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Removal of Orange G from Aqueous Solutions by Activated Carbon Obtained from Agricultural Wastes: Isotherm and Kinetic Studies

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We prepared activated carbon from an agricultural waste, kuppaimeni leaf (KPL, *Acalypha Indica*), karuvelai leaf (KVL, *Prosopis juliflora*) and bottle gourd shell (BGS, *Lagenaria siceraria*) powders to utilize them as adsorbents for the removal of an anionic dye, Orange G (OG) from aqueous solutions. The effect of various parameters such as initial dye concentration, time, pH and temperature were investigated in the adsorption studies of Orange G dye removal. The experimental values were in good agreement with the model predicted values. Adsorption data were modeled using Freundlich and Langmuir adsorption isotherms. The adsorption of Orange G dye by activated carbon obeys Langmuir isotherm. Adsorption kinetic data were also tested using pseudo-zero, first and second-order kinetics. Kinetic studies revealed that the adsorption follows pseudo-second-order reaction. SEM results showed that the surface of the activated carbon was turned from dark to light colour after dye adsorption.

Keywords: Orange G, Adsorbents, Adsorption isotherm, Kinetics study.

INTRODUCTION

Water is involved in all body functions: digestion, assimilation, elimination, respiration, maintaining temperature (homeostasis) integrity and the strength of all body structures [1]. Today, the water is polluted with hundreds of toxins and impurities. Our drinking water today, far from being pure, contains some two hundred deadly commercial chemicals [2]. In the world wide undesirable environmental problem is water pollution and it requires solutions. Most of the industries like paper printing, colour photography, pharmaceutical, leather, cosmetics, plastic and other industries to produce a lot of wastewater, which contains a number of contaminants, toxic compounds and many different dyes [3,4]. Most of the organic dyes are hazardous and it may affect aquatic and human life causing various diseases and disorders [5]. Orange G is a mono-azo, negatively charged dye and widely used in printing and textile industries. The dye is reported to be highly toxic to human beings due to its carcinogenic and teratogenic nature [6]. In the present investigation, activated carbon was prepared from an agricultural waste, kuppaimeni leaf (KPL), karuvelai leaf (KVL) and bottle gourd shell (BGS) powders to use them as adsorbents for the adsorptive removal of a toxic dye, Orange G (OG) from its aqueous solutions. The various parameters influencing the removal process of Orange G dye on to the adsorbents were investigated. Kinetics, isotherm and thermodynamic studies were carried out for a better understanding of the adsorption process. Scope for adsorbent regeneration was also explored in order to make the treatment process cost effective.

EXPERIMENTAL

Preparation of activated carbon adsorbent: The bio-wastes kuppaimeni leaf, karuvelai leaf and bottle gourd shell were collected from the countryside in India used in the present study. The collected samples were washed thoroughly with deionized water to remove adhering dirt particles from the surface and then dried by oven (70 °C) for 24 h. 50 g of dried samples were put in a container and 100 mL concentrated HNO_3 was added as impregnating reagent and then kept for 24 h. After the acid was filtered out the samples were washed with distilled water till neutral pH. The activated product was then washed with deionized water until the pH of the washing solution reached 6-7, then dried at 80 °C, for 7 h, crushed and sieved then stored in plastic bottle for further experimental work.

Preparation of Orange G stock solution (OG): The Orange G (C.I. 16230) used in this work was purchased from Merck. The stock solution of Orange G dye was prepared by

dissolving the appropriate amount of dye in distilled water to the concentration of 500 mg/L. The experimental solutions were obtained by diluting the stock solution in accurate proportions to the required initial concentrations.

Characterization of adsorbents: Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology of the adsorbents. The surface morphological features of the adsorbents before and after the adsorption of dye were studied by SEM (VEGA3 TESCON), available at Gandhigram Rural University, Dindigul, India.

