

Removal of Safranin-O dye from aqueous solution using acid activated red mud

A

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DECLARATION

I **Miss. Kajal Kiran Dehury**, NIT, Rourkela declare that all my research works are original & no part of this thesis has been submitted for any other degree or diploma. All the given information & works done are true to my sense & knowledge.

(Kajal Kiran Dehury)

Date:

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CERTIFICATE

This is to certify that the dissertation entitled “Removal of Safranin-O dye from aqueous solution using acid activated red mud” being submitted by Kajal Kiran Dehury, Roll number 412CY2009, Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University/Institute for the award of any Degree or Diploma.

The present study is a valuable contribution for the advancement of knowledge in the field of material chemistry and its environmental application.

NIT Rourkela

Prof. R. K. Patel

Date:

(Supervisor)

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1. Introduction

Dyes have wide application and found in all segment of environment. Safranin-O is considered as a highly toxic substance but use in food industry, textile industry, paper industry, rubber industry, etc. Presence of high concentration of Safranin-O in aquatic system has a tremendous effect on the health of human, animals and plants. Contamination of Safranin-O in water can cause allergic dermatitis, skin irritation, cancer and mutation in humane being. Efforts have been already initiated to eliminate Safranin-O from water. Many methods have been reported in literature for elimination of dyes from waste water such as photo catalytic degradation, chemical degradation, micellar enhanced filtration, cation exchange membrane, electrochemical degradation, adsorption/precipitation process, integrated chemical biological degradation, integrated iron (30 photo assisted biological treatment, solar-photo-Fenton reagent and biological treatment scheme and adsorption on activated charcoal [1]. Red mud could be the appropriate adsorbent for the elimination of Safranin-O from aqueous solution. Keeping this in vision, the alteration of wastes into active adsorbents for wastewater management could therefore improve the environmental performance. Thus, the choice of appropriate adsorbent is tedious. Numerous methods such as coagulation, photo degradation and ozonation are available for the management of industrial wastewaters. These approaches are expensive, yield concentrated sludge's or are inadequate to treat large volumes of effluent without the risk of clogging. Investigation is therefore required to develop new alternate environmental friendly applications.

Maximum of the dyes are carcinogenic and toxic in nature [2]. Dyes or Colored compounds are the most effortlessly identifiable pollutants in the environment. Maximum of the industries

use dyes and pigments to color their products. Today, release of dye-bearing wastewater into natural streams and rivers from textile, paper, carpet and printing industries have a austere problem since dyes impart toxicity to aquatic life and are harmful to the aesthetic nature of the environment. Existence of dyes in water bodies restricts sunlight penetration and photosynthetic process and inhibit the development of biota and tendency to chelate metal ion [3]. Usually, the dye-bearing wastewater is released directly into the adjacent water sources such as rivers, lakes and seas. Textile dyeing method is a chief source of contamination of water responsible for the continuous pollution of the environment. Contamination of drinking water above 0.1 mg/L can make it unsuitable for human consumption [4]. Above 7.0×10^5 tones and around 10000 different types of dyes and pigments are produced worldwide yearly.

The objective of this study was to investigate the adsorption potential of waste red mud for the removal of Safranin-O dye from aqueous solutions. The effect of several parameters such as contact time, initial pH of the solution, Safranin-O dye concentration, adsorbent (activated red mud) concentration, effect of temperature etc., was studied. The adsorption mechanisms of Safranin-O dye ions onto activated red mud were estimated in terms of thermodynamics and kinetics. The adsorption isotherms were described by using Langmuir and Freundlich models.

1.1. Literature review

Safranin-O, also known as basic red 2, is a basic dye. Basically, safranines are the azonium compounds of symmetrical 2,8-dimethyl-3,7-diamino-phenazine (**Fig. 1**).

