Equilibrium, kinetics and mechanism modeling and simulation of basic and acid dyes sorption onto jute fiber carbon: Eosin yellow, malachite green and crystal violet single component systems

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Abstract

Batch experiments were carried out for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon (JFC). The operating variables studied are the initial dye concentration, initial solution pH, adsorbent dosage and contact time. Experimental equilibrium data were fitted to Freundlich, Langmuir and Redlich–Peterson isotherm by non-linear regression method. Langmuir isotherm was found to be the optimum isotherm for eosin yellow/JFC system and Freundlich isotherm was found to be the optimum isotherm for malachite green/JFC and crystal violet/JFC system at equilibrium conditions. The sorption capacities of eosin yellow, malachite green and crystal violet onto JFC according to Langmuir isotherm were found to 31.49 mg/g, 136.58 mg/g, 27.99 mg/g, respectively. A single stage batch adsorber was designed for the adsorption of eosin yellow, malachite green and crystal violet onto JFC based on the optimum isotherm. A pseudo second order kinetic model well represented the kinetic uptake of dyes studied onto JFC. The pseudo second order kinetic model successfully simulated the kinetics of dye uptake process. The dye sorption process involves both surface and pore diffusion with predominance of surface diffusion at earlier stages. A Boyd plot confirms the external mass transfer as the rate limiting step in the dye sorption process. The influence of initial dye concentration on the dye sorption process was represented in the form of dimensionless mass transfer numbers ($Sh/Sc^{0.33}$) and was found to be agreeing with the expression:

$$\frac{Sh}{Sc^{0.33}} = xC_0^y.$$

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Keywords: Adsorption; Eosin yellow; Malachite green; Crystal violet; Jute fiber carbon; Kinetics; Equilibrium; Diffusion; Isotherm

1. Introduction

Color is a visible pollutant and presence of even very minute amount of coloring substance makes it undesirable due to its appearance [1]. The removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Currently adsorption processes are proved to be an effective process for the removal of pollutants from wastewaters [1–3]. The treatment of dye wastewaters by adsorption technique is receiving growing attention since the standards for quality of effluent disposal

are becoming increasingly more rigid. Activated carbon is the most commonly used adsorbent and is proved to be an effective process for the removal of various pollutants from wastewaters. However the activated carbon processes are found to be an expensive treatment process because of the high cost of activated carbon. The use of high cost activated carbons based on the non-renewable and relatively expensive starting materials such as coal is unjustified in most pollution control processes [4]. This has prompted several researchers for searching or in the production of carbon based adsorbents from a range of residues mainly industrial or agricultural by products. The production of carbons from these wastes or residuals will also reduce the cost of carbon based adsorbents and also save the non-renewable natural resources and produce a valuable product with potential applications in pollution control [4].

Nomenclature

A	Redlich–Peterson isotherm constant
B	Redlich–Peterson isotherm constant
C	concentration at any time t (mg/L)
C_e	amount of dye adsorbed at equilibrium (mg/L)
C_0	initial dye concentration (mg/L)
C_1	concentration of dye solution in stage 1 of a multistage system (mg/L)
d_p	particle diameter (cm)
D_{AB}	diffusivity of dye in distilled water (cm^2/s)
g	Redlich–Peterson isotherm constant
JF	jute fibre
JFC	jute fibre carbon
k_i	intraparticle diffusion coefficient (mg/g min$^{0.5}$)
k_2	reaction rate constant (g/mg min)
K_a	Langmuir isotherm constant (L/mg)
K_F	Freundlich isotherm constant (mg/L)(L/g)^n
K_s, β	external mass transfer coefficient (cm/s)
m, M	mass of adsorbent (g)
M_B	molecular weight of dye used
q	amount of dye adsorbed at any time t (mg/g)
q_e	amount of dye adsorbed at equilibrium (mg/g)
q_m	monolayer sorption capacity (mg/g)
q_0	amount of dye adsorbed when time $t = 0$ (mg/g)
q_1	amount of dye adsorbed in stage 1 (mg/g)
$r_{rapid\ phase}$	rate of dye uptake in initial rapid phase (mg/g min)
$r_{slower\ phase}$	rate of dye uptake in initial rapid phase (mg/g min)
r^2	coefficient of determination
S	surface area per unit volume of particle free slurry (cm^{-1})
Sc	Schmidt number $= \nu/D_{AB}$
Sh	Sherwood number $= K_s d_p/D_{AB}$
t	contact time (min)
T	solution temperature (K)
V_A	molal volume of dye used
V	volume of solution to be treated (L)
x	empirical constant
x_1	empirical constant
y	empirical constant
y_1	empirical constant
Z_{pHC}	zero point charge of adsorbent

Greek symbols

β	external mass transfer coefficient (cm/s)
ε_p	bed porosity
μ_B	viscosity of water at temperature (T)
ρ	bulk density of adsorbent (g/cm^3)
Φ	association factor of water

The literature survey revealed that several industrial and agricultural wastes like sewage sludge [4], waste apricot [5], hardwood saw dust [6], rice husk [7], pine wood saw dust [8], waste tyres [9] have been used for the preparation of activated carbon for the adsorption of dyes from their aqueous solution. In the present research, carbon derived jute fiber, an agricultural waste was used as an adsorbent for the removal of eosin yellow, crystal violet and malachite green from their aqueous solutions. EY, CV and MG were selected as model compounds in order to check the applicability of the JFC to remove dyes from their aqueous solutions. The sorption of eosin yellow, malachite green and crystal violet at solid/liquid interfaces has been studied extensively under equilibrium conditions. Further the kinetics and the mechanistic steps involved in the sorption process were evaluated at different initial methylene blue concentrations. The kinetics of eosin yellow, malachite green and crystal violet sorption onto jute fiber carbon at unknown initial concentrations was successfully simulated using a pseudo second order kinetic expression. A single-stage batch sorber has been designed for the removal of eosin yellow, malachite green and crystal violet by jute fiber carbon based on the equilibrium data obtained.

2. Materials and methods

2.1. Adsorbent

Sun-dried jute fiber, *Corchorus capsularis*, was carbonized with 15% phosphoric acid (PA) in the weight ratio 1:3 (JF:PA). The carbonization and activation were completed by heating for 12 h in a hot air oven. The resulting carbon was washed with distilled water till a constant pH of the slurry was reached. The carbon was then dried for 4 h at 100 °C in a hot air oven. The dried material were then ground and sieved to get particle of uniform geometrical dimensions (0.025 cm). The procedure described by Boehm was used to determine the acid and basic groups [10]. Phosphoric-acid-treated jute fiber carbon (JFC) is characterized and is presented in Table 1.

Table 1
Characteristics of jute fiber carbon (JFC)

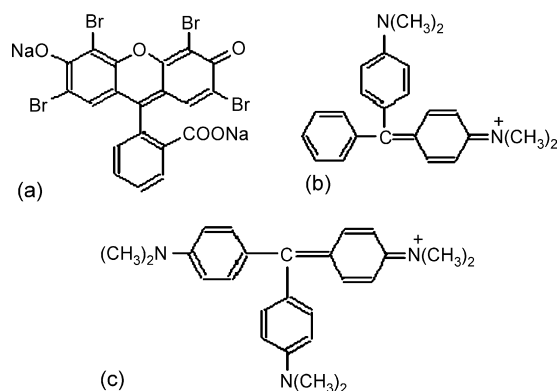| Surface and physical properties of JFC	Parameter value
Bulk density (g/ml)	0.91
Particle diameter (cm)	0.025
Bed porosity, ε_p	0.40
Surface area per unit volume of particle free slurry (cm^{-1})	439.56
Porosity (%)	76.14
Moisture (%)	6.22
Ash (%)	5.22
CEC (mequiv./g)	16.28
pHzpc	4.56
Phenolic (mequiv./g)	0.0448
Lactonic (mequiv./g)	0.01
Carboxylic (mequiv./g)	0.0253
C (wt.%)	50.81
H (wt.%)	4.59
N (wt.%)	<0.2

Fig. 1. (a) Structure of eosin yellow, (b) structure of malachite green, (c) structure of crystal violet.

2.2. Adsorbate

The acid dye eosin yellow used in the present experiment was obtained from Merck Ltd. The basic dyes malachite green and crystal violet was obtained from Ranbaxy chemicals, Mumbai. The structure of the eosin yellow, malachite green and crystal violet used in the present study was shown in Fig. 1(a)–(c), respectively. The details of the dyes used in the present study were given in Table 2. Synthetic stock dye solutions were prepared by dissolving one gram of dye in 1 L of double distilled water. All working solutions were prepared from the stock solutions by further dilution. NaOH and HCl solution was used for optimizing/adjusting the initial pH of the dye solution.

2.3. Process

The effect of pH on the amount of color removal was analyzed over the pH range from 3 to 8. The pH was adjusted using NaOH and HCl solutions. In this study 50 mL of dye solution of known initial dye concentration was agitated with weighed amount of jute fiber carbon for 6 h, which is more than sufficient to reach equilibrium. The contact was made using a water bath shaker at a constant temperature of 303 K and at a constant agitation speed of 120 rpm. The samples were then centrifuged and the left out concentration in the supernatant solution were analyzed using UV Spectrophotometer (Shimadzu, Model UV 1601). All the experiments were carried out using polyethy-

lene 150 mL capped conical flasks. Duplicate experiments were carried out for all the operating variables studied and only the average values were reported. The average deviation of duplicate results in the units of concentration was found to vary as ±2 mg/L.

