

Oil Cakes: Non-Conventional, Effective and Low-Cost Adsorbents for Removal of Acid Dyes from Aqueous Solution

NEHA PANDEY¹, SOMI ALI¹, MRUDULA PULIMI² and SANGEETHA SUBRAMANIAN^{1,*}

¹School of Bio Sciences and Technology, VIT University, Vellore-63 2014, India

²Center for Nanobiotechnology, VIT University, Vellore-63 2014, India

*Corresponding author: E-mail: sangeethasubramanian@vit.ac.in

Received: 31 August 2015;

Accepted: 12 November 2015;

Published online: 30 January 2016;

AJC-17753

In this study, the adsorption of Acid Red 114 and Acid Black 24 onto sesame oil cake, neem oil cake and groundnut oil cake has been investigated in aqueous solution. Surface study of the adsorbents was investigated using Fourier transform infrared spectra. The effect of operational parameters such as adsorbent dosage, dye concentration and pH on dye removal was evaluated. The intra-particle diffusion model, the pseudo-first order and the pseudo-second order were used to describe the kinetics data. Equilibrium isotherms were analyzed using Langmuir, Freundlich and Temkin adsorption models. The experimental data fitted well to the pseudo-second order kinetics model for dyes. The results indicated that isotherm data followed Langmuir isotherm. Dye desorption studies in aqueous solution at pH 7 showed that acetone is favourable for desorption. It can be concluded that oil cakes could be effectively employed as an effective biosorbent for the removal of dyes.

Keywords: Dyes, Adsorption, Isotherm, Oil cakes, Desorption.

INTRODUCTION

Textile industry in India is the second largest in the world and contributes to about 14 % of the GDP of India. Textile industry is also one of the largest consumers of water, dyes and processing chemicals leading to discharge of about 200-350 m³ of wastewater per ton of the finished product [1]. These effluents are a major source of pollution in India. The textile wastewater is coloured and has high pH, total dissolved solids and chemical oxygen demand. Among the various constituents of wastewater, dyes are arguably the most complex chemicals and the direct discharge of coloured textile effluent into the water bodies adversely affects the aesthetic quality and also dissolved oxygen content of water. Further these dyes are mutagenic and carcinogenic [2].

Stringent and rigid disposal standards of the pollution control boards has necessitated the setting up of wastewater treatment plants before the discharge of water to the environment. Also recycling of water leads to important savings in reduction of water, energy and chemical consumption. For small scale industries which cannot afford advanced treatment techniques, adsorption offers a highly efficient alternative for removal of dyes in terms of cost and ease of operation. Activated carbon is most widely used adsorbent, but its use is limited by high cost. Consequently, a number of low cost, easily

available materials are being studied for removal of different dyes from aqueous solutions (Table-1). In this study, three agriculture wastes sesame oil cake (SOC), neem oil cake (NOC), groundnut oil cake (GOC) are used as adsorbent materials to remove two industrial anionic dyes namely Acid Red 114 and Acid Black 24 from their aqueous solution. The main functional groups present in the anionic dyes are azo, anthraquinone, triphenylmethane, azine, xanthenes, nitro and nitroso [3]. The objectives of this study include studying the effect of pH, initial dye concentration, adsorbent dosage on the adsorption profile of various adsorbents. The mechanism of adsorption will be evaluated by using adsorption kinetic models and adsorption isotherm models.

EXPERIMENTAL

Adsorbent preparation: The adsorbent materials neem oil cake (NOC), sesame oil cake (SOC) and groundnut oil cake (GOC) were collected from oil producing units in Vellore district, India. The cakes were crushed, washed thoroughly with millipore water 10 times to remove dust and impurities and dried for 48 h in a hot air oven at 70 °C. The cakes were further ground and sieved to get a particles size of 36 BSS mesh size. The prepared adsorbent materials were stored in a cool, dry place and used throughout the experiment.

TABLE-1
A COMPARATIVE STUDY ON MAXIMUM ADSORPTION CAPACITY OF DIFFERENT ADSORBENT MATERIALS

| Adsorbent | Adsorbate | Q _e (maximum adsorption capacity) | References |
|---------------------------------------|-----------------|--|---------------|
| Mustard husk | Alizarin Red S | 0.5 | [5] |
| Macauba palm (Natural) | Congo Red | 32 | [6] |
| Orange peel | Direct Red 23 | 10.71 | [21] |
| Orange peel | Direct Red 80 | 21.05 | [21] |
| Surfactant modified coconut coir pith | Direct Red 12 B | 76.3 | [22] |
| Saw dust carbon | Acid yellow 36 | 183.8 | [30] |
| Rice husk carbon | Acid yellow 36 | 86.9 | [30] |
| Neem leaves | Methylene Blue | 8.76 | [32] |
| Eucalyptus wood | Congo Red | 66.66 | [33] |
| Rice husk | Methylene blue | 40.58 | [34] |
| Almond shell | Rhodamine 6G | 32.6 | [35] |
| Neem oil cake | Acid Red 114 | 31.4 | Present Study |
| Sesame oil cake | Acid Red 114 | 55.8 | Present Study |
| Ground nut oil cake | Acid Red 114 | 78.125 | Present Study |
| Neem oil cake | Acid Black 24 | 44.84 | Present Study |
| Sesame oil cake | Acid Black 24 | 35.33 | Present Study |
| Ground nut oil cake | Acid Black 24 | 113.63 | Present Study |

Adsorbate: In this study, commercial synthetic dyes namely Acid Red 114 (Acid Red RS) and Acid Black 24 (Grey WS) purchased from Colourtex, India were used as adsorbates. The dyes were acidic in nature and were used as such without any further modifications or purification. Stock solution of 1000 mg/L was prepared using distilled water. After complete wavelength scan by spectrophotometer (SHIMADZU UV-2401PC), the maximum wavelength was found to be 470 nm and 570 nm for Acid Red 114 and Acid Black 24, respectively.

Batch adsorption studies: The effect of pH on adsorption was measured by adding a fixed amount of adsorbents (2 g/L) to the replicate flasks containing 20 mL of 50 mg/L dye solutions. The dye solutions were adjusted to pH values ranging from pH 3 to pH 9 by using 0.1 N HCl or 0.1 N NaOH solutions. After 105 min, the mixture was centrifuged at 10,000 rpm for 10 min and the supernatant was analyzed at the respective λ_{\max} value of Acid Red 114 and Acid Black 24 using a UV-visible spectrophotometer (SHIMADZU UV-2401PC).

The amount of adsorption at equilibrium q_e (mg/g) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e represents the initial and equilibrium dye concentration (mg/L), respectively. V is the volume of the solution (mL) and W the weight of adsorbent material used (g).