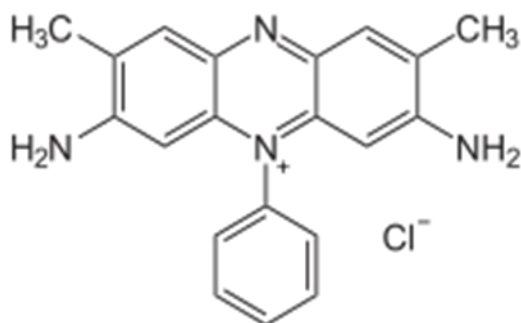


Fig. 1. Structure of Safranin-O

The dye Safranin-O (molecular formula:-, $C_{20}H_{19}N_4Cl$, mol wt: 350.8 gm/mol, absorption spectra: 518 nm) is the dye widely used in textile industry is creating hazard due to its disposal into water bodies [8]. Safranin-O can be obtained by oxidation of one molecule of a para-diamine with two molecules of a primary amine, by the condensation of para-aminoazo compounds with primary amines and by the action of para-nitrosodialkylanilines with secondary bases such as diphenylmetaphenylenediamine. Safranin-O is an amorphous powder, showing a characteristic like readily solubility in water and dye of blue or violet. Safranin-O form stable

monacid salts and are strong bases. The alcoholic solution of safranines shows a yellow-red fluorescence. Phenosafranine in the Free State is not very stable; its chloride forms green plates.

1.2. Aims and objective:

The aim and objective of the present work for the study of adsorption of Safranin-O by using ARM for the action of remedying Safranin-O has following objectives:

- Preparation and characterization of ARM
- To the removal efficiency of Safranin-O by ARM
- To know the optimum condition for maximum efficiency of Safranin-O removal by varying pH, time, adsorbent dose and temperature

Chapter 2

2. Materials and Methods

2.1. Materials

All chemicals used in this study were of AR grade and the red mud was obtained from Vedanta Private Limited, Lanjigarh, Odisha. All the glassware's used was of borosil and tarson. In all experiments, Millipore water was used for preparation, dilution and analytical purposes of

the solutions. Stock solutions of the Safranin-O were prepared by dissolving 1mg of Safranin-O in 1 L of milipore water. Different concentrations of test solutions of Safranin-O were prepared by proper dilution of the stock solutions.

2.2. Preparation of acid activated red mud

In a 1000 ml beaker approximately 10 gm of red mud was added to 190 gm milipore water and stirred to form a slurry, to which 18 gm of 31 wt% HCl was added. The resulting solution was heated at 60 °C for 20 min and diluted with water to make total volume of 800 cm³ with constant stirring. Liquid Ammonia solution (specific gravity ~0.880) was added slowly with constant stirring until a pH of 8 and resulting precipitate was heated at 50 °C for 10 min with constant stirring. The precipitate was separated by filtration, washed 3 times with distilled water dried overnight in oven at 110 °C and finally calcined in air at 700 °C for 2 hours which is referred as an activated red mud (ARM).

2.3. Characterization of Adsorbent

The X-ray diffraction (XRD) of red mud was determined by using Philips X'Pert X-ray diffractometer with a Cu K α radiation generated at 35 kV and 30 mA. Scattering angle 2 θ was ranged from 10° to 80° at a scanning rate of 2 degree/minute and was analyzed using standard software provided with the instrument. The surface micro-morphology of materials was investigated using scanning electron microscope (SEM).

2.4. Batch Experiments

Adsorption of Safranin-O on to HCl activated red mud was studied at room temperature by batch. A fixed amount of dry adsorbents 0.25 g was added to a series of capped volumetric poly lab plastic bottles containing 50 mL of 50 ppm Safranin-O solution and shaken at 400 rpm using a temperature-controlled water bath with shaker. The bottles were capped tightly for all

tests to avoid change in concentration, due to evaporation. The pH was adjusted to the desired level by adding required amounts of 0.1 M HCl or 0.1 M NaOH solutions. A number of experimental parameters such as adsorbent dose (0.1-1.0 g), contact time (15–90 min), initial concentration of adsorbate (10-50 ppm), pH (2–12) and temperature (35–65 °C) which affect the adsorption process have been studied to investigate the removal process. The solutions were stirred using magnetic stirrer at about 150 rpm for 1 h. After stirring for a period of predetermined time, the solutions were allowed to settle for 10 min and the samples were centrifuged at 3000 rpm for 10 min and filtered through Whatman 42 filter paper. The filtrate was used for the analysis of remaining Safranin-O concentration in the solution.