Adsorption equilibrium studies: Batch experiments were carried out to evaluate the effect of contact time, initial dye concentration, solution pH and temperature for the removal of Orange G dye on kuppaimeni leaf, karuvelai leaf and bottle gourd shell adsorbents from aqueous solutions. Adsorption experiments were carried out in 250 mL Erlenmeyer flasks. Adsorption of Orange G onto kuppaimeni leaf, karuvelai leaf and bottle gourd shell were studied for a fixed amount of adsorbent (2 g/L) to a series of Orange G dye solution at various initial concentrations (20-60 mg/L) at constant pH (dye pH) and temperature (303 K). The concentration of Orange G was determined at λ_{max} = 485 nm, by using UV-visible spectrophotometer. The amount of dye adsorbed on the adsorbent was estimated by the difference between the initial concentration in aqueous solution and that found in the supernatant. The amount of dye-adsorbed q_e (mg g^{-1}) was determined by

$$q_e = \frac{(C_i - C_e)}{W} \times V$$

The percentage of dye removal is calculated by the following equation:

$$\text{Removal of dye } (\%) = \left(\frac{C_o - C_t}{C_o} \right) \times 100$$

where, C_o is the initial concentration of dye at time t = 0 (mg/L), C_e is the equilibrium concentration of dye (mg/L), V is the volume of dye solution (L) and W is the mass of adsorbent used (g). C_t (mg/L) is the concentration of dye at time t.

RESULTS AND DISCUSSION

Scanning electronic microscope analysis: The surface morphology of before and after adsorption of adsorbents karuvelai leaf, kuppaimeni leaf and bottle gourd shell were investigated by SEM (Fig. 1). The particles were found to be clumped together as a result of the formation of a weak van der Waal bond between the particles. The particles appear to be smooth and very distinguished dark spots which can be taken as a sign for effective acid treatment.