Blank experiments were carried out with dye solution and without adsorbent to ensure that no dye was adsorbed onto the walls of the conical flasks.

The effect of jute fiber carbon on the amount of dye adsorbed was obtained by agitating 50 mL of dye solution of known initial dye concentration with different weighed amount of jute fiber carbon till equilibrium is reached.

Equilibrium studies were carried out at a constant solution temperature of 303 K. Equilibrium experiments were performed by contacting weighed amount of jute fiber carbon particles with 50 mL of dye solution of different initial dye concentration for 6 h.

Kinetic experiments were carried out using six sets of 150 mL capped conical flasks. In this study, weighed amount of JFC was loaded into the six sets of conical flask containing 50 mL of dye solution of known initial concentration. The flasks were then subjected to agitation using water bath shakers for different contact time intervals. Flasks were taken from the shakers at regular time intervals and the left out concentration in the dye solution was estimated. Unless specified all the experiments were carried out a pH of 8 for the sorption of malachite green and crystal violet onto jute fiber carbon. In the case of eosin yellow, unless specified all the experiments were carried out a pH of 3. All the experiments were carried out at a constant agitation speed of 150 rpm. The range of operating variables studied and the operating conditions studied were shown in Table 3.

Table 2
Information of the dyes used

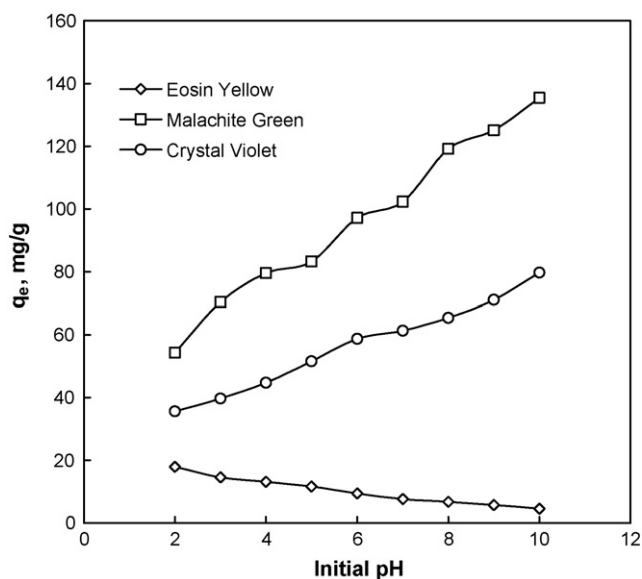| Name of dyes			
CI name	Acid red 87 (AR87)	Basic green 4 (BG4)	Basic violet 10 (BV10)
Color index number	45380	42000	42555
Empirical formula	$C_{20}H_6O_5Br_4Na_2$	$C_{23}H_{25}N_2Cl$	$C_{25}H_{30}N_3Cl$
Molecular weight	691.9	365	408
Dye content	90%	90%	80%
λ_{max}	518	617	593

Fig. 2. Effect of pH on the sorption of eosin yellow, malachite green and crystal violet onto activated carbon (operating conditions—eosin yellow/JFC system, C_0: 40 mg/L, M: 0.1 g/0.05 L; operating conditions—malachite green/JFC system, C_0: 200 mg/L, M: 0.05 g/0.05 L; operating conditions—crystal violet/JC system, C_0: 40 mg/L, M: 0.02 g/0.05 L).

Table 3
Operating variables and experimental conditions (parameters inside the square brackets refers to the fixed experimental conditions)

Initial dye concentration and contact time (kinetic studies)	JFC mass (g)	pH	Equilibrium studies
Eosin yellow/jute fiber carbon system (operating variables)			
C_0 (mg/L): 10, 20, 30, 40; time (min): 0, 5, 10, 20, 30, 50, 80, 120, 150, 180, 220, 250, 280 [V: 0.05 L, M: 0.05 g; pH: 3]	0.025, 0.05, 0.075, 0.1, 0.15, 0.2 [C_0: 40 mg/L; V: 0.05 L, pH: 3]	3, 4, 5, 6, 7, 8 [C_0: 40 mg/L; M: 0.1 g; V: 0.05 L]	C_0 (mg/L): 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 [V: 0.05 L, M: 0.05 g; pH: 3]
Malachite green/jute fiber carbon system (operating variables)			
C_0 (mg/L): 50, 100, 150, 200; time (min): 0, 5, 10, 20, 30, 50, 80, 120, 150, 180, 220, 250, 280 [V: 0.05 L, M: 0.05 g; pH: 8]	0.02, 0.04, 0.05, 0.075, 0.1, 0.15, 0.175 [V: 50 mL, C_0: 200 mg/L; pH: 8]	3, 4, 5, 6, 7, 8 [C_0: 200 mg/L; M: 0.05 g; V: 0.05 L]	C_0 (mg/L): 50, 75, 100, 125, 150, 175, 200, 225, 250, 275 [V: 0.05 L, M: 0.05 g; pH: 8]
Crystal violet/jute fiber carbon system (operating variables)			
C_0 (mg/L): 20, 30, 40, 50; time (min): 0, 5, 10, 20, 30, 50, 80, 120, 150, 180, 220, 250, 280 [V: 0.05 L, M: 0.05 g; pH: 8]	0.01, 0.02, 0.03, 0.04, 0.05 [V: 50 mL, C_0: 40 mg/L; pH: 8]	3, 4, 5, 6, 7, 8 [C_0: 40 mg/L; M: 0.02 g; V: 0.05 L]	C_0 (mg/L): 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 [V: 0.05 L, M: 0.05 g; pH: 8]

2.4. Dye uptake

The amount of dye sorbed onto unit weight of jute fiber carbon and % color removal were calculated using Eqs. (1) and (2), respectively:

$$q = \frac{(C_0 - C)V}{M} \tag{1}$$

$$\% \text{ removal} = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 is the initial dye concentration (mg/L); C the concentration of dye at any time t; V the volume of solution (L); M is the mass of jute fiber carbon (g).
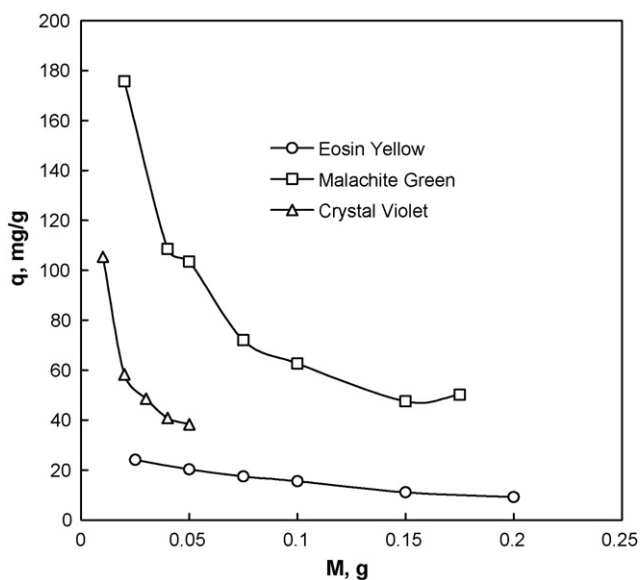

Fig. 3. Effect of jute fiber carbon mass on the sorption of dyes (operating conditions—eosin yellow/JFC system, C_0: 40 mg/L, V: 0.05 L; operating conditions—malachite green/JFC system, C_0: 200 mg/L, V: 0.05 L; operating conditions—crystal violet/JC system, C_0: 40 mg/L, V: 0.05 L).

3. Results and discussions

3.1. Effect of pH

Fig. 2 shows the effect of initial solution pH on the amount of dye adsorbed (mg/g) at equilibrium conditions for the uptake of eosin yellow, malachite green and crystal violet onto jute fiber carbon. From Fig. 2, it was observed that the amount of eosin yellow adsorbed onto jute fiber carbon linearly gets decreased with increase in pH. The amount of dye adsorbed gets decreased from 14.576 to 6.73 mg/g for an increase in pH from 3 to 8. An opposite effect was observed for the sorption of malachite green and crystal violet onto activated carbon. The amount of malachite green adsorbed onto jute fiber carbon was found to increase from 70.3 to 119.14 mg/g for an increase in pH from 3 to 8. Similarly for crystal violet/jute fiber carbon system, the amount of dye adsorbed was found to increase from 39.68 to 65.39 mg/g. This behavior can be explained on the basis of change in surface charge of the jute fiber carbon. In the case of eosin yellow, an

Table 4
Isotherm parameters for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon (q_m: mg/g, K_a: L/mg; K: $(mg/g)(L/g)^n$; n: dimensionless; A: L/g; B: $(L/mg^{1-(1/A)})$; g: dimensionless)

Isotherms	Eosin yellow	Malachite green	Crystal violet
Langmuir			
q_m	31.489	136.586	27.999
K_a	0.063	0.072	0.227
r^2	0.979	0.943	0.956
Freundlich			
K	4.583	32.290	12.519
$1/n$	0.421	0.285	0.182
r^2	0.901	0.983	0.979
Redlich–Peterson			
A	1.989	9.838	6.347
B	0.0632	0.072	0.227
g	1	1	1
r^2	0.979	0.943	0.956

anionic dye, at higher pH, the OH$^-$ ions compete effectively with dye anions causing a decrease in q_e. At lower pH, the surface of carbon gets negatively charged, which enhances the negatively charged dye anions through electrostatic force of attraction.