Chapter 3

3. Result and discussion

3.1. Characterization of Adsorbent

SEM pictures provide surface morphology of the RM samples at micro-scale. From **Fig. 2**, the contrast in surface features between the raw RM which is relatively smooth and flat, and the acid treated specimen, RM-HCl, provides clear visual evidence for the new surface area generated by strong acid treatment. The acid treated sample shows many new cavities and

coarsened exterior probably due to removal of some acid-soluble salts. After heat treatment, RM-HCl exhibits a morphology similar to the RM-HCl but with additional porosity

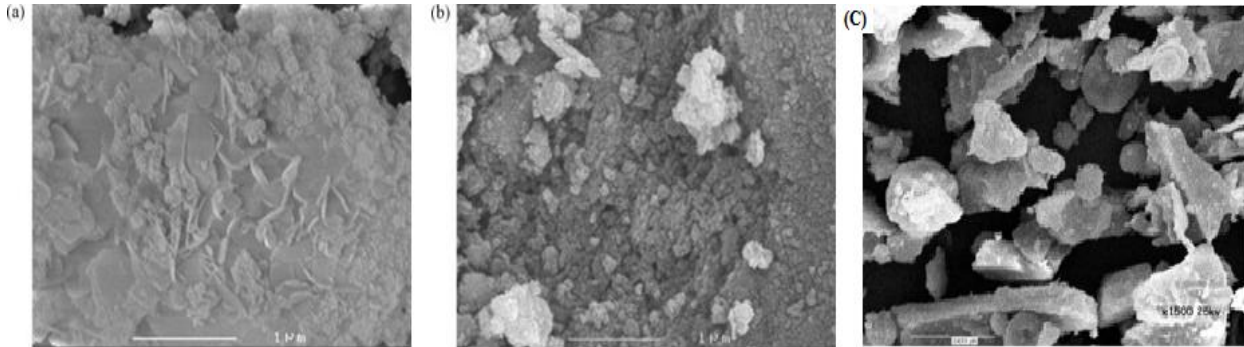


Fig. 2. SEM micrograph of (a) Raw Red mud (b) HCl activated red mud before adsorption (c) HCl activated red mud after adsorption

The XRD patterns show a remarkable difference between acid treated samples and the acid-thermally treated samples, which suggests that phase transformation has taken place shown in **Fig. 3**. After acid treatments, the calcite phase present in the raw RM disappears. The acid-thermal treatment creates a new phase of magnetite, which is attributed to the decomposition of goethite. The intensities of hematite also show a significant enhancement, making them the dominant phases in RM-HCl.