The percent dye removal for adsorption process was calculated from the following equation:

$$\frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100 \quad (2)$$

For evaluating the optimal dosage of adsorbent, varying concentrations of NOC (2-8 g/L), SOC (2-8 g/L) and GOC (0.5-4 g/L) were mixed with 20 mL of 100 mg/L dye solutions of Acid red and Acid Black 24. For measuring adsorption kinetics, the concentration of Acid Red 114 dye was varied from 25 to 100 mg/L and Acid Black 24 dye from 50 to 125 mg/L. To measure the adsorption, samples were collected at pre-determined time interval of 15 min for duration of 105

min. For the study of effect of initial dye concentration and adsorbent dosage, experiments were maintained at pH 3; temperature 37 °C and agitating speed of 110 rpm was used for all the adsorption experiments.

Batch desorption studies: The adsorbent materials namely NOC, SOC and GOC that were used for adsorption process were separated from the aqueous solution by centrifuging at 10,000 rpm for 15 min. Desorption experiments were carried out by treating the dye loaded adsorbent material (10 mg) with 5 mL of different solvents for 120 min. The three solvents used were ethanol (50 and 80 % v/v), methanol (50 and 80 % v/v) and acetone (50 and 80 % v/v). Treated solution was centrifuged and supernatant was analyzed for dye desorption and recovery of dye was calculated.

RESULTS AND DISCUSSION

FTIR analysis: For the determination of functional groups present in NOC, SOC, GOC and their interaction with Acid Red 114 and Acid Black 24, FTIR analysis was performed by using KBr disk. The FTIR analysis of RNOC (Acid Red 114 with NOC), RSOC (Acid Red 114 with SOC), RGOC (Acid Red 114 with GOC), GNOC (Acid Black 24 with NOC), GSOC (Acid Black 24 with SOC) and GGOC (Acid Black 24 with GOC) are shown in Fig. 1. The significant peaks of RNOC had been shifted from 3431.65 to 3441.01, 3140.11 to 3419.79 and 1076 to 1087.85. In case of RSOC, the significant shifts were 3419.79 to 3444.87, 1153.43 to 1093, 1089.78 to 1037.70 and 802.39 to 781. The significant peaks of GNOC had been shifted from 3431.36 to 3441.01, 1157.29 to 1149.57 and 1031.92 to 1024.20. In case of GGOC, the shifts were 3446.79 to 3441.01, 3143.97 to 3132.40, 1743.65 to 1737 and 1026.13 to 1031.92. The band around 3400 cm^{-1} confirmed the O-H stretching [4]. Band between 1300 and 1000 cm^{-1} confirmed C-O-C stretching [5]. The band around 1735 cm^{-1} indicate the C=O stretching [6], peak around 1600 cm^{-1} represents the C=O stretching with the NH_2 [7]. The vibration less than 1000 cm^{-1} represent the sulfur and phosphate groups [8]. Results showed that the material has characteristic peaks of different functional groups, which are able to interact with the adsorbate. The

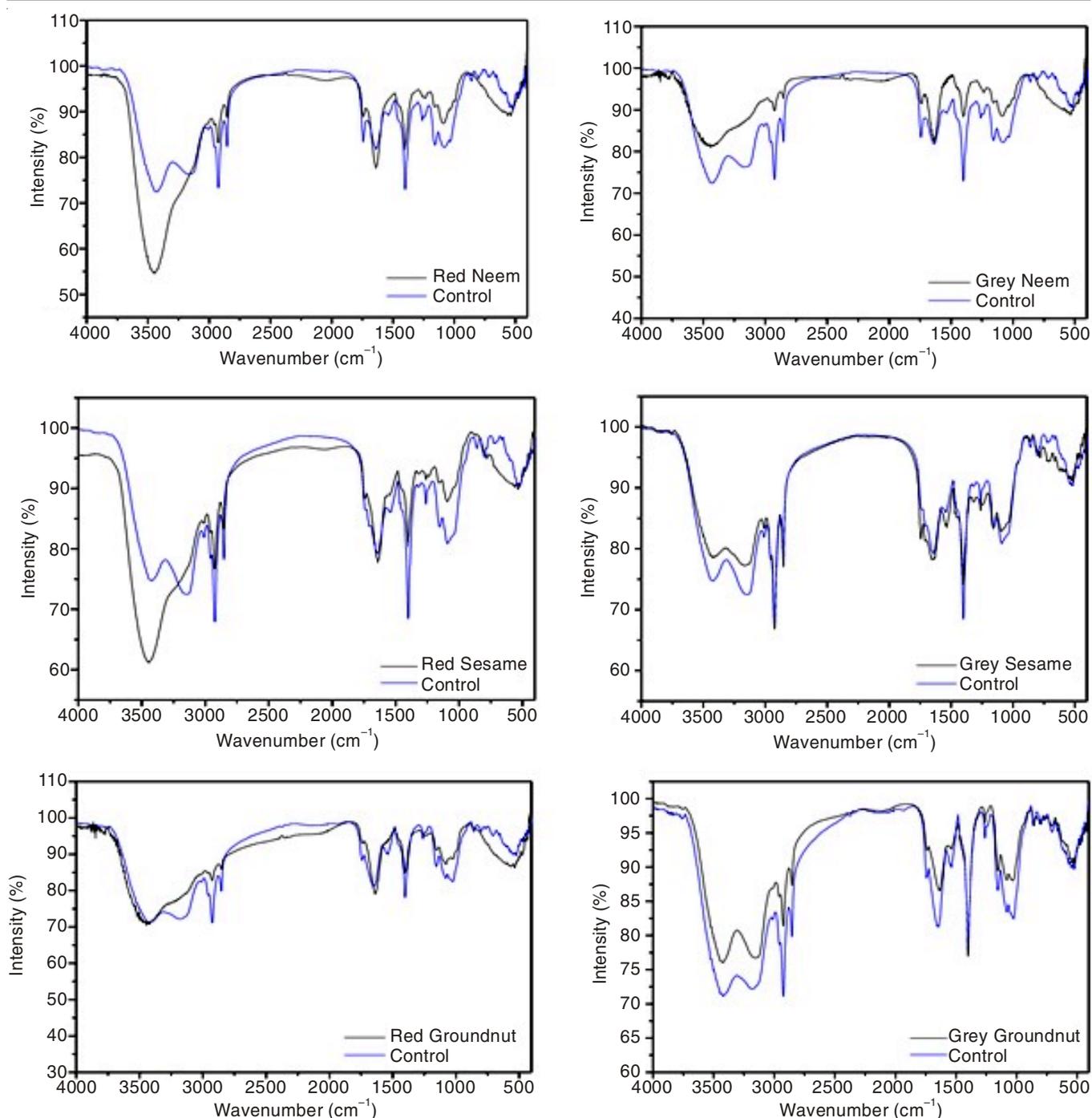


Fig. 1. FTIR spectra of the adsorbent materials (NOC, SOC and GOC) before (control) and after adsorption of Acid Red 114 and Acid Black 24 under acidic condition

disappearance of various peaks and the occurrence of new peaks were observed which was the indication of the adsorption process.