In the case of basic dyes, malachite green and crystal violet, at lower pH, the H+ ions will compete with dye cations causing a decrease in q_e value. This can be observed from the higher and lower sorption capacity of malachite green and crystal violet at higher and lower pH, respectively.

The variation in the dye uptake with respect to the initial solution pH can be explained on the basis of the zero point charge, Z_{pHC} of the JFC particles. For JFC, the zero point charge was estimated to be as 4.56 (Table 1). Above this pH (Z_{pHC}), the surface of JFC will acquire a negative surface charge leading to increased dye cations uptake due to electrostatic force of attraction. This can be visualized from the favorbale uptake of cationic

dyes, malachite green and crystal violet at higher pH. At pH lower than Z_{pHC} the JFC surface will acquire positive charges leading to increased dye anions uptake due to electrostatic force of attraction. From Fig. 2, it can be observed that the eosin yellow, an anionic dye uptake was found to be more favorable at a lower pH of 3.

3.2. Effect of adsorbent mass

Fig. 3(a)–(c) shows the plot of equilibrium uptake capacity, q_e (mg/g) and % color removal against jute fiber carbon mass (g) for the sorption of eosin yellow, malachite green and crystal violet respectively. From Fig. 2(a)–(c) it was observed that the amount of dye adsorbed onto unit weight of adsorbent gets decreased with increasing jute fiber concentration. The dye uptake decreased from 24.128 mg/g to 9.206 mg/g for an
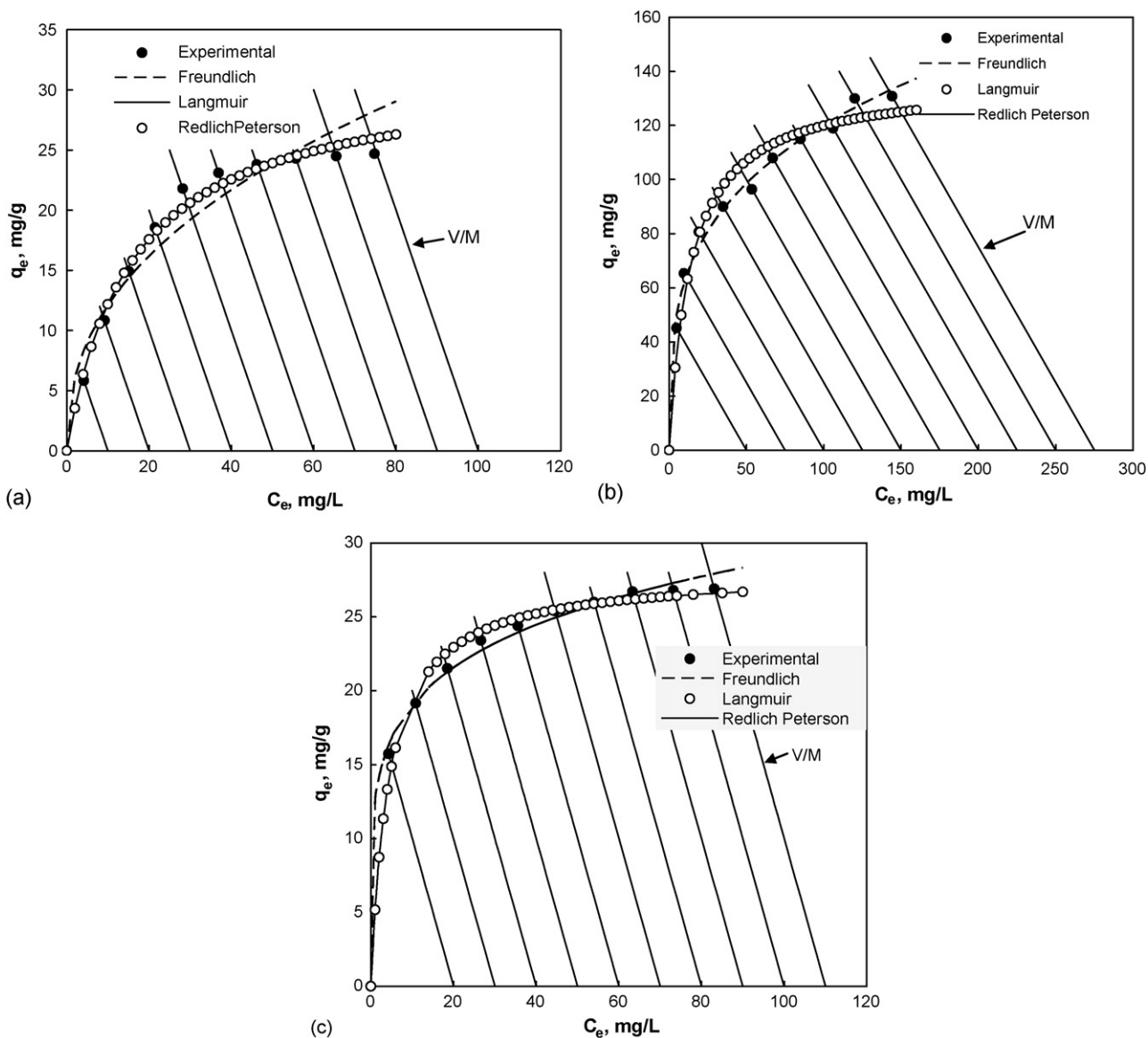

Fig. 4. (a) Experimental data and isotherms for eosin yellow onto jute fiber carbon at 303 K (*V/M*: 0.05 L/0.05 g). (b) Experimental data and isotherms for malachite green onto jute fiber carbon at 303 K (*V/M*: 0.05 L/0.05 g). (c) Experimental data and isotherms for crystal violet onto jute fiber carbon at 303 K (*V/M*: 0.05 L/0.05 g).

increase in adsorbent mass from 0.025 g to 0.2 g for eosin yellow. In the case of malachite green and crystal violet the amount of dye adsorbed decreased from 175.7 mg/g to 50.085 mg/g and 105.4 mg/g to 38.372 mg/g for am increase in adsorbent from 0.02 g to 0.17 g and 0.01 g to 0.05 g, respectively. Whereas for all the three dye sorption systems, the % color removal increases with increasing adsorbent dose. The % eosin yellow removal increased 30.16–92.06% for an increase in adsorbent mass from 0.025 g to 0.2 g. Similarly in the case of malachite green and crystal violet sorption onto jute fiber carbon, the % color removal was found to increase from 35.14% to 87.65% and 52.7% to 95.93% for an increase in adsorbent mass from 0.02 g to 0.175 g and 0.01 g to 0.05 g, respectively. The decrease in q_e value may be due to the splitting effect of flux (concentration gradient) between sorbate and sorbent with increasing jute fiber concentration causing a decrease in amount of dye adsorbed onto unit weight of carbon. The increase in % color removal is because, at higher carbon concentration, there is a very fast superficial adsorption onto the carbon surface that produces a lower solute concentration in the solution than when carbon concentration is lower. The relation between the amount of dye sorbed and the initial jute fiber carbon loading fits the Eqs. (3)–(5) for the sorption of eosin yellow, malachite green and crystal violet, respectively:

$$q_e = \frac{m}{0.2092m^{1.4663}}; \quad r^2 = 0.998 \tag{3}$$

$$q_e = \frac{m}{0.0634m^{1.6098}}; \quad r^2 = 0.9978 \tag{4}$$

$$q_e = \frac{m}{0.0305m - 0.0002}; \quad r^2 = 0.9978. \tag{5}$$

3.3. Sorption equilibrium and process design

The experimental equilibrium data of eosin yellow, malachite green and crystal violet onto jute fiber carbon was fitted to the three widely used isotherms Freundlich [11], Langmuir [12] and Redlich–Peterson [13] isotherms by non-linear regression method. For non-linear regression method, a trial and error procedure which is applicable to computer operation was developed and used to determine the isotherm parameters by maximizing the respective coefficient of determination, r^2 between the experimental and the isotherms using the solver add-in with Microsoft's spreadsheet, Microsoft's Excel. The Freundlich, Langmuir and Redlich–Peterson isotherms were given by Eqs. (6)–(8), respectively:

$$q_e = K_F C_e^{1/n} \tag{6}$$

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{7}$$

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{8}$$

Fig. 4(a)–(c) shows the experimental equilibrium data and the predicted isotherms for eosin yellow, malachite green and crystal violet onto jute fiber carbon at 305 K. The predicted isotherm constants and their corresponding r^2 valued were shown in Table 4. From Table 4, it was observed that the Langmuir
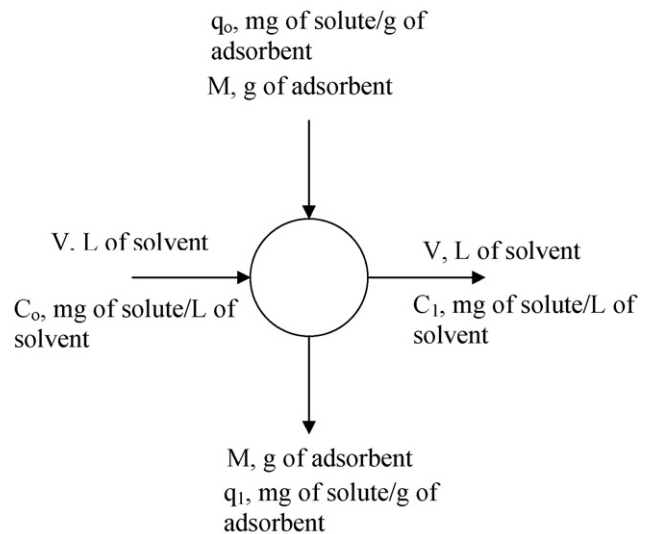