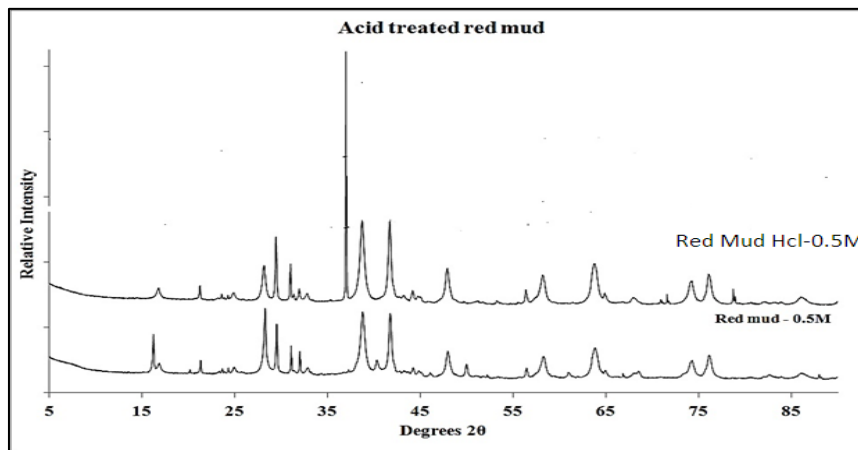


Fig. 3. XRD of red mud before and after adsorption

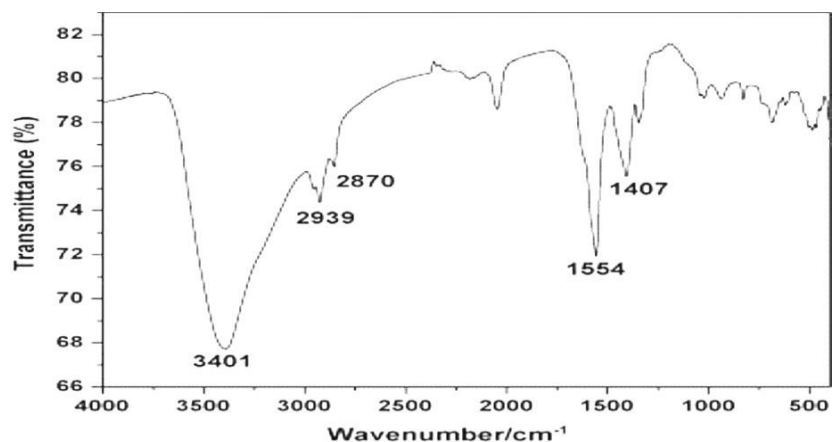


Fig. 4. IR spectra of Safranin-O

Fig. 4. shows the FTIR analysis of Safranin-O. The weak peaks located at 2870 cm⁻¹ and 2939 cm⁻¹ are assigned to symmetric and asymmetric C–H stretches. The peak at 3401 cm⁻¹ can be attributed to N–H stretching vibration of the –NH₂ group. The peak at 1554 cm⁻¹ can be attributed to N–H bending vibration of the –NH₂ group

3.2. Effect of adsorbent dose

Adsorption of Safranin-O at different adsorbent dose was studied for initial Safranin-O concentration of 50 mg/L to know the rate and equilibrium data. The sensitivity of Safranin-O efficiency to adsorbent dose was tested by taking different dose rate of 0.1-1.0 mg/L red mud and a constant test solution of Safranin-O concentration and pH. The result are presented in **fig. 5**. The figure shows increasing Safranin-O removal efficiency and decreasing pseudo equilibrium solution concentration with increasing RM dose. This implies that sorption sites depend on the availability of binding sites. Thus the removal of Safranin-O was increased with increasing red mud dosage, which is due to the increase in surface area of the red mud.

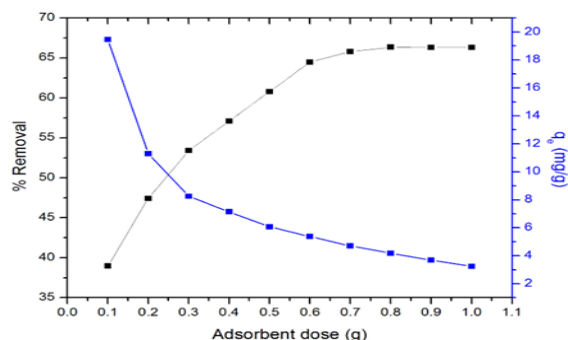


Fig. 5. Adsorbent dose versus percentage removal of Safranin-o by activated red mud with initial concentration of 50 mg/L, temperature 27 °C

3.3. Effect of pH

Adsorption of Safranin-O at different adsorbent dose was studied for initial Safranin-O concentration of 50 mg/L to know the rate and equilibrium data. The result are presented in **Fig. 6.** It is evident from the figure that adsorption capacity is maximum at pH 8. When the solution has higher pH the surface of red mud carries more negative charge, whereas Safranin-O is a positively charged molecule which can bind the negative charge of red mud.

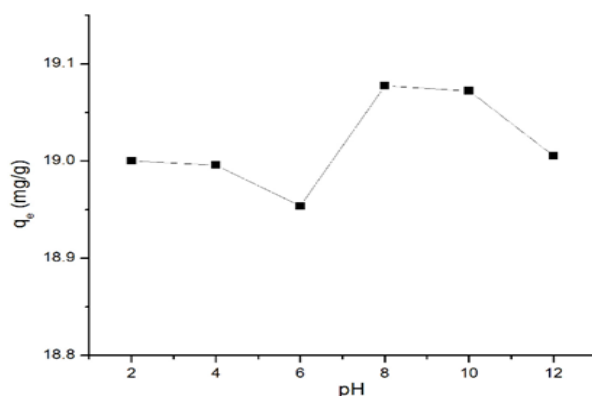


Fig. 6. pH dose versus percentage removal of Safranin-o by activated red mud with initial concentration of 50 mg/L, temperature 27 °C and adsorbent dose 0.25 mg/g.

3.4. Effect of contact time

The experimental result portrayed in **Fig. 7.** The adsorption capacity increases 5 mg/g – 8 mg/g at 20 min. The plot denotes the first uptake of adsorbate species (5 mg/g during 20 min and even 9 mg/g during 40 min) during the initial stages and after 40 min there was establishment of equilibrium. Fast removal of Safranin-O during initial stages attributed to boundary layer

diffusion. The rapid rate of removal during the inceptive stage was attributed to numerous vacant surface sites accessible for adsorption. During later stages with progressing duration adsorption sites were exhausted, competition between adsorbate molecules was intensified, repulsive forces among the adsorbate molecules eventuated on the surface of adsorbent molecules. Hence conditions exhibited during later stages steered uptake of Safranin-O by transport from external to internal sites of the adsorbent liable for slow process governing the adsorption. Hence the rate of uptake was slow during later stages of adsorption.