Effect of pH: pH plays an important role in the adsorption process as it controls the rate of adsorption in aqueous medium [9]. Fig. 2 compares the adsorption of both the dyes to NOC, SOC and GOC for an incubation period of 105 min (temperature 37 °C, 110 rpm). As the pH was increased from 3 to 7, the dye uptake for Acid Red 114 was found to decrease from 18.34 to 10.30 mg/g, 18.58 to 11.43 mg/g and 19.4 to 11.2 mg/g for NOC, SOC and GOC, respectively. Similarly for Acid Black 24, the dye uptake was found to decrease from 16.35 to

12.70 mg/g, 15.53 to 11.484 mg/g, 20 to 13 mg/g for NOC, SOC and GOC, respectively. The percent removal for both the dyes using adsorbent materials (NOC, SOC and GOC) was highest at pH 3 and decreased with the further increase in pH. At lower pH, there is availability of positively charged protons and hence the negatively charged dye molecules were easily adsorbed on adsorbent materials through the electrostatic force of attraction. Similar activity of dyes was reported in literature [10-12]. Adsorption was carried out at pH 3 for all further experiments.

Effect of initial dye concentration and contact time: Initial dye concentration is an important factor, as it gives the

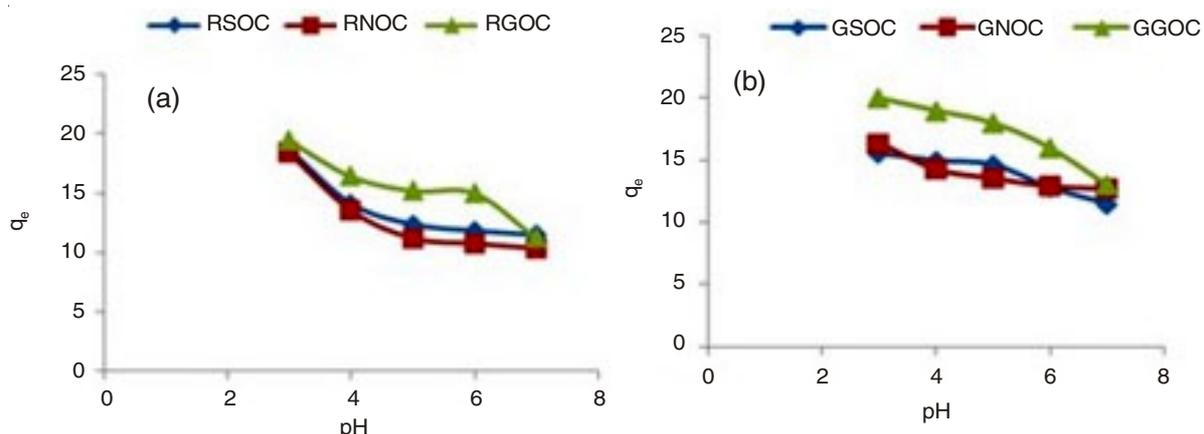


Fig. 2. Effect of pH on dye adsorption (a) Acid Red 114 by NOS, SOC and GOC (b) Acid Black 24 by NOS, SOC and GOC (2 g/L Adsorbent dosage, 50 mg/L initial dye concentration, 100 rpm agitation speed and 37 °C)

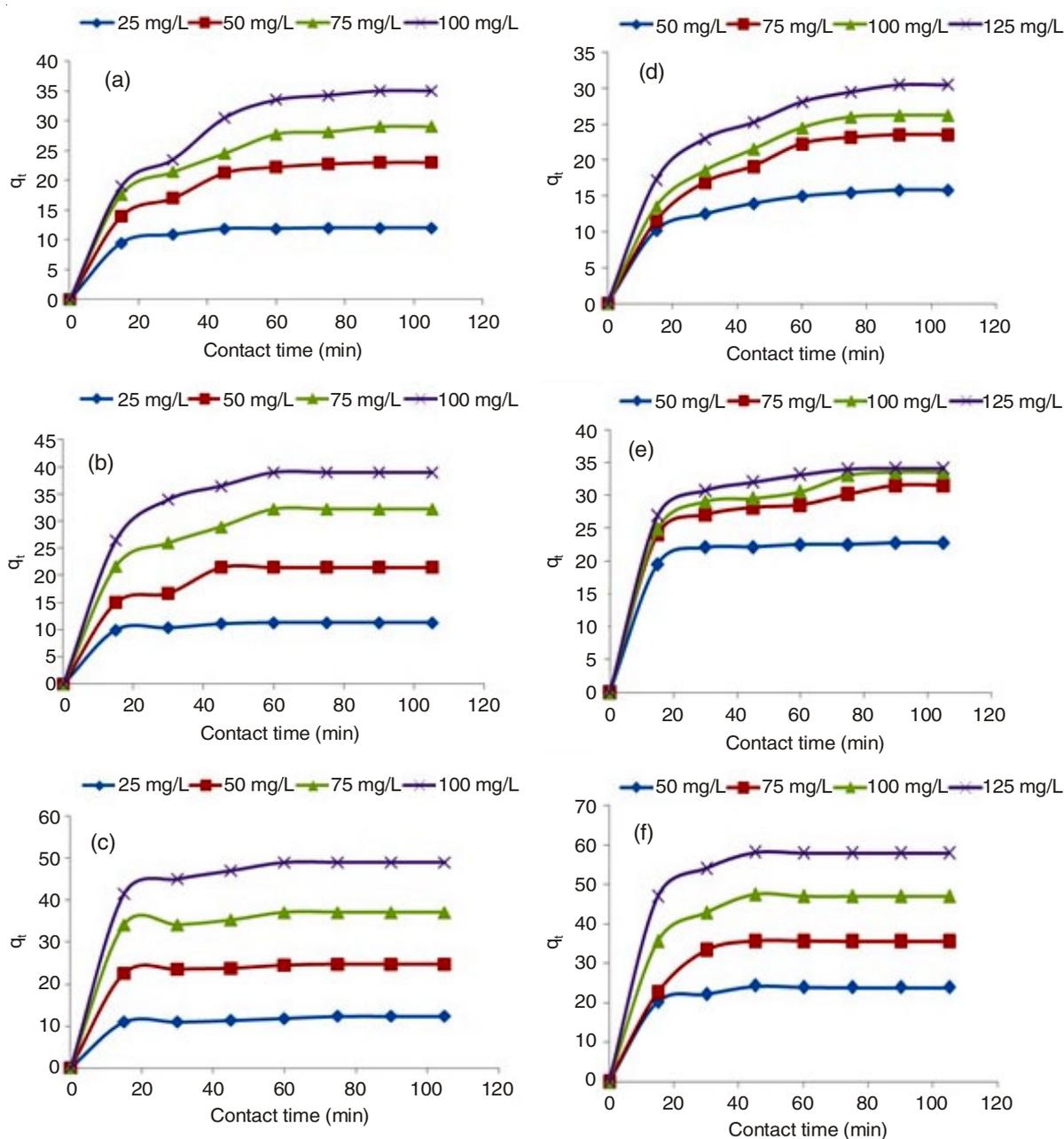


Fig. 3. Effect of contact time and initial dye concentration on the adsorption of Acid Red 114 with (a) NOC (b) SOC (c) GOC and Acid Black 24 with (d) NOC (e) SOC (f) GOC (37 °C temperature, 2 g/L adsorbent dosage, pH 3 and agitation speed of 110 rpm)