Fig. 5. Single stage batch adsorber.

and Redlich–Peterson isotherm well represent the equilibrium uptake of eosin yellow by jute fiber carbon. Freundlich isotherm was found to be the best fit isotherm for the sorption of malachite green and crystal violet onto activated carbon. In addition from Table 4, it can be observed that for all the three dye activated carbon systems, Redlich–Peterson isotherm exactly overlapped the Langmuir isotherm with same r^2 value. Thus by non-linear method, Redlich–Peterson is a special case of Langmuir when the constant g equals unity, which is in good agreement with the previous findings [14–20]. Based on the best fit isotherm, a single stage adsorber as shown in Fig. 5 was designed for different solution volumes. The design objective is to reduce the dye solution of volume V, L from an initial dye concentration of C_0–C_1 (mg/L). The amount of adsorbent is M and the solute loading on the adsorbent changes from q_0 (mg/g) to q_1 (mg/g). At time $t = 0$, $q_0 = 0$ and as time proceeds the mass balance equated the dye removed from the liquid to that picked up by the solid. The mass balance equation for the sorption system in Fig. 5 can be written as

$$V(C_0 - C_1) = M(q_1 - q_0) = Mq_1 \tag{9}$$

At equilibrium conditions,

$$C_1 \rightarrow C_e \quad \text{and} \quad q_1 \rightarrow q_e \tag{10}$$

Since the equilibrium studies confirm that the equilibrium data for eosin yellow onto jute fiber carbon follows a Langmuir isotherm equation, Langmuir isotherm was used for batch adsorber design. The Eq. (10) can be rearranged as

$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{q_m K_a C_e/(1 + K_a C_e)} \tag{11}$$

For malachite green and crystal violet sorption onto jute fiber carbon, Freundlich isotherm was use for batch sorber design as follows:

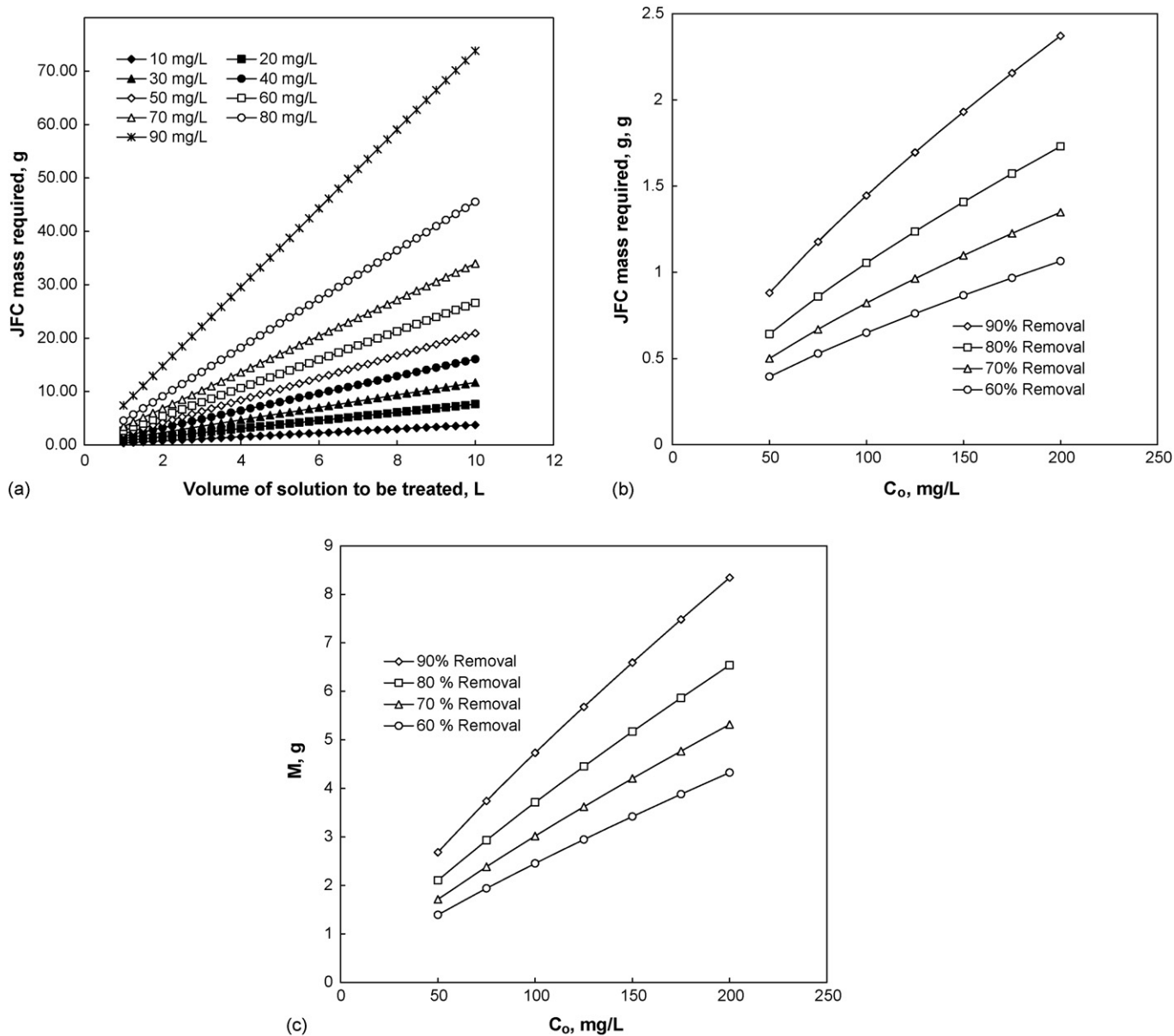$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{K_F C_e^{1/n}} \tag{12}$$

Fig. 6. (a) Design plot generated using Langmuir isotherm for the 90% removal of eosin yellow for different dye solution volumes at different initial dye concentration. (b) Design plot generated using Freundlich isotherm for the different % removal of malachite green for a fixed dye solution volume of 1 L for different initial dye concentration. (c) Design plot generated using Freundlich isotherm for the different % removal of crystal violet for a fixed dye solution volume of 1 L for different initial dye concentration.

Except for 100% removal conditions, Eqs. (11) and (12) can be used to calculate the amount of dose required for the required % removal of dye from aqueous solution for any initial solution concentration. Fig. 6(a) shows the amount of carbon required for the desired % removal of eosin yellow for different solution volumes. From Fig. 6(a), for an initial dye concentration of 100 mg/L and for 90% removal of eosin yellow, the amount of jute fiber carbon required was estimated to be 0.37 g, 0.75 g, 1.12 g, 1.49 g, 1.87 g, 2.24 g, 2.61 g, 2.99 g and 3.73 g for solution volume of 1 L, 2 L, 3 L, 4 L, 5 L, 6 L, 7 L, 8 L and 9 L, respectively.

The amount of jute fiber carbon required to remove 90% of malachite green and crystal violet from their aqueous solution of volume 1 L at different initial dye concentrations were calculated using Eq. (12) and are shown in Fig. 6(b) and (c), respectively. From Fig. 6(b) and (c), the amount of jute fiber carbon required to remove 90% of dye from aqueous solution can be predicted for any initial dye concentration for a fixed *V*.