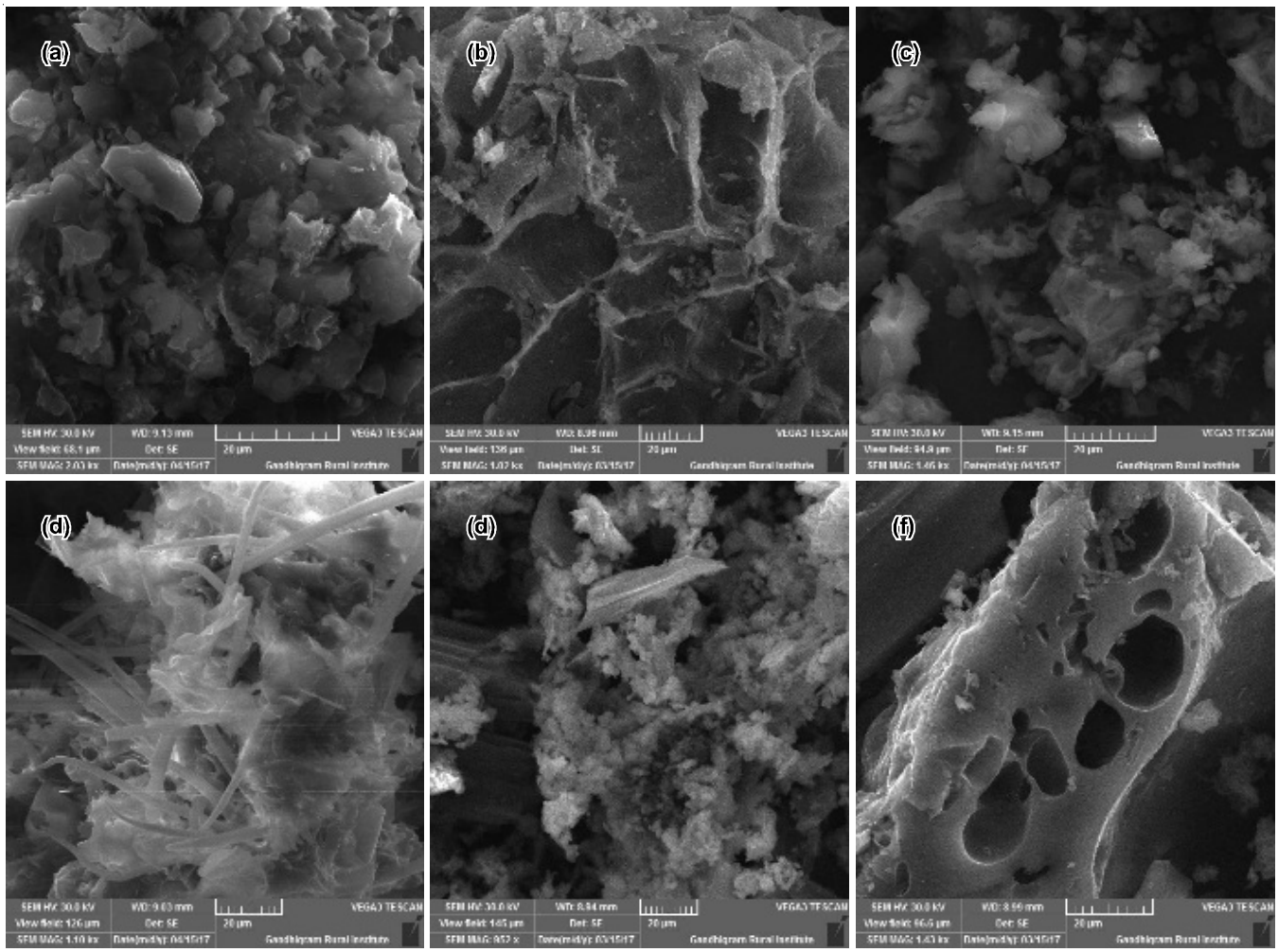

Fig. 1. SEM images of adsorbents kuppaimeni leaf, karuvelai leaf and bottle gourd shell before (a, c and e) and after (b, d and f) adsorption of Orange G dye

Effect of contact time and initial dye concentration: Effect of initial dye concentration on adsorption of Orange G onto kuppaimeni leaf, karuvelai leaf and bottle gourd shell were investigated at 40 mg/L concentration of Orange G Fig. 2 shows the effect of contact time on the removal of Orange G by kuppaimeni leaf, karuvelai leaf and bottle gourd shell at 303 K. The adsorbed amount of Orange G increases sharply with time in the initial stage and then progressively increases to reach equilibrium value in approximately 90 min. However, the experimental data are measured after 180 min to make sure that full equilibrium has been attained. The removal of Orange G is quite rapid initially. The initial faster rate may be due to the accessibility of uncovered surface area of the adsorbent. Because of the adsorption kinetics depends on the nature and the concentration of the active sites of the adsorbent, which are responsible for the interaction with Orange G. The same trend is observed for the adsorption of Orange G dye using carbon mesoporous material [7].

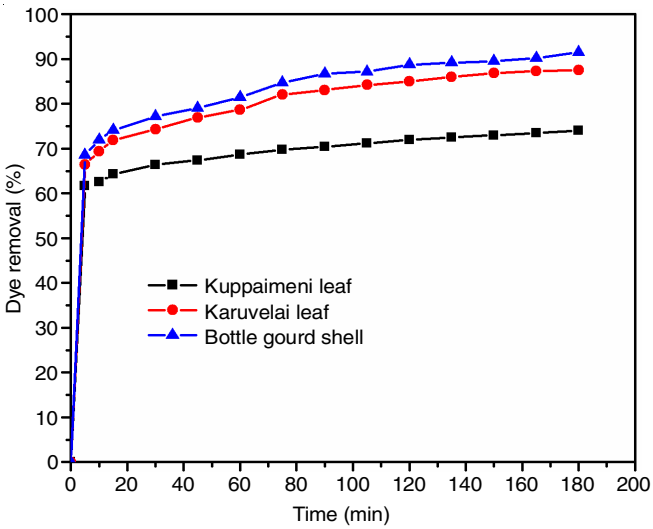

Fig. 2. Effect of initial Orange G concentration on the uptake of Orange G by kuppaimeni leaf, karuvelai leaf and bottle gourd shell

Effect of pH: Another important role of adsorption process is pH because pH decides the nature of the adsorbent surface when it comes in contact with the adsorbate solution. For the present investigation of the effect of pH on the removal of Orange G, the pH of the dye solution varied from 4.4 to 12.4 using 1 N HCl and 1 N NaOH. The percentage of dye removal efficiency as a function of pH, is shown in Fig. 3 for the initial dye concentrations of 40 mg/L, adsorbent dosage of 2 mg/L and a shaking time of 15 min of operation. From the Fig. 3, it is clear that removal of dye was higher at lower pH. Removal of kuppaimeni leaf, karuvelai leaf and bottle gourd shell increased from 72.4 to 88.3, 74.2 to 93.9 and 79.6 to 97.9 % by decreasing the pH from 12.4 to 4.4. At acidic pH, the adsorbent surface becomes positively charged, which favours the anionic dye species. The tendency of decreasing trend of removal of dye on increasing pH of dye solution may be ascribed to the deprotonation of the adsorbent surface.