immediate relation between the available binding sites on the adsorbent surface and initial dye concentration. So, at lower concentration of dye, availability of active site is more as compared to higher concentration [13]. Effect of initial dye concentration and contact time for all combinations is shown in Fig. 3. For Acid Red 114, it was evident from the figures that the q_e value increased for NOC, SOC and GOC, when the dye concentration increases from 25 to 100 mg/L. Similarly, for Acid Black 24 the q_e value increased when the dye concentration increased from 25 to 100 mg/L. It was observed that the q_t value increased with contact time and concentration until it attained equilibrium. It was also clear that the adsorption rate depended on the initial dye concentration and it was faster during the initial period of time and becomes slower as the contact time increased due to decrease in the concentration which acted as driving force. For higher initial dye concentration, the initial rate of adsorption is greater since the mass transfer driving force increased [14]. Equilibrium time was the same irrespective of initial dye concentration for particular adsorbent material [15]. Equilibrium time for all the combinations for different initial dye concentration with NOC and SOC was found to be 60 min and for GOC it was 30 min. Rapid establishment of the equilibrium was an indication for the efficient use of adsorbent material for the dye removal from wastewater. The contact time profiles of all combinations were smooth and continuous curves, suggesting monolayer coverage of dye on adsorbent surface [16,17].

Effect of adsorbent dosage: The per cent removal of dye from the aqueous solution increased with the increase in adsorbent dosages, as the number of active sites available for adsorption was more, at constant dye concentration [18,19]. A plot of percent removal vs. dosage is given in Fig. 4. It was observed that with further increase in adsorbent dosage the percent removal did not get altered due to the reduction in concentration gradient of dye at the surface of adsorbent material. A similar effect of dosage was observed on dye removal from cashew nut shell [20].

Adsorption kinetics: Information on the kinetics of dye adsorption is required for selecting optimum operating conditions for full-scale batch dye removal processes. Mathematical models that can describe the behaviour of a batch biosorption process operated under different experimental conditions are very useful for scale-up studies or process optimization [21]. The two important aspects for parameter evaluation of the adsorption study are the kinetics and equilibrium of adsorption.

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer, several kinetics models are used to test the experimental data.

Intra-particle diffusion model: Intra-particle diffusion model was studied to identify the diffusion mechanism. This model is common to most of the adsorption processes.

$$q_t = k_{id}t^{1/2} + C \quad (3)$$

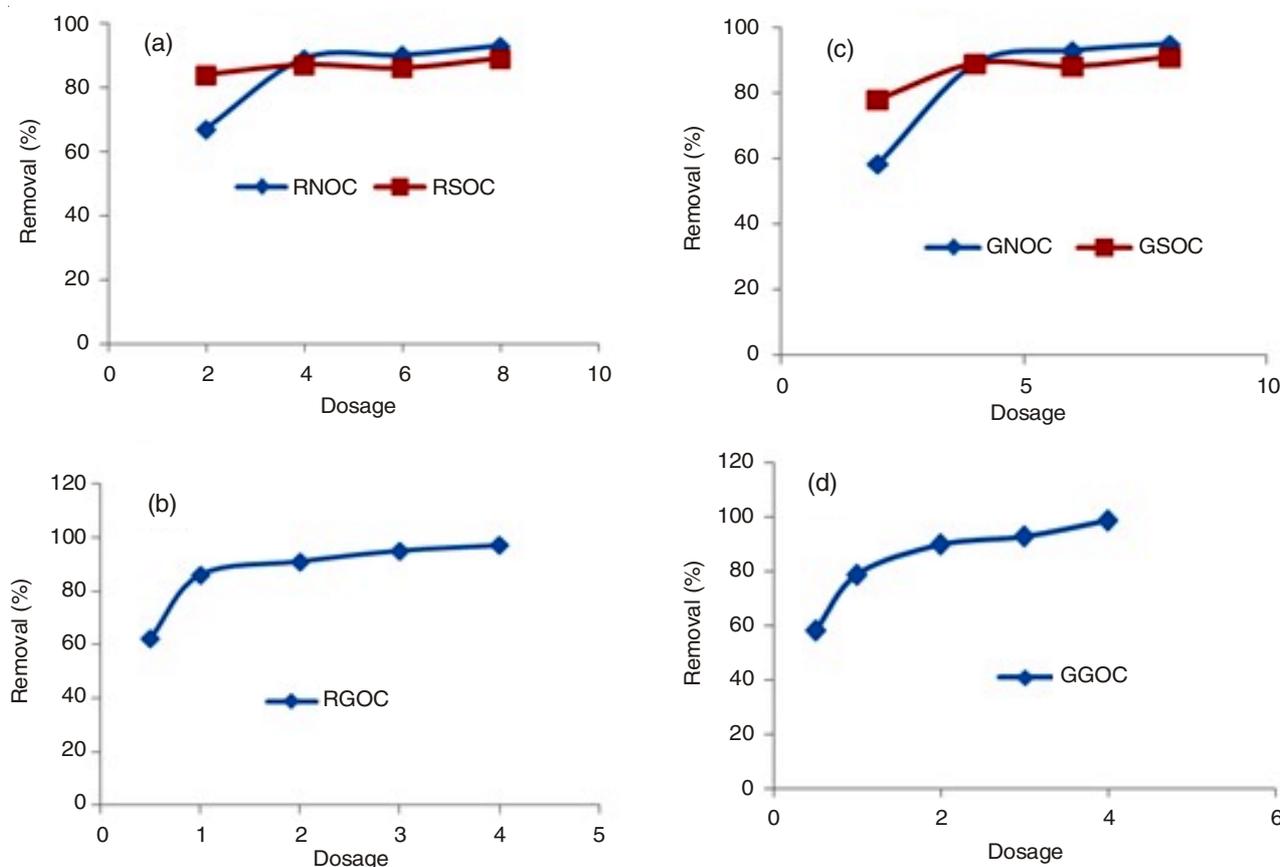


Fig. 4. Effect of adsorbent dosage on the adsorption of Acid red 114 by (a) NOC and SOC (2-8 g/L dosage) (b) GOC (0.5-4 g/L dosage) and Acid Black 24 by (c) NOC and SOC (2-8 g/L dosage) (d) GOC (0.5-4 g/L dosage) (100 mg/L initial dye concentration, 100 rpm agitation speed, 37 °C, pH 3)

where, k_{id} is the intra-particle diffusion rate constant and C is the intercept. Plot of q_t versus $t^{1/2}$ would give a linear relationship (Fig. 5). Intra-particle diffusion would be a controlling step in adsorption if it passes through the origin [20]. Intra particle model usually follows the three steps: the first portion of the graph plot represents the boundary layer diffusion. The second portion represents the intra particle diffusion. Last and third portion is the plateau stage in which the intra-particle diffusion is slow due to the less concentration of the dye left in the solution [22,23]. All the constants of the model are tabulated in Table-2. As observed from Fig. 5, adsorption plots of Acid Red 114 with NOC, SOC and GOC were not linear for the complete time which suggested more than one process responsible for adsorption process. Linear portion did not pass

through the origin, so the adsorption is not controlled by intra-particle diffusion alone and boundary layer diffusion possibly controlled the adsorption to some extent. Similar behaviours of plots were observed for adsorption of Acid Black 24 with NOC, SOC and GOC. The value of intercept C for all the combination increased with the increase in initial dye concentration representing the increasing effect of boundary layer on adsorption process [23]. Similar works of intra-particle diffusion were reported in literature [10,24,25].

