the AO7 removal percent increased from 35% to 98% when biosorbent dosage increased from 1 to 8 g/L. Biomass dosage

increased to 8 g/L and remained approximately constant with further increases in biosorbent dosage. On the basis of both biosorption capacity and the removal percentage, an optimum biosorbent dosage of 8 g/L was selected for all further experiments. The effect of pH on dye uptake in the batch process was studied by varying the pH from 3 to 11 (Fig. 7). The biosorption of AO7 on dried Rice Stem decreased significantly with increasing solution pH from 3 to 11.

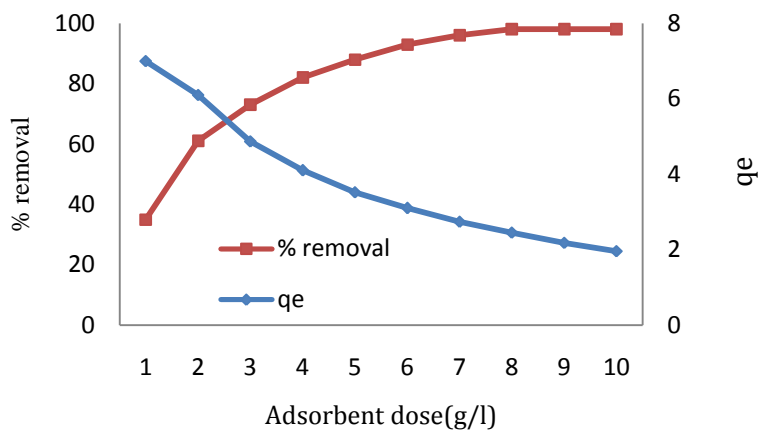


Fig6. Effect of adsorbent dose on removal efficiency of AO7 (contact time = 90 min, PH = 3, AO7 concentration: 10ppm)

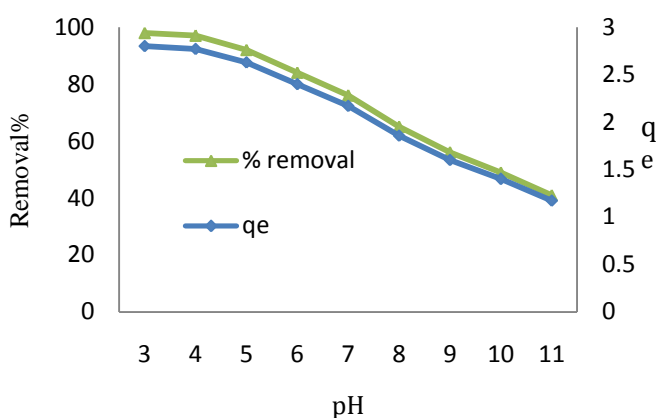


Fig7. Effect of pH on removal efficiency of AO7 (contact time = 90 min, dosage: 10g/l, AO7 concentration: 10ppm)

3.3. Adsorption kinetics and isotherms:

The results obtained by the adsorption of dye were analyzed by the well-known models of Langmuir, Freundlich and Temkin and BET. The results showed that AO7 dye on dried Rice Stem fitted according to Freundlich Model isotherm model ($R^2=0.998$). Furthermore it agreed with BET isotherm ($R^2=0.991$) that better than Langmuir ($R^2=0.941$) and Temkin

model ($R^2=0.962$). The isothermal models and adsorption kinetics is shown in Fig. 4 and 5. The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant which means the uptake process follows the pseudo-second-order expression with Correlation coefficients were always greater of 0.99.

Table 4. The adsorption isotherms constants for the removal AO7

Langmuir Model			Freundlich model			Temkin Model			BET Model		
q_m	b	R^2	n	K	R^2	b	k_t	R^2	A	X_m	R^2
10.2	0.94	0.941	1.4	3.5	0.998	64.4	4.21	0.962	20.4	0.197	0.991

Table 5. The adsorption kinetic model constants for the removal AO7

Pseudo Second-order model			Pseudo First-order model			Elovich			Intraparticle diffusion		
k_2	R^2	q	K_1	R^2	q	α	β	R^2	K_{dif}	C	R^2
0.124	0.999	9.6	0.113	0.949	8.1	6.9	0.21	0.911	1.74	12.2	0.906