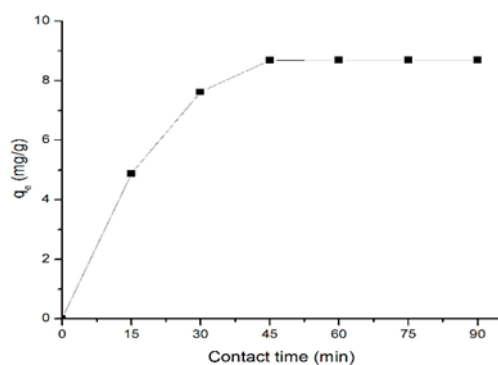


Fig. 7. Contact time versus adsorption capacity of Safranin-O by activated red mud with initial concentration of 50 mg/L, temperature 27° C and adsorbent dose 0.25 mg/g.

3.5. Effect of initial concentration

Batch experiment was performed to investigate the effect of initial Safranin-O from 10 mg/L to 50 mg/L with optimum adsorption dose of Safranin-O adsorption on HCl activated red mud shown in **Fig. 8**. The rise of adsorption capacity decreases with temperature. At lower temp (308 K) adsorption capacity is maximum.

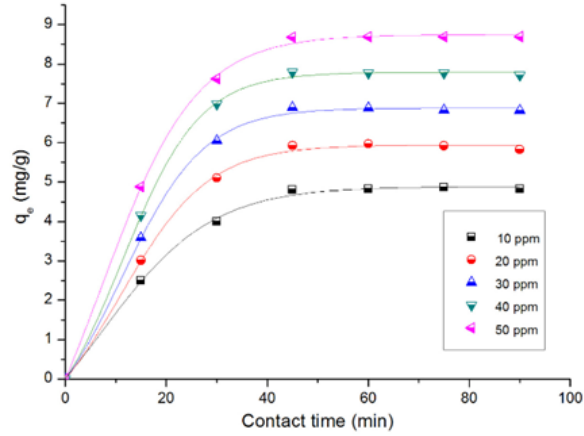


Fig. 8. Contact time versus adsorption capacity of Safranin-o by activated red mud with initial concentration of 50 mg/L, temperature 27° C, adsorbent dose 0.25 mg/g and time 30 min.

3.6. Effect of temperature and thermodynamic study

Thermodynamic parameter such as free energy change (G°), enthalpy change (H°) can be calculated using the following equation:

$$\Delta G = -RT \ln K_c \quad (1)$$

$$\log K_c = \left[\left(\frac{\Delta S}{R} \right) - \left(\frac{\Delta H}{RT} \right) \right] \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

Where K_c is the equilibrium constant, R is the universal rate constant (mol/K), T is the temperature (K).

The Van't Hoff equation in chemical thermodynamics relates the change in the equilibrium constant (K_{eq}) of a chemical equilibrium to the change in temperature, T , given the standard

enthalpy change, ΔH^0 for the process shown in **Fig. 8**. With the increase in temperature, the adsorption increases with indicate the process is exothermic.

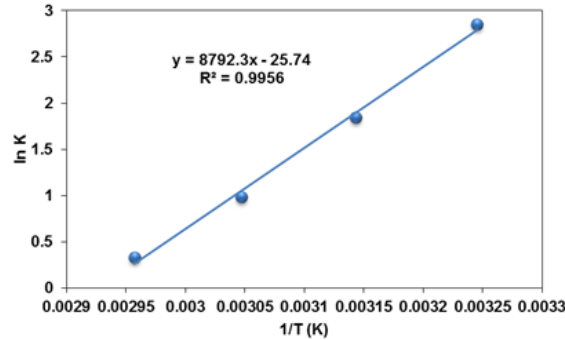


Fig. 8. Van't Hoff plot

3.7. Adsorption Isotherm

Experimental data were analyzed with adsorption isotherm models including Langmuir and Freundlich isotherms. Langmuir adsorption isotherm states that adsorption takes place at specific homogenous sites within adsorbent and has found successful application to many sorption process of monolayer adsorption. The Langmuir isotherm can be written in the following form:

$$\frac{C_e}{q_e} = \frac{1}{(q_m b)} + \frac{C_e}{q_m} \quad (4)$$

Where q_e the adsorbed amount of the dye is, q_m is the monolayer adsorption capacity, C_e is the equilibrium concentration of the dye in the solution. The linear plot of C_e/q_e versus C_e (**Fig. 9**) with correlation coefficient R^2 was found to be 0.9999, 0.9973, 0.9980 for temperature 308, 318 and 328 K, indicates the accuracy of Langmuir isotherm shown in fig .This indicates a monolayer adsorption of Safranin-O onto the adsorbent surface. The maximum adsorption capacity (q_m) and binding energy constant (b) of activated red mud for Safranin-O was 8.9471 mg/g and 1.0265 L/mg, respectively according to Langmuir model.

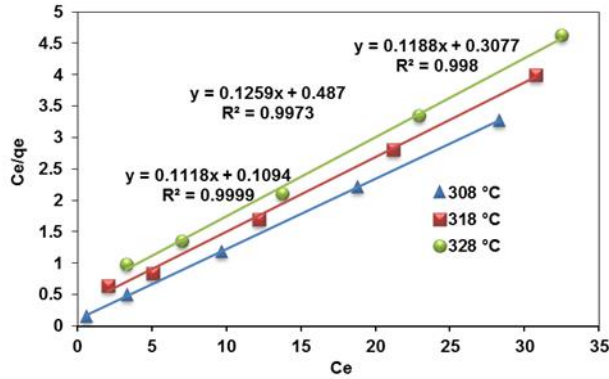


Fig. 9. Langmuir isotherm plot

The Freundlich isotherm is employed to describe heterogenous system. The linear form of Freundlich equation is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where C_e is the adsorption capacity (mg/g) and n is the empirical parameter. The value of K_f , $1/n$ and R^2 are 5.8741, 0.1237, and 0.9257 respectively (**Fig. 10**).

The value of Langmuir and Freundlich isotherm parameter was given in **Table 1**. Higher value of correlation coefficient of Langmuir isotherm indicates that adsorption data fits better with Langmuir equation then by Freudlich isotherm.

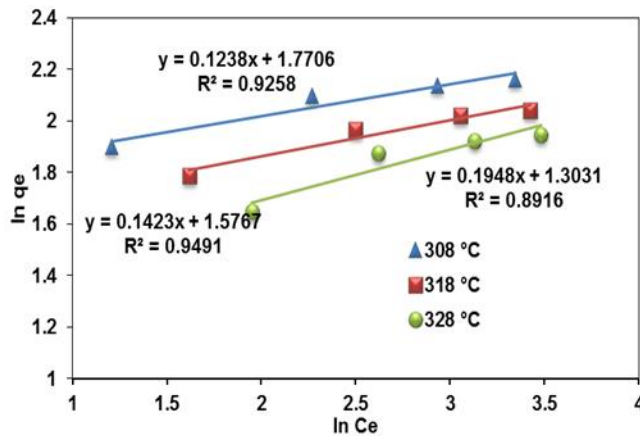


Fig. 10. Freundlich isotherm plot

Table 1: Langmuir isotherm, Freundlich isotherm data at different Temperature

Model	Parameters	Temperature (K)		
		308	318	328
Langmuir Isotherm	q_m (mg/g)	8.9471	8.4193	7.9423
	b (L/mg)	1.0265	0.3859	0.2585
	R^2	0.9998	0.9979	0.9973
Freundlich Isotherm	K_f	5.8741	4.8391	3.6808
	$1/n$	0.1237	0.1422	0.1948
	R^2	0.9257	0.9491	0.8916

3.8. Kinetic Study

Adsorption of Safranin-O at different contact time was studied keeping constant the Safranin-O concentration (50 ppm), the adsorbent dose (0.25 gm), and pH 8 of the solution. The adsorption capacity was found to increase from 1-9 mg/g for contact time of 10-45 min. It is clear from the figure that the Safranin-O rate is high at the beginning of the adsorption, due to available adsorption site, which are open and Safranin-O interact easily with these adsorption sites.

The rate constant K_1 for the adsorption of Safranin-O was studied by Lagergren rate equation, for initial Safranin-O concentration of 50 ppm. Pseudo-first-order rate expression of Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303} \right) \quad (6)$$

where q_e and q_t are the amount of Safranin-O adsorbed (mg/g) at equilibrium at time t (min). k_1 is the pseudo-first order rate constant (min^{-1}). The k_1 and correlation coefficient R^2 were calculated from the slope of linear plot of $\log(q_e - q_t)$ versus 't' at different time intervals (**Fig. 11**). The k_1 and R^2 was found to be 0.0062 and 0.577, respectively, indicating that the adsorption of Safranin-O into ARM did not follow pseudo-first-order rate model.