In order to analyze the adsorption kinetics of the dyes on the three adsorbent materials (NOC, SOC and GOC) based on chemical reaction, pseudo-first order and pseudo second order were studied. The linearized form of the first order model (Lagergren equation) is given in the following equation:

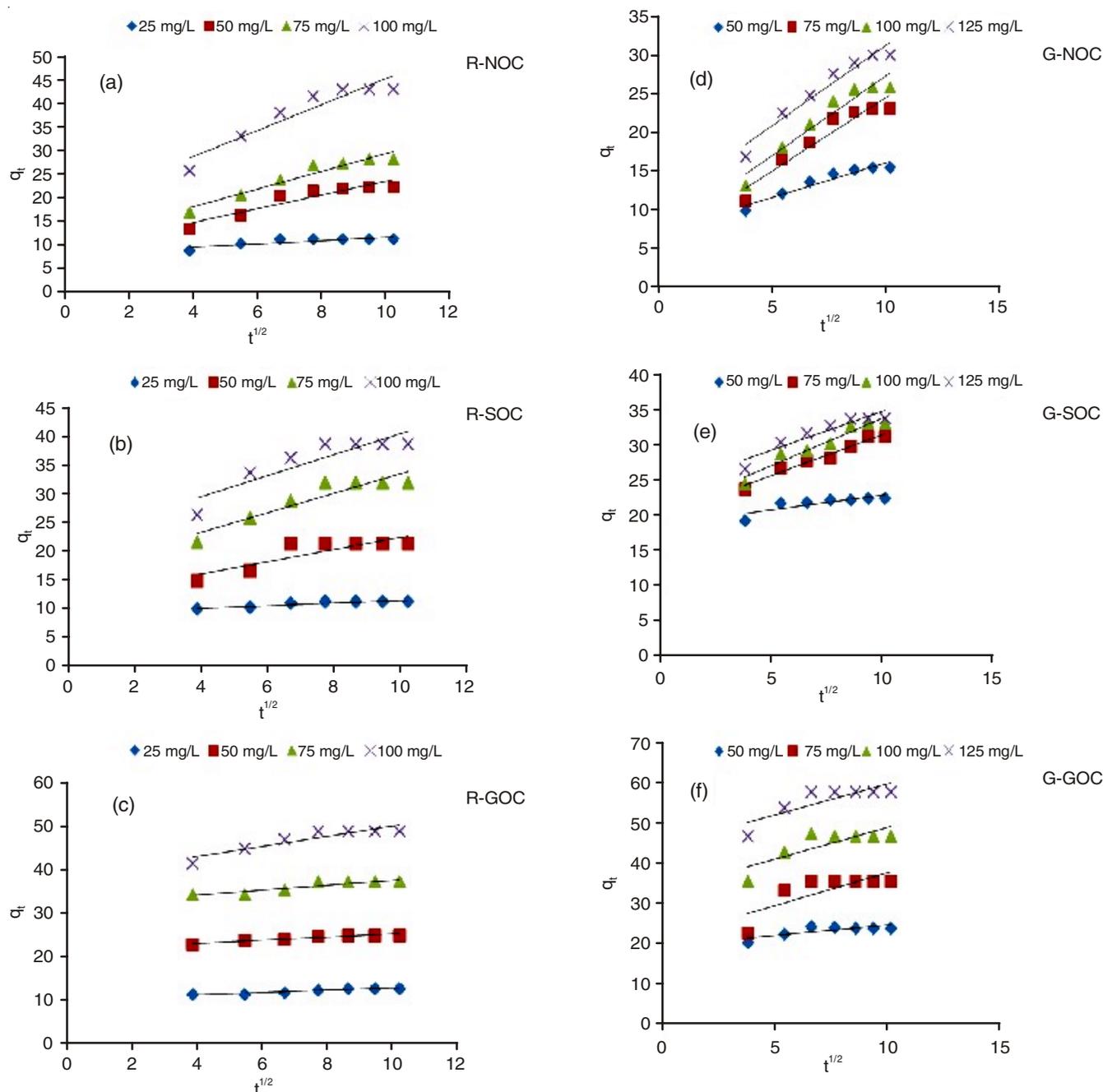


Fig. 5. Intraparticle diffusion plot for the adsorption of Acid red 114 on (a) NOC, (b) SOC, (c) GOC and Acid Black 24 by (d) NOC, (e) SOC and (f) GOC for varying initial dye concentrations (37 °C, pH 3, 110 rpm agitation speed, 2 g/L adsorbent dosage)

TABLE-2
INTRAPARTICLE DIFFUSION CONSTANT AND CORRELATION COEFFICIENT FOR ADSORPTION OF ACID RED 114 AND ACID BLACK 24 ONTO NOC, SOC AND GOC

| Concentration (mg/L) | k_{id} | c (intercept) | R^2 | Acid Red 114 | | | | | |
|----------------------|----------|-----------------|-------|--------------|-----------------|-------|----------|-----------------|-------|
| | | | | k_{id} | c (intercept) | R^2 | k_{id} | c (intercept) | R^2 |
| | RNOC | | | RSOC | | | RGOC | | |
| 25 | 0.34 | 8.85 | 0.71 | 0.23 | 9.28 | 0.83 | 0.26 | 9.76 | 0.90 |
| 50 | 1.45 | 9.59 | 0.86 | 1.06 | 11.98 | 0.74 | 0.36 | 21.35 | 0.91 |
| 75 | 1.87 | 11.34 | 0.93 | 1.70 | 16.70 | 0.86 | 0.58 | 31.61 | 0.84 |
| 100 | 2.78 | 11.37 | 0.89 | 1.83 | 22.45 | 0.79 | 1.17 | 38.28 | 0.85 |
| | GNOC | | | GSOC | | | GGOC | | |
| 25 | 0.89 | 7.46 | 0.93 | 0.43 | 18.81 | 0.72 | 0.51 | 19.32 | 0.65 |
| 50 | 1.90 | 5.78 | 0.91 | 1.16 | 20.03 | 0.96 | 1.65 | 20.99 | 0.59 |
| 75 | 2.07 | 6.89 | 0.93 | 1.35 | 20.41 | 0.93 | 1.59 | 32.95 | 0.66 |
| 100 | 2.09 | 10.7 | 0.94 | 1.09 | 23.94 | 0.88 | 1.54 | 44.37 | 0.68 |

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The linearized pseudo-second order rate equation is given under:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where, q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the adsorption rate constant of pseudo-first-order and pseudo second order adsorption, respectively. The linear plots of $\log(q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively [26]. The rate constants k_1 and k_2 for both dyes can be obtained from the plot of experimental data and are tabulated in Table-3. In present study, pseudo second order (Fig. 6) had shown a good fit with correlation coefficient ($R^2 > 0.98$) compared to pseudo first order so it can be concluded that the adsorption mechanism might be chemisorption according to the literature [27].