A similar trend is also observed for the adsorption of Orange G on polystyrene modified chitin [8].

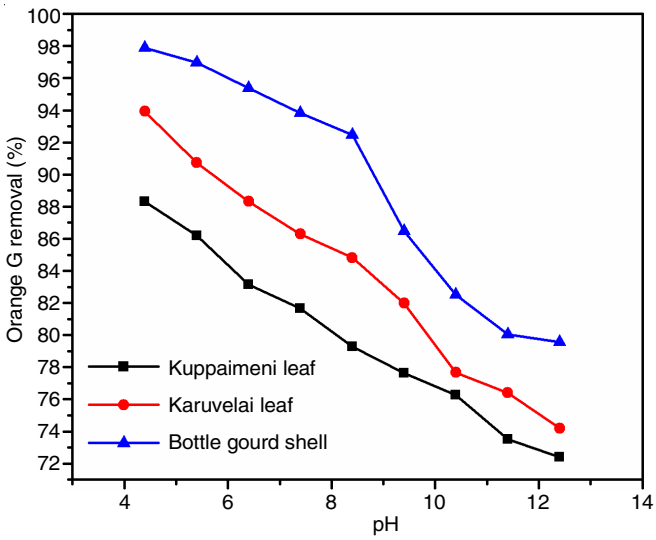

Fig. 3. Effect of initial pH on the uptake of Orange G by kuppaimeni leaf, karuvelai leaf and bottle gourd shell (Concentration = 40 mg/L, T = 303 K, Dose = 2 g/L and Time = 15 min)

Effect of temperature: The percentage of Orange G adsorption was studied at different temperature in the range of 293-313 K. The results of percentage of Orange G removal obtained are presented in Fig. 4. The percentage of Orange G removal increases with decrease in temperature. This may be due to desorption caused by an increase in the obtainable thermal energy. The higher mobility of the adsorbate induces at higher temperature this may be due to causing desorption. Then the quantity of adsorption was found to increase as the temperature decreased (exothermic process). A related reported by others previously for adsorption of Orange G onto modified sawdust [9].

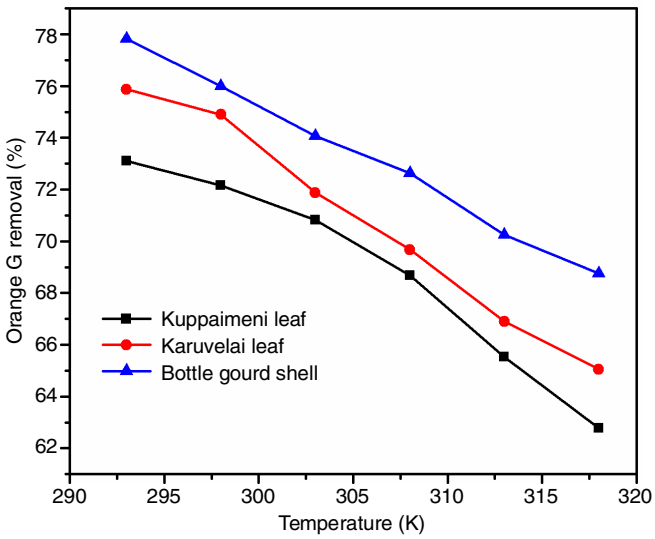

Fig. 4. Effect of temperature on the uptake of Orange G by kuppaimeni leaf, karuvelai leaf and bottle gourd shell (Concentration = 40 mg/L, T = 303 K, Dose = 2 g/L and Time = 15 min)

Langmuir isotherm: The Langmuir isotherm monolayer adsorption model as expressed by the equation below [10]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$

where C_e is equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), Q_o (mg/g) and b (mg/L) are Langmuir constants related to adsorption capacity and rate adsorption, respectively. The values of Langmuir constants Q_o and b were determined from the slope and the intercept of the linear plot of C_e/q_e *vs.* C_e (Table-1).