3.4. Adsorption kinetics

Fig. 7(a)–(c) shows the effect of initial dye concentration on the rate of eosin yellow, malachite green and crystal violet uptake respectively by jute fiber carbon. From Fig. 7(a)–(c), for all the three dyes studied, it was observed that the amount of dye adsorbed gets increased with increasing initial dye concentration and contact time. From Fig. 7(a), for eosin yellow/jute fiber carbon system, it was observed that the rate of dye uptake was found
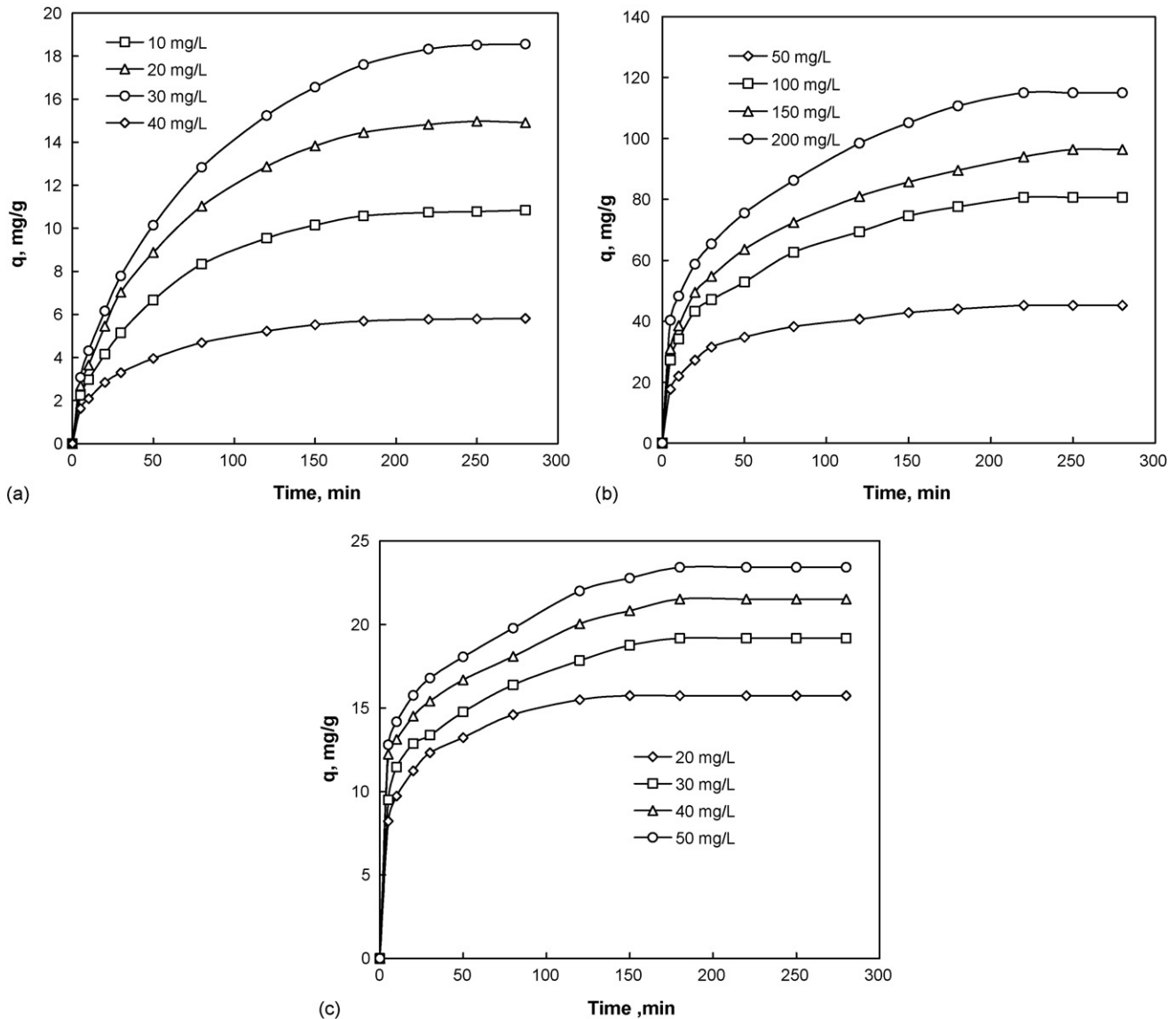
Fig. 7. (a) Kinetics of eosin yellow uptake by jute fiber carbon at different initial dye concentration (*M*: 0.05 g, *V*: 0.05 g). (b) Kinetics of malachite green uptake by jute fiber carbon at different initial dye concentration (*M*: 0.05 g, *V*: 0.05 g). (c) Kinetics of crystal violet uptake by jute fiber carbon at different initial dye concentration (*M*: 0.05 g, *V*: 0.05 g).

to be very rapid for the initial contact period of 50 min and thereafter the dye uptake process tends to proceed at a very slower rate and finally reaches saturation. The saturation time was found to be 220–280 min depending on the initial dye concentration. The predicted rate of reaction, *r*, for both the initial rapid phase and in the later slower phase for the sorption of eosin yellow onto jute fiber carbon is shown in Fig. 8(a). From Fig. 8(a), it is observed that the rate of dye uptake in the initial rapid phase, $r_{rapid\ phase}$, was found to be increasing as 0.079 mg/g min, 0.133 mg/g min, 0.177 mg/g min and 0.203 mg/g min for an initial dye concentration of 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L, respectively. Similarly the rate of dye uptake for the slower phase, $r_{slower\ phase}$, was also found to be increasing as 0.008 mg/g min, 0.018 mg/g min, 0.026 mg/g min and 0.037 mg/g min for an initial dye concentration of 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L, respectively. The rate of eosin yellow uptake by jute

fiber carbon for different initial dye concentration in Fig. 7(a) fits Eqs. (13) and (14) for the initial rapid phase and the later slower phase, respectively:

$$r_{rapid\ phase} = 0.09 \ln C_0 - 0.1305; \quad r^2 = 0.9949 \tag{13}$$

$$r_{slower\ phase} = 0.0009 C_0 - 0.0012; \quad r^2 = 0.9978 \tag{14}$$

In the case of basic dyes malachite green and crystal violet sorption onto jute fiber carbon, the rate of dye uptake was found to be rapid for the first 50 min (Fig. 7(b) and (c)) and thereafter sorption was found to proceed at a slower rate and finally reaches saturation. The saturation was reached in 220 min irrespective of the initial malachite green concentration. In the case of crystal violet the saturation was reached in 150 min irrespective of initial dye concentration.
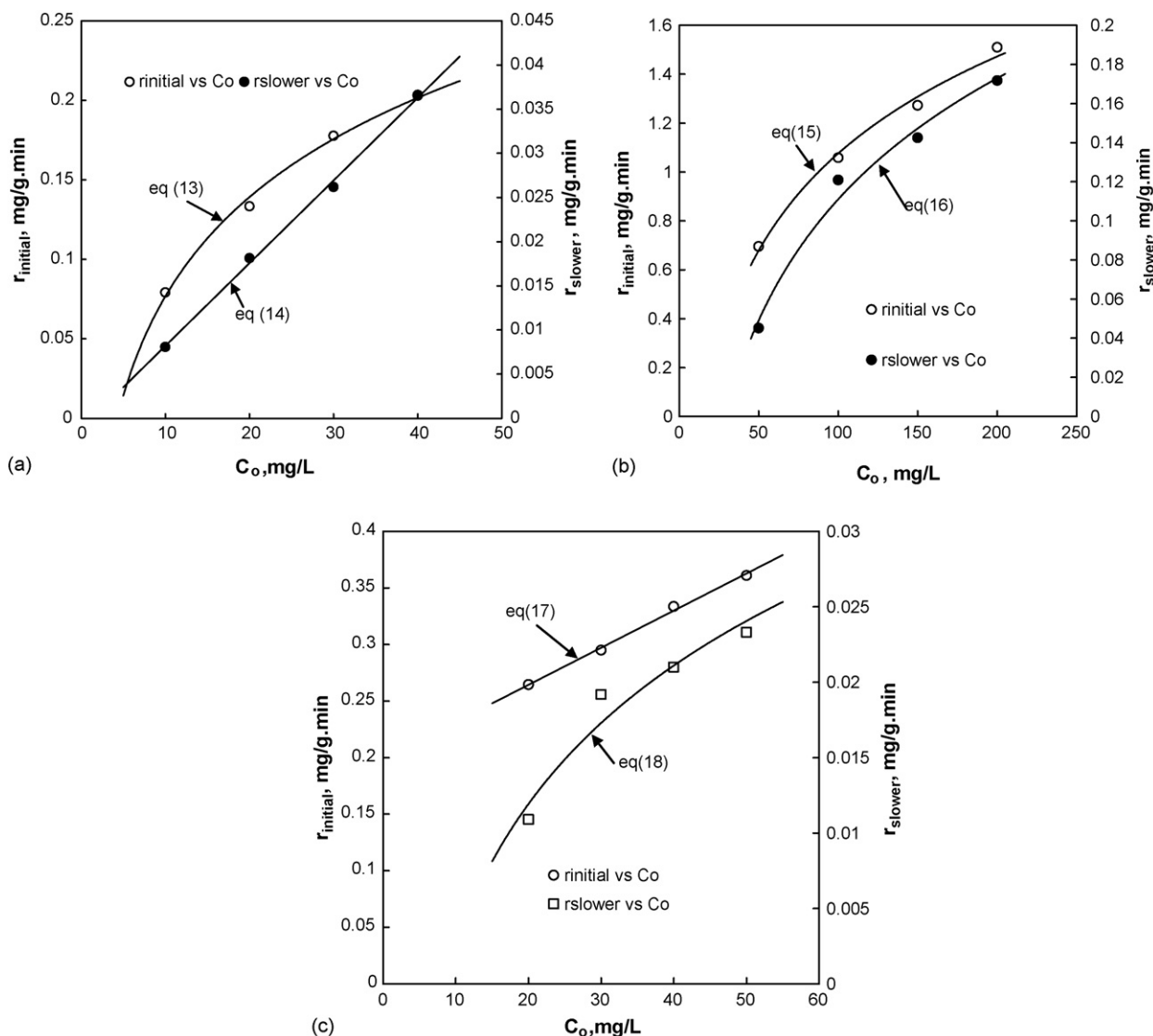
Fig. 8. (a) Effect of initial dye concentration on the rate of dye uptake of eosin yellow by jute fiber carbon. (b) Effect of initial dye concentration on the rate of dye uptake of malachite green by jute fiber carbon. (c) Effect of initial dye concentration on the rate of dye uptake of crystal violet by jute fiber carbon.