Adsorption isotherm: The equilibrium sorption isotherm is necessary in the design of sorption system. The adsorption isotherm describes how the solutes interact with the adsorbent and assesses the distribution of solute between the solid and the liquid phase by measuring the distribution coefficient.

The adsorption data in Fig. 7 is fitted to the Langmuir model. Langmuir isotherm model assumes the monolayer adsorption on structurally and energetically homogeneous active sites and predicts the monolayer coverage at the outer surface of adsorbent [20].

The linear form of Langmuir isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_e b} + \frac{C_e}{Q_e} \tag{7}$$

The maximum adsorption capacity Q_e and the constant b are calculated by a plot of C_e/q_e vs. C_e . The slope of the graph ($1/Q_e$) and the intercept ($1/Q_e b$) are used to calculate the maximum adsorption capacity Q_e and the constant b , respectively (Fig. 7). Dimensionless equilibrium constant R_L is the important characteristic of Langmuir adsorption isotherm and is calculated as follows [28]:

$$R_L = \frac{1}{1 + bC_e} \tag{8}$$

TABLE-3
KINETIC CONSTANTS FOR ADSORPTION OF ACID RED 114 AND ACID BLACK 24 ONTO NOC, SOC AND GOC

| Conc. (mg/L) | Pseudo first order kinetics | | Pseudo second order kinetics | |
|---------------|-----------------------------|-------|------------------------------|-------|
| | K_1 | R^2 | K_2 | R^2 |
| Acid Red 114 | | | | |
| RNOC | | | | |
| 25 | 0.074 | 0.88 | 0.023 | 0.99 |
| 50 | 0.061 | 0.98 | 0.003 | 0.98 |
| 75 | 0.046 | 0.96 | 0.002 | 0.99 |
| 100 | 0.054 | 0.97 | 0.001 | 0.99 |
| RSOC | | | | |
| 25 | 0.057 | 0.88 | 0.031 | 0.99 |
| 50 | 0.021 | 1.00 | 0.005 | 0.99 |
| 75 | 0.039 | 0.99 | 0.005 | 0.99 |
| 100 | 0.053 | 0.99 | 0.003 | 0.99 |
| RGOC | | | | |
| 25 | 0.022 | 0.82 | 0.018 | 0.99 |
| 50 | 0.020 | 0.89 | 0.018 | 0.99 |
| 75 | 0.025 | 0.87 | 0.008 | 0.99 |
| 100 | 0.045 | 0.99 | 0.006 | 0.99 |
| Acid Black 24 | | | | |
| GNOC | | | | |
| 50 | 0.045 | 0.98 | 0.0048 | 0.99 |
| 75 | 0.057 | 0.95 | 0.0016 | 0.99 |
| 100 | 0.046 | 0.98 | 0.0015 | 0.99 |
| 125 | 0.042 | 0.97 | 0.0017 | 0.99 |
| GSOC | | | | |
| 50 | 0.012 | 0.36 | 0.0181 | 0.99 |
| 75 | 0.025 | 0.94 | 0.0039 | 0.99 |
| 100 | 0.041 | 0.82 | 0.0035 | 0.99 |
| 125 | 0.037 | 0.97 | 0.0053 | 0.99 |
| GGOC | | | | |
| 50 | 0.039 | 0.89 | 0.0175 | 0.99 |
| 75 | 0.056 | 0.82 | 0.0043 | 0.99 |
| 100 | 0.058 | 0.89 | 0.0052 | 0.99 |
| 125 | 0.057 | 0.89 | 0.0058 | 0.99 |

b represents Langmuir constant. The value of R_L is used to determine whether the adsorption isotherm is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The values of Q_e , b , R_L and R^2 are tabulated in Table-4. The values of R^2 were in the range of 0.93 to 0.97 and 0.97 to 0.99 for Langmuir isotherms of the adsorption of Acid Red 114 and Acid Black 24, respectively.