The Langmuir equation can be expressed in terms of dimensionless separation factor R_L, defined by equation [11]:

$$R_L = \frac{1}{1 + bC_o}$$

The R_L value reveals the nature of the isotherm: favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), respectively [12,13].

The R_L values for kuppaimeni leaf, karuvelai leaf and bottle gourd shell were calculated as 0.521, 0.444 and 0.356 respectively, with coefficients of determination (R^2) 0.997, 0.998 and 0.993 respectively. This indicates that the adoption is favourable (Table-1). The comparisons of maximum monolayer adsorption capacity of Orange G on various adsorbents are listed in Table-2. Kuppaimeni leaf, karuvelai leaf and bottle gourd shell have relatively large adsorption capacity of 37.45, 46.9 and 39.68 mg/g and this is indicating that three adsorbents could be considered as an effective adsorbent for the removal of Orange G from aqueous solution.

Freundlich isotherm: Freundlich isotherm is applicable to adsorptions on heterogeneous surfaces involving the interaction between the adsorbed molecules. The equation for the Freundlich model is represented as below [19]:

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

where q_e is the amount of adsorbate adsorbed at equilibrium per unit mass of the adsorbent (mg/g), K_F is the Freundlich constant, 1/n is the heterogeneity factor which is related to the adsorption intensity and C_e is the equilibrium concentration (mg/L). The 1/n and K_F values obtained from the plot of log q_e against log C_e as slope and intercept. The Freundlich isotherms plots for the adsorption of Orange G onto kuppaimeni leaf, karuvelai leaf and bottle gourd shell were used to determine K_F and n values, which are the characteristic constants that reveal the nature of the adsorption as listed in Table-1.

The heterogeneity factor n for Orange G on kuppaimeni leaf, karuvelai leaf and bottle gourd shell is largely of $n > 1$ indicating favourable adsorption. The R^2 values suggest that the Langmuir isotherm provides a good fit to isotherm dada for Orange G on kuppaimeni leaf, karuvelai leaf and bottle gourd shell (Table-1).

Pseudo-first-order kinetic model: The Lagergren pseudo-first-order kinetic model equation is [24]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

where q_t (mg/g) is the amount of dye adsorbed at time (t), k_1 (1/min) is the first-order rate constant and q_e (mg/g) is the amount of Orange G adsorbed on the surface at equilibrium. The value of k_1 for Orange G adsorption by kuppaimeni leaf, karuvelai leaf and bottle gourd shell was determined from the slope of the linear plot of log ($q_e - q_t$) against time (t) (Fig. 5).

TABLE-1
VARIOUS EQUILIBRIUM ISOTHERM COEFFICIENTS OBTAINED FOR ADSORPTION OF ORANGE G ON KUPPAIMENI LEAF, KUPPAIMENI LEAF AND BOTTLE GOURD SHELL

Adsorbents	Langmuir isotherm model				Freundlich isotherm model		
	Q_o	b	R_L	R^2	K_F	n	R^2
Kuppaimeni leaf	37.45	0.0370	0.521	0.997	1.517	1.261	0.985
Kuppaimeni leaf	46.90	0.0451	0.444	0.997	2.153	1.286	0.982
Bottle gourd shell	39.68	0.0702	0.356	0.992	2.669	1.408	0.993

TABLE-2
COMPARISON OF ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS FOR ORANGE G DYE