The effect of initial malachite green concentration and initial crystal violet concentration sorption onto jute fiber carbon on the rate of dye uptake in the both the rapid phase and slower phase are shown in Fig. 8(b) and (c), respectively. From Fig. 8(b) and (c), it can be observed that for both malachite green and crystal violet onto jute fiber carbon the rate of dye uptake (both in the rapid and slower phase) was found to be increasing with increase in initial dye concentration. The rate of malachite green uptake in the initial rapid phase was found to increase from 0.695 mg/g min to 1.51 mg/g min for an increase in initial dye concentration from 50 mg/L to 200 mg/L. Similarly the rate of malachite green uptake in the slower phase was found to increase from 0.045 mg/g min to 0.172 mg/g min for an increase in initial dye concentration from 50 mg/L to 200 mg/L The influence of initial malachite concentration on the rate of dye uptake in the initial rapid phase and slower phase fits the Eqs. (15) and (16), respectively:

$$r_{\text{rapid phase}} = 0.5726 \ln C_0 - 1.5611; \quad r^2 = 0.9909 \tag{15}$$

$$r_{\text{slower phase}} = 0.0893 \ln C_0 - 0.3001; \quad r^2 = 0.9846 \tag{16}$$

Similarly the effect of initial crystal violet concentration on the rate of dye uptake in the initial rapid phase and slower phase were calculated and it fits the Eqs. (17) and (18), respectively:

$$r_{\text{rapid phase}} = 0.0033 C_0 - 0.1987; \quad r^2 = 0.9961 \tag{17}$$

$$r_{\text{slower phase}} = 0.0132 \ln C_0 - 0.0278; \quad r^2 = 0.9404. \tag{18}$$

3.5. Kinetic modeling and simulation

The transient behavior of eosin yellow, malachite green and crystal violet uptake by jute fiber carbon following the pseudo

Table 5
Pseudo second order kinetic constants for the sorption of dyes onto jute fiber carbon (q_e: mg/g; C_0: mg/L; k_2: g/mg min)

C_0	$q_{e,experimental}$	$k_2 \times 10^{-3}$	$q_{e,predicted}$	r^2
Eosin yellow/jute fiber carbon				
10	5.82	6.7	6.339	0.991
20	10.84	2.3	12.313	0.997
30	14.91	1.5	17.247	0.997
40	18.56	0.9	21.856	0.994
Malachite green/jute fiber carbon				
50	45.16	1.4	47.499	0.999
100	80.7	0.5	86.958	0.996
150	96.39	0.4	103.22	0.995
200	115	0.3	124.33	0.995
Crystal violet/jute fiber carbon				
20	15.73	7.9	16.264	0.999
30	19.164	4.2	20.044	0.998
40	21.51	3.9	22.427	0.998
50	23.41	3.6	24.431	0.998

second order kinetics can be represented by Ref. [21]:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{19}$$

Integrating Eq. (19) with respect to the limits, $q = 0$ at time $t = 0$ and $q = q$ at time $t = t$, the simplified linear expression of first order and second order expressions can be obtained as follows [22]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{20}$$

Thus the kinetics of dye sorption onto jute fiber carbon following the pseudo second order kinetic process can be analyzed from the plot of t/q versus t. Eq. (20) can be used to predict the amount of dye adsorbed at equilibrium conditions, q_e (mg/g) [22]. Previously the pseudo second order kinetic expression was used to obtain a pseudo isotherm based on the q_e values predicted theoretically using the pseudo second order kinetic expression [14,23,24].

Fig. 9(a)–(c) shows the plot of t/q versus t for different initial eosin yellow concentration, malachite green and crystal violet concentrations. The second order kinetic constant and the amount of dye adsorbed, q_e can be predicted theoretically from the intercept and slope of Fig. 9(a)–(c) using Eq. (10). The calculated rate constant k_2, theoretically predicted q_e and their corresponding r^2 values were shown in Table 5. From Table 5, the very higher r^2 value for all the dyes studied confirms that for all the range of initial dye concentrations studied, the sorption kinetics of eosin yellow, malachite green and crystal violet follows a pseudo second order process. In addition from Table 5, it was also observed that the theoretically predicted q_e values well agree with the experimentally obtained q_e values. Thus the pseudo second order kinetic expression can be used to predict successfully the amount of dye adsorbed at equilibrium using the kinetic experimental data. Based on the best fit of experimental kinetic data in the pseudo second order kinetic expression, the

generalized pseudo second order expression for the sorption of eosin yellow, malachite green and crystal violet are predicted and are given by Eqs. (21)–(23), respectively:

$$q = \frac{(C_0/6.2812C_0^{2.3872})(0.5149C_0 + 1.5669)^2 t}{1 + (C_0/6.2812C_0^{2.3872})(0.5149C_0 + 1.5669)} \tag{21}$$

$$q = \frac{(C_0/3698.8C_0 - 162,547)(0.5149C_0 + 1.5669)^2 t}{1 + (C_0/3698.8C_0 - 162,547)(0.5149C_0 + 1.5669)t} \tag{22}$$

$$q = \frac{(C_0/376.2C_0 - 4658.6)(0.2688C_0 + 11.382)^2 t}{1 + (C_0/376.2C_0 - 4658.6)(0.2688C_0 + 11.382)t} \tag{23}$$

Eqs. (21)–(23) can be used to predict the q value at any time and for any initial dye concentration required at a given V/M ratio of 1/1. A simple template was formed using Microsoft's Spreadsheet, Microsoft excel to simulate the kinetics of eosin yellow, malachite green and crystal violet sorption using Eqs. (21)–(23), respectively. The simulated kinetics of eosin yellow, malachite green and crystal violet onto jute fiber carbon for different initial dye concentration were shown in Fig. 10(a)–(c), respectively. From Fig. 10 also shows some of the experimental kinetic data of eosin yellow onto jute fiber carbon. From Fig. 10(a), it can be observed that the simulated kinetic data very well represent the experimental sorption of eosin yellow onto jute fiber carbon. In addition, from Fig. 10(b) and (c), it was observed that the simulated kinetics very well exploits and interpolated the kinetics of sorption of malachite green and crystal violet onto jute fiber carbon for higher initial dye concentration. Thus the pseudo second order kinetic model can be used in successfully simulating the kinetics of eosin yellow, malachite green and crystal violet sorption onto jute fiber carbon.

3.6. Adsorption mechanism

In general the sorption process involves multisteps mainly the surface diffusion followed by the intraparticle diffusion. From mechanistic view point t is necessary to identify the steps involved during adsorption [25], described by external mass transfer (boundary layer diffusion) and intraparticle diffusion. According to previous studies, the intraparticle diffusion plot may represent multilinearity, representing the different stages in adsorption [26–28]. An intraparticle diffusion parameter, k_i (mg/g min$^{0.5}$) is defined as [29]

$$k_i = \frac{q}{t^{0.5}} \tag{24}$$

In theory the plot between q and $t^{0.5}$ is given by multiple regions representing the different steps involved in the adsorption process [26–28]. The intraparticle diffusion plot for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon was shown in Fig. 11(a)–(c), respectively. From these figures it was observed that there were two linear portions. A first linear portion ended with a smooth curve followed by a second linear portion. The double nature of the curve reflects the two-stage external mass transfer followed by
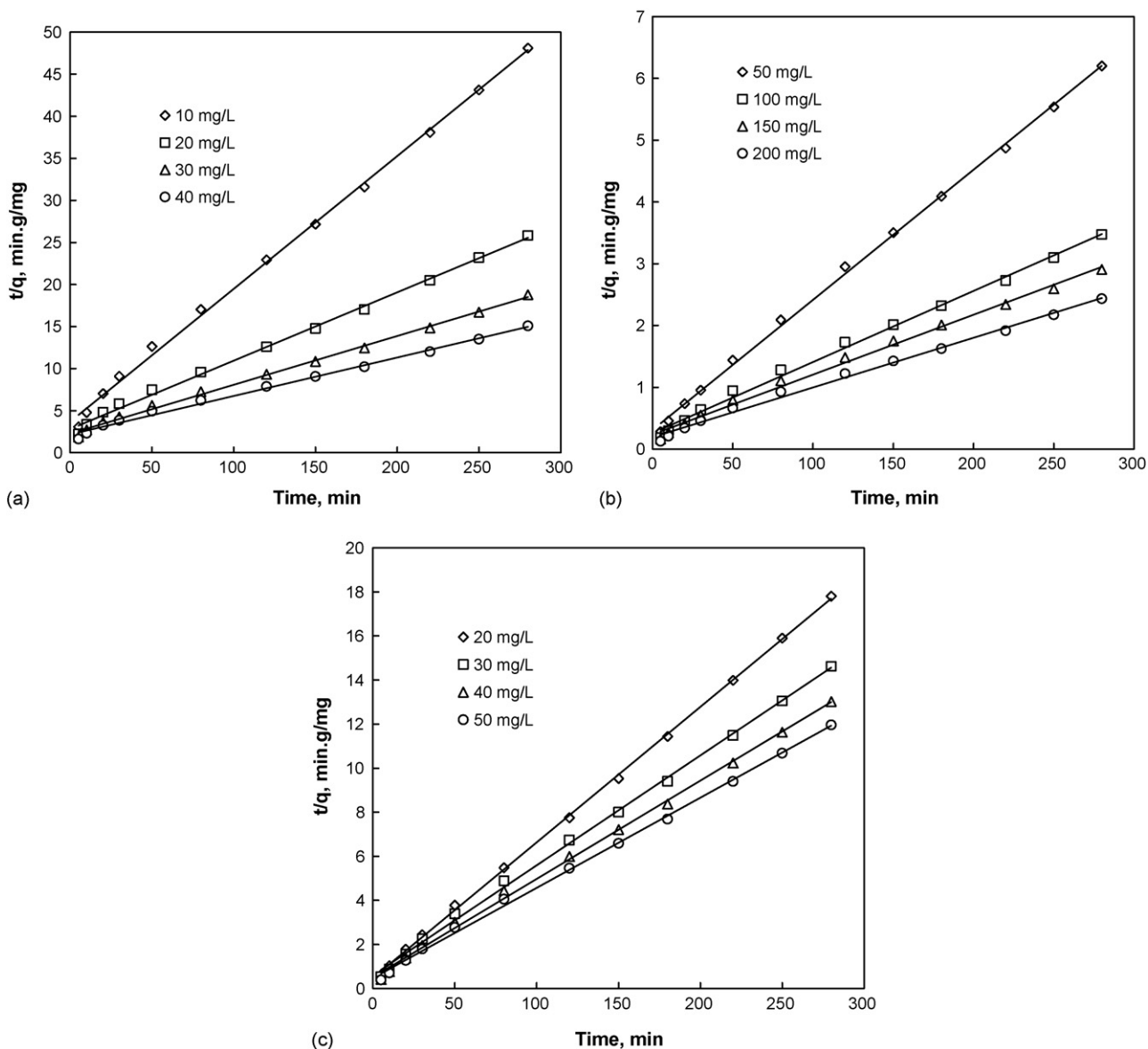
Fig. 9. (a) Pseudo second order kinetics for the sorption of eosin yellow onto jute fiber carbon (M: 0.05 g, V: 0.05 L). (b) Pseudo second order kinetics for the sorption of malachite green onto jute fiber carbon (M: 0.05 g, V: 0.05 L). (c) Pseudo second order kinetics for the sorption of crystal violet onto jute fiber carbon (M: 0.05 g, V: 0.05 L).