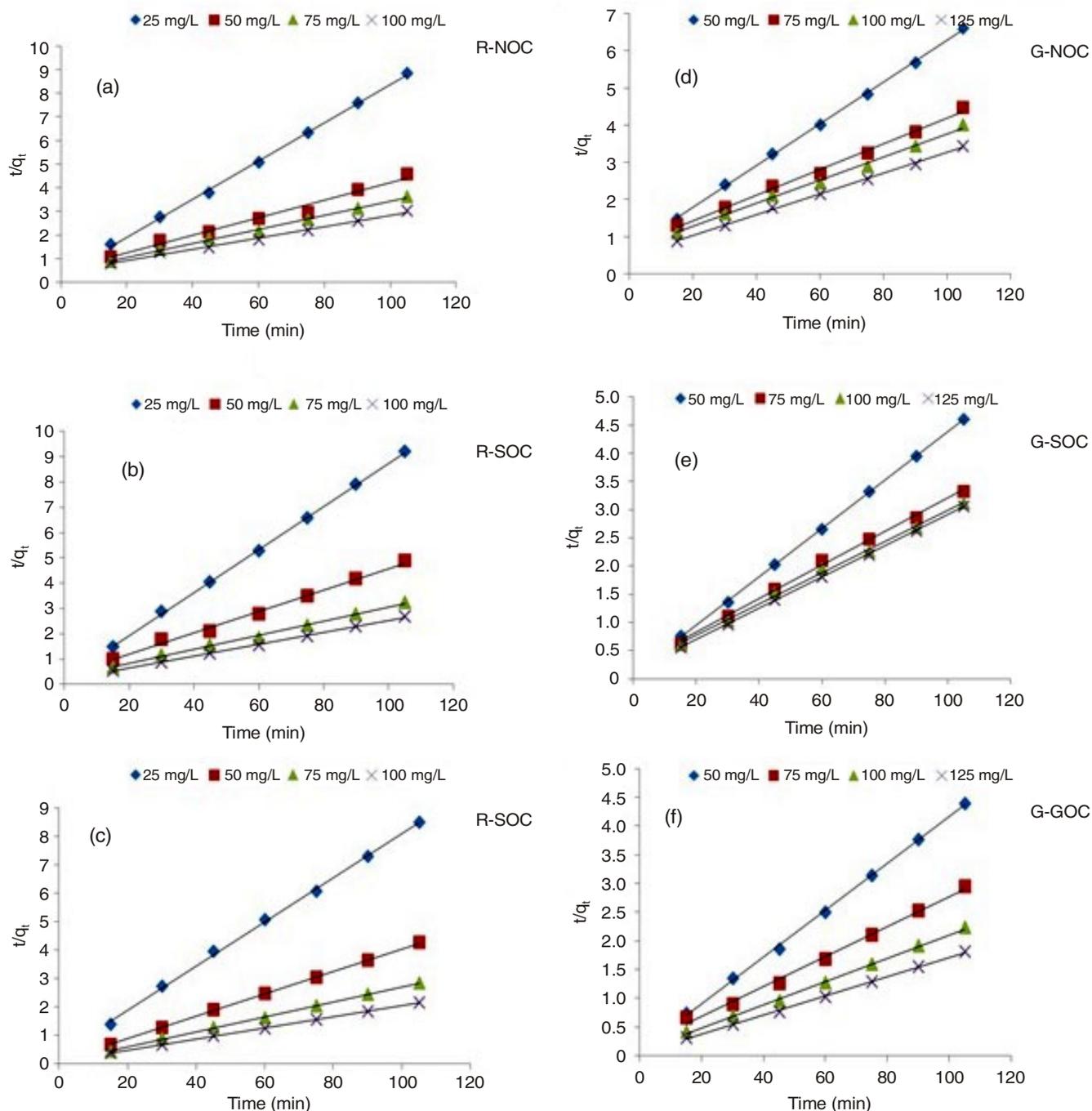


Fig. 6. Pseudo second order kinetics for adsorption of Acid red 114 by (a) NOC, (b) SOC, (c) GOC and Acid Black 24 by (d) NOC, (e) SOC and (f) GOC. (37 °C, pH 3, 110 rpm agitation speed, 2 g/L adsorbent dosage)

| TABLE-4 ADSORPTION ISOTHERM CONSTANTS FOR ACID RED 114 AND ACID BLACK 24 ON NOC, SOC AND GOC | | | | | | | | | | |
|---|-------------------|-----------------------|----------------------|----------------|--|------|----------------|-----------------|-------|----------------|
| Adsorbent | Langmuir isotherm | | | | Freundlich isotherm | | | Temkin isotherm | | |
| | b | Q _e (mg/g) | R _L range | R ² | K _F (mg/g (mg/g) ^{1/n}) | N | R ² | A | B | R ² |
| Acid Red 114 | | | | | | | | | | |
| NOC | 0.289 | 31.4 | 0.12-0.03 | 0.97 | 11.71 | 3.97 | 0.95 | 5.24 | 6.27 | 0.98 |
| SOC | 0.108 | 55.8 | 0.27-0.08 | 0.97 | 7.29 | 1.76 | 0.97 | 0.87 | 14.75 | 0.95 |
| GOC | 0.901 | 78.125 | 0.04-0.01 | 0.93 | 35.9 | 1.53 | 0.91 | 8.41 | 17.96 | 0.97 |
| Acid Black 24 | | | | | | | | | | |
| GNOC | 0.033 | 44.84 | 0.37-0.19 | 0.97 | 4.27 | 2.09 | 0.92 | 0.267 | 10.71 | 0.95 |
| GSOC | 0.507 | 35.33 | 0.04-0.01 | 0.99 | 19.44 | 6.71 | 0.85 | 65.3 | 4.32 | 0.85 |
| GGOC | 0.117 | 113.63 | 0.15-0.06 | 0.99 | 14.07 | 1.53 | 0.99 | 1.007 | 25.16 | 0.98 |

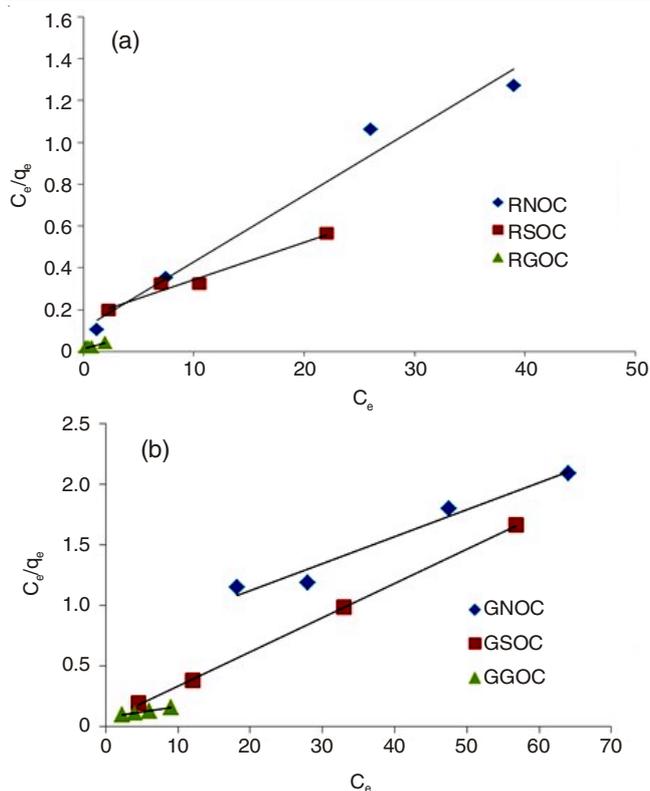


Fig. 7. Langmuir plot for (a) adsorption of Acid red 114 and (b) Acid Black 24 (37 °C, pH 3, 110 rpm agitation speed, 2 g/L adsorbent dosage)

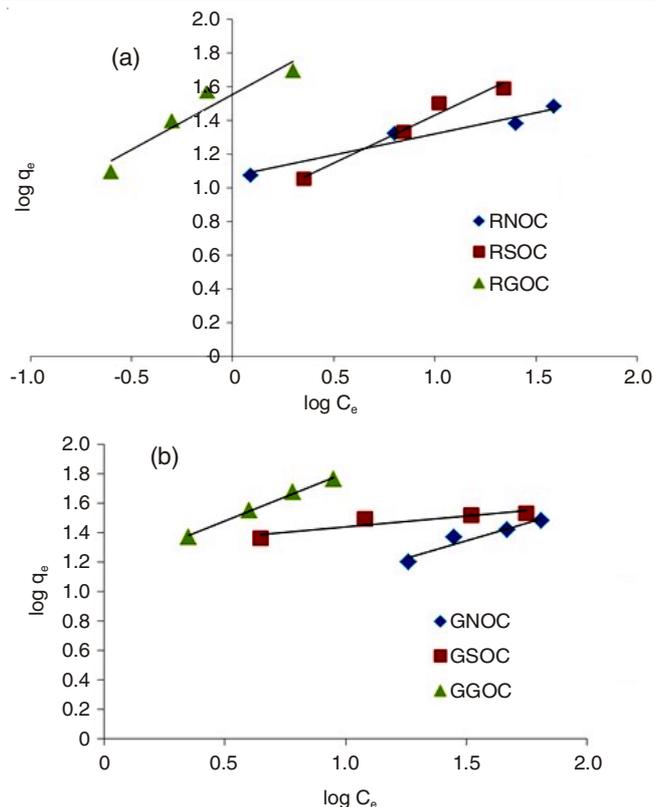


Fig. 8. Freundlich isotherm for (a) adsorption of Acid red 114 and (b) Acid Black 24 (37 °C, pH 3, 110 rpm agitation speed, 2 g/L adsorbent dosage)

Freundlich isotherm is used to describe the adsorption on the surface that has heterogeneous energy distribution [29]. The linear form of Freundlich can be given as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (9)$$

K_F and $(1/n)$ are the adsorption capacity and the measure of adsorption intensity or surface heterogeneity, respectively (Fig. 8). Langmuir is favourable if the value of $1/n$ comes under the range $(0 < 1/n < 1)$ [29] and R^2 represents correlation coefficient. The values of K_F , n and R^2 are tabulated in Table-4. For Freundlich isotherms R^2 values were in the range of 0.91 to 0.97 for adsorption of Acid Red 114 and 0.85 to 0.99 for Acid Black 24.