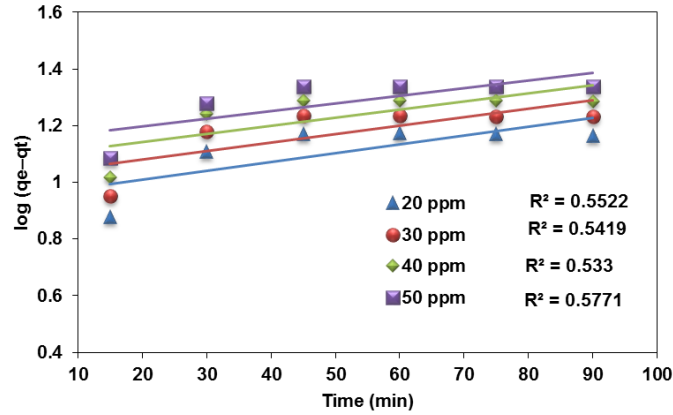


Fig. 11. Pseudo-first-order kinetic model for Safranin-O adsorption

The pseudo-second order rate expression is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) and calculated from the slope and intercept of the plot t/q_t versus time ‘ t ’ (**Fig. 12**). The values of k_1 , k_2 , and R^2 was shown in **Table 2**.

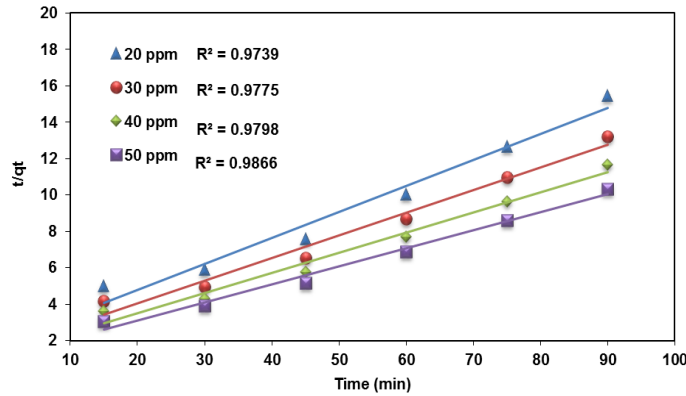


Fig. 12. Pseudo-second-order kinetic model for Safranin-O adsorption

Table 2. Kinetics constants and related regression coefficients.

Initial concentration (mg/L)	Safranin-O	Pseudo-first-order Model			Pseudo-second-order Model		
		q_e (mg/g)	k_1	R^2	q_e (mg/g)	k_2	R^2
20		2.5792	0.0071	0.5522	6.9836	0.0107	0.9739

30	2.7798	0.0068	0.5419	8.0358	0.0099	0.9775
40	2.9625	0.0065	0.5330	9.0197	0.0095	0.9798
50	3.1374	0.0062	0.5771	10.0594	0.0088	0.9866

From the Table 2 is was observed that high value of R^2 indicates that adsorption follow pseudo-second-order kinetics.

Chapter 4

4. Conclusion

From the result we concluded that red mud which is a waste was successfully utilized for the removal of Safranin-O from water. The red mud was activated by using dil. HCl and subsequently excess acid was neutralized by dil. Ammonium hydroxide. The ARM was used as an adsorbent which was tested for leaching of any constituent. It was conformed that the material was used for the removal of Safranin-O. When red mud was added to the solution of Safranin-O, the concentration of Safranin-O was drastically decreased. The optimum condition of adsorbent dose: 0.25 gm, pH: 8, temperature: 35 °C, initial concentration: 50 ppm, the removal is Safranin-O is maximum i.e 8.9 mg/g. From SEM report it is confirmed that it is porous in nature. The R^2

value was found to be 0.9866 at temperature 308 K which indicates that fit with Langmuir isotherm model. From the thermodynamic parameters, it is evident that the process is exothermic in nature. The above data indicates that the material is suitable for removal of Safranin-O from water.

Future work:

- Detailed characterization of the material synthesized before and after the experiment.
- Study of various isotherm models
- Practical application of the material
- Use of low cost materials for the neutralization of red mud.

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