4. Discussion

The specific surface area of adsorbent was one of the most important parameters on adsorption ability. The specific surface area is related to the number of active adsorption sites of dried Rice Stem. The adsorption increased with the specific surface area and pore volume of the sorbent. The surface area of dried Rice Stem was 82 m²/gr. which it indicated that the modified Rice Stem area have relatively good ability to remove the pollutants. The amount of specific surface area, is greater than other adsorbent such as red mud, azolla and lemna minor(8, 9, 33). The specific surface area for Azolla, Lemna and red mud is 36, 30 and 28m²/gr, respectively (23). In intense absorption peaks at around 3424-3429 cm⁻¹ correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds. Thus, showing the presence of “free” hydroxyl groups on the adsorbent surface(26). The peaks at 2918-9 and 1382 cm⁻¹ corresponded to the C–H symmetric stretch of the methylene groups (–CH₂) and deformation vibration of methyl groups (–CH₃)(14). The peak at 16.29-31 cm⁻¹ was attributed to a C=O stretching vibration of carboxylate (–COO⁻) or a N–H deformation vibration of amide I groups. The peaks at 1256-9 and 1031-9cm⁻¹ were due to the C–O stretching vibration of ketones, aldehydes

and lactones or carboxyl groups. However, some shifts in wave numbers from 1629 cm⁻¹ to 1631 cm⁻¹, 1256 cm⁻¹ to 1259.2cm⁻¹, and 1031 cm⁻¹ to 1038 cm⁻¹ were noticed in the spectra of dried Rice Stem before and after use(26). The shifts in wave numbers suggested that amide, hydroxy; carboxylate and C–O groups could participate in AO7 biosorption on the surface of dried Rice Stem. The initial high biosorption rate of AO7 on dried Rice Stem within the first 60 min was attributed to the high availability of binding sites on the surface of dried Rice Stem, and the subsequent lower biosorption rate after 60 min was decreased availability of binding sites on the surface of dried Rice Stem due to absorption of initial AO7 molecules. Similar results were observed for biosorption of reactive dyes by other adsorbent(8, 9). It is similar to dye removal by canola adsorbent. The optimum contact time was 45min which it can probably describe by greater contact surface of Canola adsorbent. Because the increasing of specific surface area can lead to more adsorption percentage in lower time (30). Biosorption increased with increasing initial concentrations of AO7 from 10 to 500 mg/L, while the AO7 removal efficiency decreased. This was due to an increased driving force from the concentration gradient at higher initial AO7

concentrations. In contrast, the higher the initial AO7 concentrations the lower the availability of adsorption sites and consequently the percentage of dye removal decrease(8, 34). Lower biosorption capacity of AO7 at a higher dosage of biosorbent is probably due to decrease of the surface area of the biosorbent by the overlapping or aggregation during the sorption. However, the higher dosage of biosorbent in the solution, the greater the availability of active sites for AO7, leading to the higher AO7 removal. The results obtained were similar and supported by other researchers(19, 26). One of the most important factors affecting the biosorption of AO7 on dried Rice Stem was the acidity of the solution, since the PH of the dye solution influences not only the surface charge of the biosorbent and the dissociation of functional groups of the active sites on the surface of the biosorbent, but also the aqueous chemistry of the dye. The biosorption decreased significantly with increasing solution pH from 3 to 11, the deprotonation of functional groups, such as phenolic-OH and COOH, occurred and electrostatic interaction between the dye cations and active sites on the surface of the biomass becomes consequently favourable. Similar results were observed in studies on the removal of dyes using azolla treated HCL and biosorption of dye other researchers(8, 9). The biosorption of sorbate (AO7) onto the adsorbent (dried Rice Stem) was modelled using the Langmuir, Freundlich, Tekmin, BET equations. The Langmuir isotherm assumes monolayer coverage of a sorbate on to the solid surface of adsorbent, uniform energy

of sorption, and no transmigration of sorbate in the plane of the Surface. While freundlich, Tekmin, BET equations are based on the hypothesis of multi-layer biosorption(35). The correlation coefficient (R^2) for Langmuir isotherm was 0.941, which was slightly poorer than the R^2 value obtained from the Temkin and BET and Freundlich equations indicating that the Freundlich model better fitted the equilibrium obtained in this study. This suggested that the biosorption of AO7 onto dried Rice Stem may be due to biosorption of multi-layer to the functional groups as binding sites on the surface of the biomass. The Freundlich biosorption constants of n and K_F were 1.4 and 3.5, respectively. A $1/n$ value between 0 and 1 indicates that biosorption of AO7 on dried Rice Stem was favourable. The results obtained were similar and supported by other researchers(17, 36). In this study the obtained q_e value in concentration of 100 mg/l was 14.1mg/g which this value is greater than obtained q_e for Lemna (9.8mg/g) and Azolla (11.2mg/g), however the q_e of this study is less compare to q_e of Canola (17.8mg/g) which it probably is due to presence of greater specific surface area in studied adsorbent than the Azolla and Lemna (23). The correlation coefficient (R^2) in pseudo second- order model was better than the first order model, Elovich, Intraparticle diffusion, correlation coefficients. This kinetic study confirmed that biosorption of AO7 on dried Rice Stem was a multi step process, involving in biosorption on the external surface and diffusion into the interior with external surface chemical sorption being the rate-

controlling step(9, 37). Based on the results, the dried Rice Stem can be used as an effective and low cost adsorbent to treat effluent containing dye. The removal efficiency depends upon parameters such as initial dye concentration, adsorbent dose, pH, and contact time. The data were best fitted on Freundlich isotherm pseudo second- order kinetic.

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