Temkin model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions and the adsorption is a uniform distribution of maximum binding energy [24]. The linear form of the equation can be given as follows:

$$q_e = B \ln A + B \ln C_e \quad (10)$$

where, $B = RT/b$; T is the absolute temperature in Kelvin; B is Temkin constant which is related to heat of adsorption (J/mg); A is an equilibrium constant related to maximum binding energy (L/mg).

Plot of q_e vs. $\ln C_e$ is fitted linearly with the adsorption data of Acid Red 114 with NOC, SOC and GOC and shown in the Fig. 9. The values of R^2 , B and A is given in Table-4. The value of correlation factor $R^2 > 0.95$ shows better applicability of Temkin isotherm.

From Table-4, the values of R_L (Langmuir separation or equilibrium parameter, dimensionless) for the adsorption of

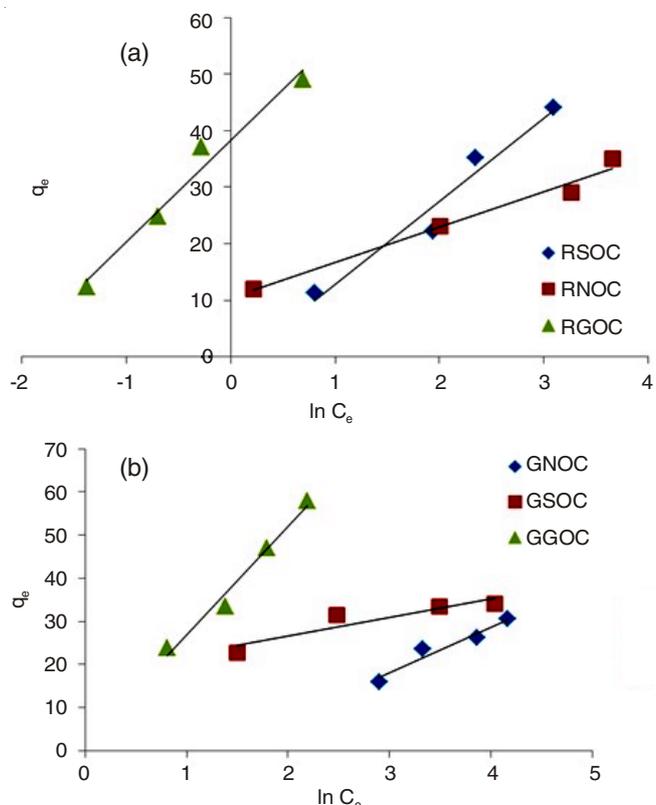


Fig. 9. Temkin isotherm for (a) adsorption of Acid red 114 (b) Acid Black 24 (37 °C, pH 3, 110 rpm agitation speed, 2 g/L adsorbent dosage)

acid dyes confirm that the oil cake surfaces are favourable for the adsorption of acid dyes under conditions used in this study.

Similar observations were reported for the adsorption of acid orange 10 dyes onto activated carbons prepared from agricultural waste bagasse [30] and also for the adsorption of methylene blue on green pea peals [31].

Desorption study: Desorption study was carried to regenerate the absorbent materials and dyes. Desorption study aided to understand the practical utility of the adsorbent material. Desorption of dyes by different oil cakes are shown in Table-5. With 50 % acetone, desorption of Acid Red 114 and Acid Black 24 from GOC and NOC showed a maximum percent recovery of 84.62 and 66.56 %, respectively. With 80 % acetone, Acid Red 114 and Acid Black 24 showed maximum percent recovery of 46 and 65 %, respectively. 54.9 and 54.4 % recovery was observed with 50 % ethanol. Acid Red 114 and Acid Black 24 with NOC showed a maximum percent recovery of 30.24 % and 45 with 80 % ethanol. With 50 % methanol, Acid Red 114 with GOC showed maximum percent recovery of 33.66 % and with 80 % methanol, Acid Red 114 with NOC showed maximum percent recovery of 40.55 %. With 50 and 80 % methanol, Acid Black 24 with NOC showed maximum percent recovery of 64 and 59 %, respectively. On comparison, recovery of dye was efficient when acetone was used as solvent.

TABLE-5
PERCENTAGE OF ACID RED 114 AND ACID BLACK
24 DYE DESORBED FROM NOC, SOC AND GOC BY
ACETONE, ETHANOL AND METHANOL

| | Acetone | | Ethanol | | Methanol | |
|---------------|---------|-------|---------|-------|----------|-------|
| | 50 % | 80 % | 50 % | 80 % | 50 % | 80 % |
| Acid Red 114 | | | | | | |
| RNOC | 66.00 | 46.00 | 54.90 | 28.72 | 13.35 | 40.55 |
| RSOC | 61.58 | 43.19 | 7.07 | 24.64 | 25.13 | 5.42 |
| RGOC | 84.62 | 27.41 | 9.86 | 30.24 | 33.66 | 2.41 |
| Acid black 24 | | | | | | |
| GNOC | 66.56 | 65.00 | 54.40 | 45.00 | 64.00 | 59.00 |
| GSOC | 31.03 | 46.39 | 42.17 | 28.02 | 38.56 | 37.66 |
| GGOC | 17.33 | 1.99 | 34.10 | 37.80 | 32.96 | 11.94 |

Conclusion

The present work results showed that all the three adsorbent materials exhibited good potential for the removal of Acid Red 114 and Acid Black 24 from aqueous solutions. The optimum pH for the removal of both the dyes using NOC, SOC and GOC was found to be 3. Equilibrium data was analyzed using Langmuir, Freundlich and Temkin adsorption isotherms. The maximum adsorption capacity was exhibited by GOC with 78.12 and 113.63 mg/g for Acid Red 114 and Acid Black 24, respectively. Pseudo-second order kinetics was favourable for the present experiment. The experimental results showed that

intra-particle diffusion and boundary layer phenomenon controlled the adsorption process. FTIR was used to study the dye interaction with adsorbent, oil cakes. Desorption was favourable with acetone when compared to methanol and ethanol for the recovery of acid dyes.

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