Adsorbent	Q_o (mg/g)	Reference
Activated carbon of *Thespesia populnea* pods	9.129	[14]
Modified sawdust	5.480	[9]
Bagasse fly ash	18.796	[15]
Perchloric acid activated saw dust	64.93	[16]
Magnetic Biochar	32.36	[17]
Modified chitin	17.86	[8]
Paper mill sludge (activated at 500 °C)	62.3	[18]
Zinc oxide loaded activated carbon	153.85	[19]
Hydrothermally synthesized Co_3O_4 nanostructures	33.3	[20]
Hydrothermally synthesized α-Fe_2O_3 nanostructures	53.2	[20]
Hydrothermally synthesized $CoFe_2O_4$ nanostructures	62.0	[20]
Saw dust activated with perchloric acid	64.93	[16]
Saw dust activated with H_2SO_4	0.4045	[21]
Paper mill sludge (25 °C)	62.3	[22]
LDH	76.4	[23]
Kuppaimeni leaf	37.45	Present Study
Kuppaimeni leaf	46.90	Present Study
Bottle gourd shell	39.68	Present Study

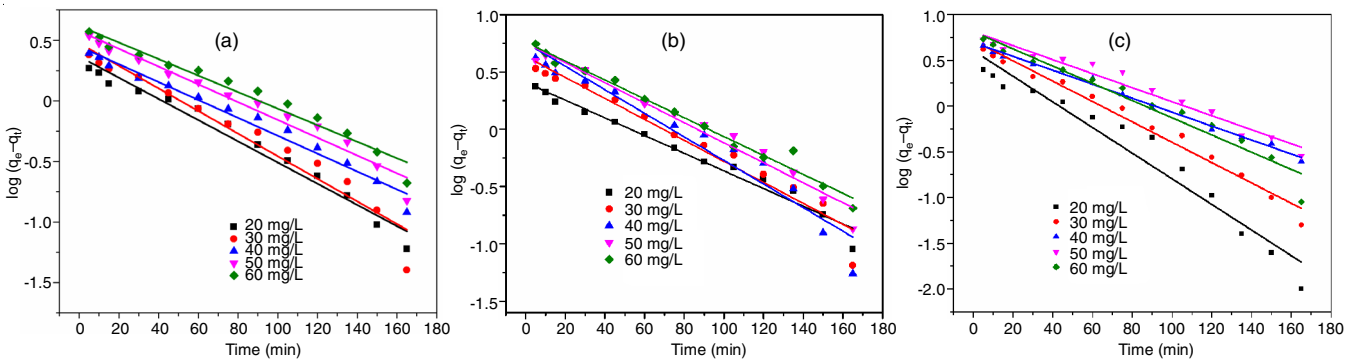

Fig. 5. Pseudo-first-order kinetics for adsorption of Orange G onto (a) kuppaimeni leaf (b) karuvelai leaf and (c) bottle gourd shell

Pseudo-second-order kinetic model: The following pseudo-second-order kinetic equation is used to analyze the adsorption kinetic data:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right) t$$

where k_2 is the second-order rate constant (g/mg min). The linear plot of t/q_t against time (t) is shown in Fig. 6. From the slope and intercept of the linear plot, q_e and k_2 are calculated. For the present three adsorbents, calculated q_e values for the second order plots are in good agreement with the experimental values of q_e with small deviations and higher R^2 values suggested that the Orange G sorption system follows second-order kinetics. The pseudo-second-order rate constants k_2, expected and calculated q_e values and the corresponding linear regression correlation coefficient R^2 and calculated h values for Orange G on kuppaimeni leaf, karuvelai leaf and bottle gourd shell are given in Table-3.

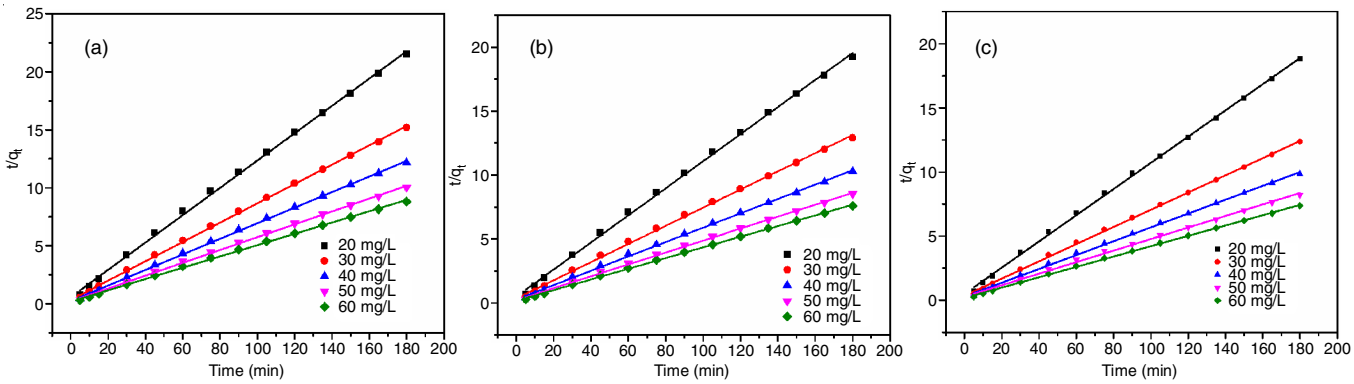

Fig. 6. Pseudo-second-order kinetics for adsorption of Orange G onto (a) kuppaimeni leaf (b) karuvelai leaf and (c) bottle gourd shell

TABLE-3
COMPARISON OF PSEUDO-FIRST-ORDER AND PSEUDO-SECOND ORDER ADSORPTION RATE CONSTANTS AND EXPERIMENTAL AND CALCULATED q_e VALUES OBTAINED AT ORANGE G ON DIFFERENT AGRICULTURAL WASTE

Concentration (mg/L)	Pseudo-first order				Pseudo-second order		
	k_1 (min^{-1})	q_e (exp) (mg/g)	q_e (cal) (mg/g)	R^2	k_2 (g/mg min)	q_e (cal) (mg/g)	R^2
Kuppaimeni leaf							
20	0.0202	8.365	2.324	0.972	0.0082	8.4889	0.999
30	0.0215	11.805	2.994	0.942	0.0023	12.0048	0.999
40	0.0170	14.805	2.824	0.975	0.0014	14.8943	0.999
50	0.0171	17.955	3.779	0.966	0.0006	18.1818	0.999
60	0.0157	24.445	4.155	0.964	0.0005	20.538	0.999
Karuvelai leaf							
20	0.0178	9.370	4.008	0.972	0.0057	9.455	0.999
30	0.2109	13.940	5.211	0.951	0.0018	14.096	0.999
40	0.0237	17.505	4.964	0.936	0.0009	17.829	0.999
50	0.0201	21.140	6.515	0.967	0.0005	21.725	0.999
60	0.0189	23.700	6.822	0.981	0.00031	23.975	0.999
Bottle gourd shell							
20	0.0323	9.555	2.564	0.944	0.0053	9.787	0.999
30	0.0256	13.830	4.328	0.980	0.0018	14.098	0.999
40	0.0175	18.295	5.719	0.992	0.0008	18.525	0.999
50	0.0176	21.910	5.689	0.966	0.0006	22.227	0.998
60	0.0218	24.430	5.764	0.953	0.0003	24.765	0.999

Conclusion

Novel, low cost biosorbents *e.g.*, kuppaimeni leaf, karuvelai leaf and bottle gourd shell were prepared from the agricultural waste and are applied for the removal of Orange G dye from its aqueous solution. The surface morphological features of the adsorbents before and after the adsorption of dye were studied by SEM. Solution pH plays a prominent role in dye removal process as acidic pH condition favours uptake capacity of the adsorbents kuppaimeni leaf, karuvelai leaf and bottle gourd shell. The percentage of removal of Orange G dye is found to be maximum at pH 4.4. Solution temperature is also found to be an effective parameter and it was observed that with increasing temperature from 293 to 313 K, the dye removal percentage decreased from 73 to 63 % for kuppaimeni leaf, 75 to 65 % for kuppaimeni leaf and 78 to 68 % for bottle gourd shell which corroborates to the exothermic nature of the removal process. The equilibrium data fitted well with Langmuir's model and the Langmuir adsorption capacities are found to be 37.45 mg/g, 46.9 mg/g and 39.8 mg/g at 303 K for kuppaimeni leaf, karuvelai leaf and bottle gourd shell respectively. The process of removal of Orange G by adsorption on kuppaimeni leaf, karuvelai leaf and bottle gourd shell are governed by pseudo-second order kinetics.

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