intraparticle diffusion of dyes (eosin yellow, malachite green and crystal violet) onto jute fiber carbon particles. The slope of the second linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept of this second linear portion is proportional to the boundary layer thickness. The intraparticle diffusion of eosin yellow, malachite green and crystal violet, k_i (mg/g min$^{0.5}$), at different initial concentrations were found from the slope of the corresponding linear region of Fig. 11(a)–(c). The calculated k_i values for different dye concentrations are given in Table 6. The calculated average value of k_i were found to be 0.555 mg/g min$^{0.5}$, 3.298 mg/g min$^{0.5}$, 0.574 mg/g min$^{0.5}$ for the sorption of eosin yellow, malachite green and crystal violet onto activated carbon.

As the double nature of the intraparticle diffusion plot suggested the external mass of dye particles at initial time periods,

the rate constant corresponding to external mass transfer at these initial time intervals were calculated. The external mass transfer of eosin yellow, malachite green and crystal violet onto jute fiber carbon was analyzed using the external mass transfer model pro-

Table 6
Intraparticle diffusion coefficient for dyes onto jute fiber carbon (C_0: mg/L; k_i: mg/g min$^{0.5}$)

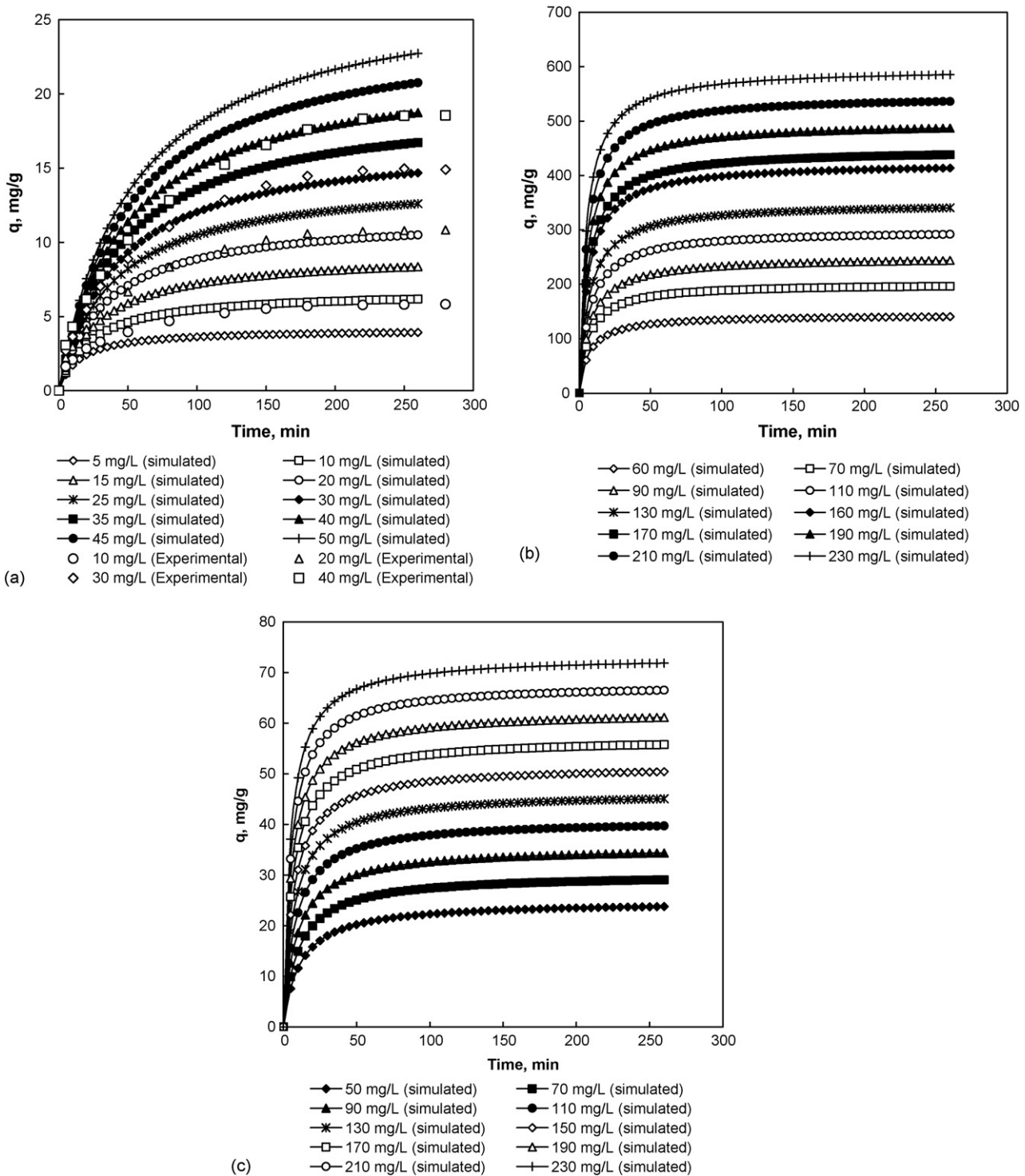| Dye/JFC system					
Eosin yellow/JFC		Malachite green/JFC		Crystal violet/JFC	
C_0	$k_i \times 10^{-2}$	C_0	k_i	C_0	$k_i \times 10^{-2}$
10	19.15	50	1.364	20	58.07
20	42.3	100	3.343	30	54.48
30	64.63	150	3.488	40	59.88
40	95.97	200	5.001	50	57.31

Fig. 10. (a) Experimental and simulated kinetics for the sorption of eosin yellow onto jute fiber carbon for V/M ratio of 0.05 g/0.05 L. (b) Simulated kinetics for the sorption of malachite green onto jute fiber carbon for a V/M ratio of 0.05 g/0.05 L. (c) Simulated kinetics for the sorption of crystal violet onto jute fiber carbon for a V/M ratio of 0.05 g/0.05 L.

posed by Furusawa and Smith [30]. The experimental data are analyzed assuming a three step model:

(1) external mass transfer of dye ions from bulk liquid to the JFC particle surface;
(2) intraparticle diffusion;
(3) adsorption at internal site.

It is assumed that step is rapid when compared to the first two steps. In a fully agitated solid/liquid adsorber, mixing in the liquid is very rapid. The change in concentration of sorbate with respect to the time is related by the equation:

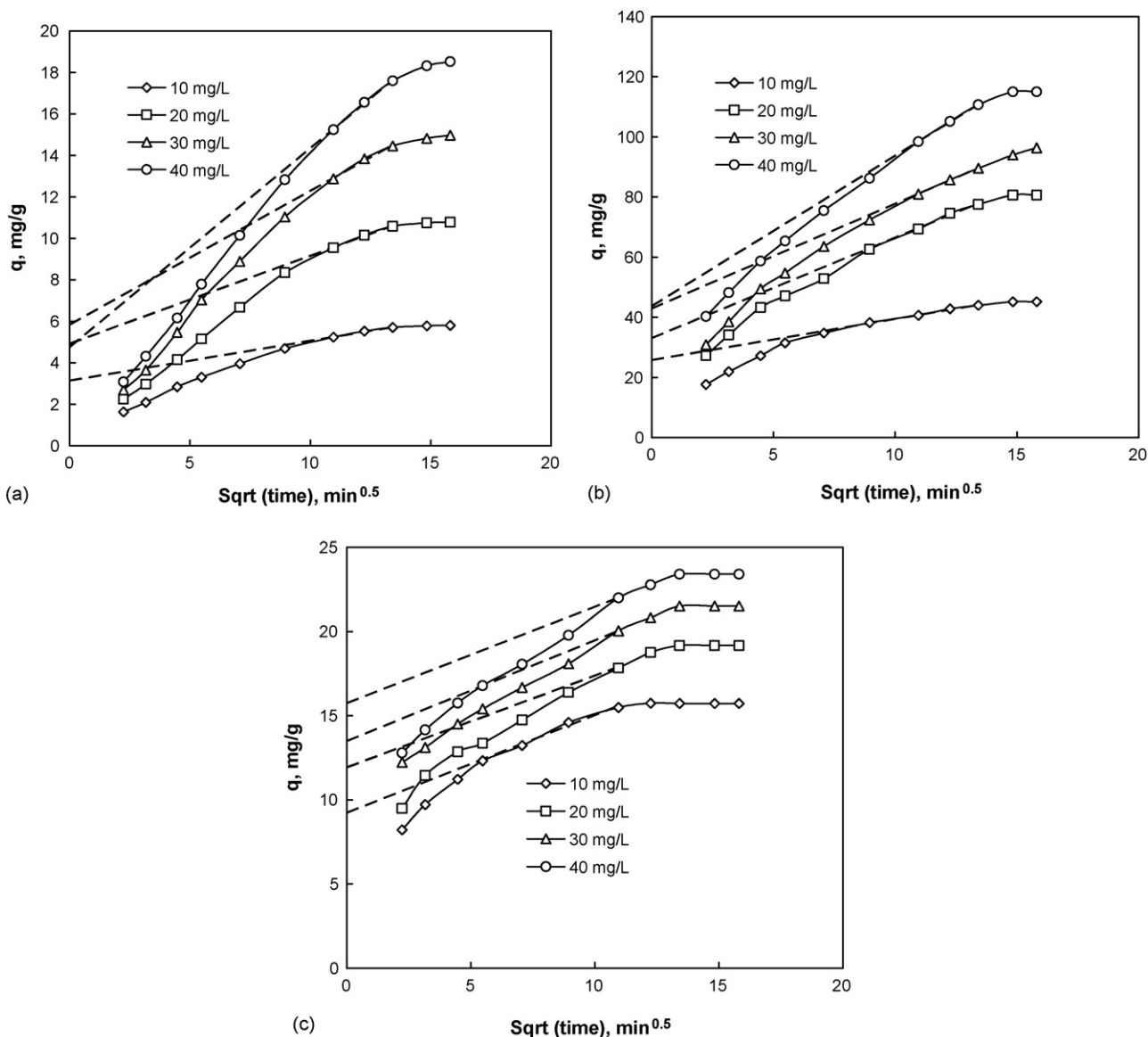$$-\frac{\mathrm{d}C}{\mathrm{d}t} = K_\mathrm{s}S(C - C_\mathrm{e}) \tag{25}$$

Fig. 11. (a) Intraparticle diffusion plot for eosin yellow onto jute fiber carbon (M: 0.05 g; V: 0.05 L). (b) Intraparticle diffusion plot for malachite green onto jute fiber carbon (M: 0.05 g; V: 0.05 L). (c) Intraparticle diffusion plot for crystal violet onto jute fiber carbon (M: 0.05 g; V: 0.05 L).

where S is the surface area of adsorbent per unit volume of particle slurry and is given by

$$S = \frac{6M}{Vd_p\rho(1 - \varepsilon_p)} \quad (26)$$

At time $t = 0$, $C_e = 0$, thus Eq. (25) becomes:

$$\left[\frac{d(C/C_0)}{dt}\right]_{t=0} = -K_s S \quad (27)$$

The external mass transfer coefficient K_s can be calculated from the slope of C/C_0 versus time t using Eq. (27). In the present investigation the K_s values were obtained using the experimental kinetic data for the first initial rapid phase of 50 min where the external mass was expected to be the dominant process. The calculated external mass transfer coefficient, K_s (cm/s), at different initial dye concentrations for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon was given in

Table 7. The calculated external mass transfer coefficients were represented in the form of dimensionless mass transfer numbers ($Sh/Sc^{0.33}$). The effect of initial dye concentration on dimensionless mass transfer numbers was shown in Fig. 12(a)–(c) respectively. The experimental data in Fig. 12(a)–(c) fits the generalized expression:

$$\frac{Sh}{Sc^{0.33}} = xC_0^y \quad (28)$$

where x and y are constants. The calculated x, y and the corresponding r^2 values for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon were shown in Table 8. From Fig. 12(a)–(c), it was observed that the mass transfer was found to get increase with increasing initial dye concentration. This is because the amount of mass transferred to the surface of sorbent per unit time will get increase with increasing initial dye concentration.
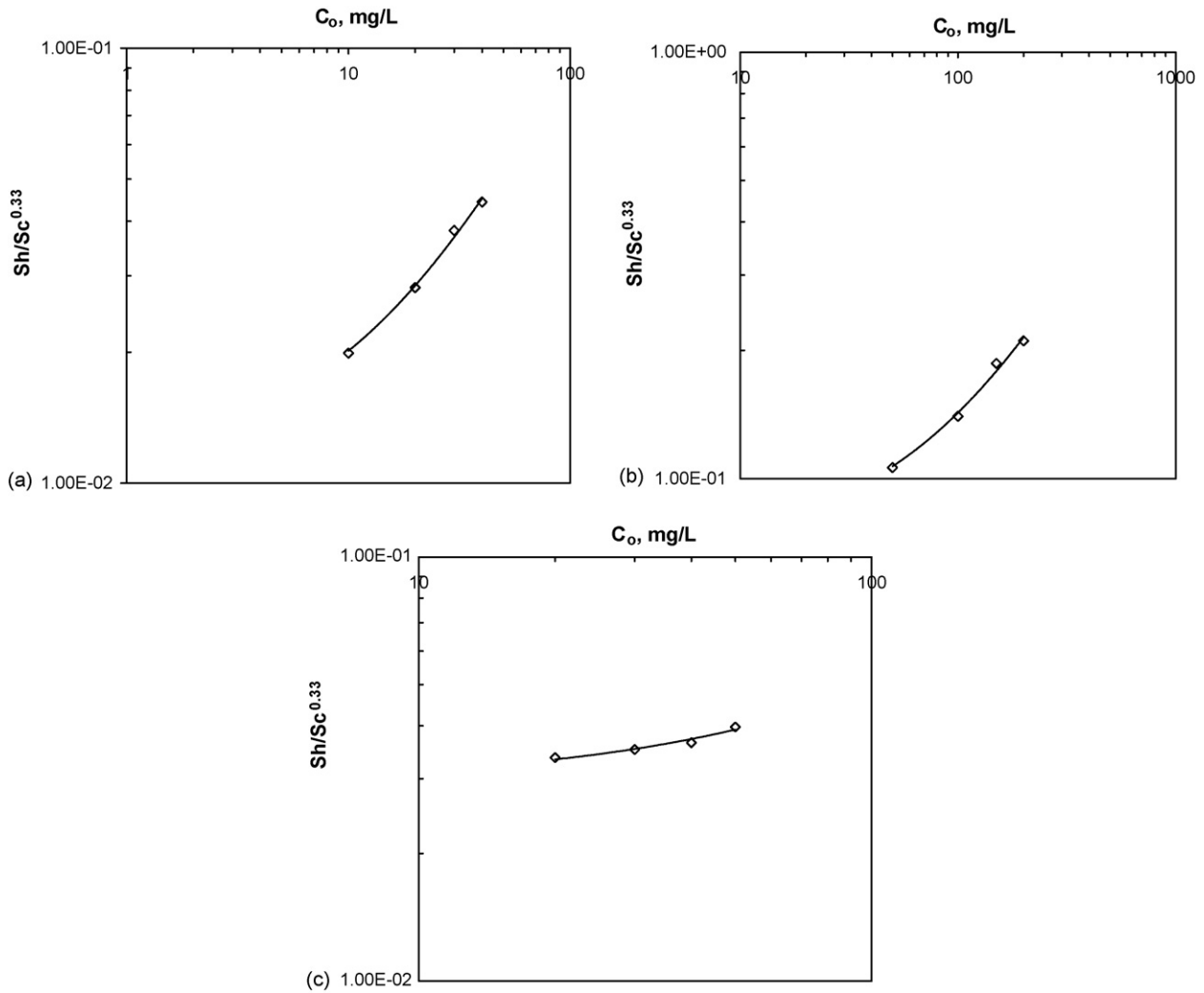
Fig. 12. (a) Effect of external mass transfer on the sorption of eosin yellow onto JFC. (b) Effect of external mass transfer on the sorption of malachite green onto JFC. (c) Effect of external mass transfer on the sorption of crystal violet onto JFC.

The Sh and Sc represents the Sherwood and Schmidt numbers and is given by equations:

$$Sh = \frac{\beta dp}{D_{AB}} \qquad (29)$$

$$Sc = \frac{\upsilon}{D_{AB}} \qquad (30)$$

Table 7
External mass transfer coefficient for the sorption of dyes onto jute fiber carbon (C_0: mg/L; k_S: cm/s)

Dye/JFC system	
C_0	K_S
Eosin yellow/JFC	
10	0.14×10^{-3}
20	1.98×10^{-3}
30	2.68×10^{-3}
40	3.11×10^{-3}
Malachite green/JFC	
50	8.44×10^{-4}
100	11.14×10^{-4}
150	14.81×10^{-4}
200	16.73×10^{-4}
Crystal violet/JFC	
20	2.31×10^{-4}
30	2.42×10^{-4}
40	2.51×10^{-4}
50	2.73×10^{-4}

Table 8
Constants 'x' and 'y' in Eq. (28)

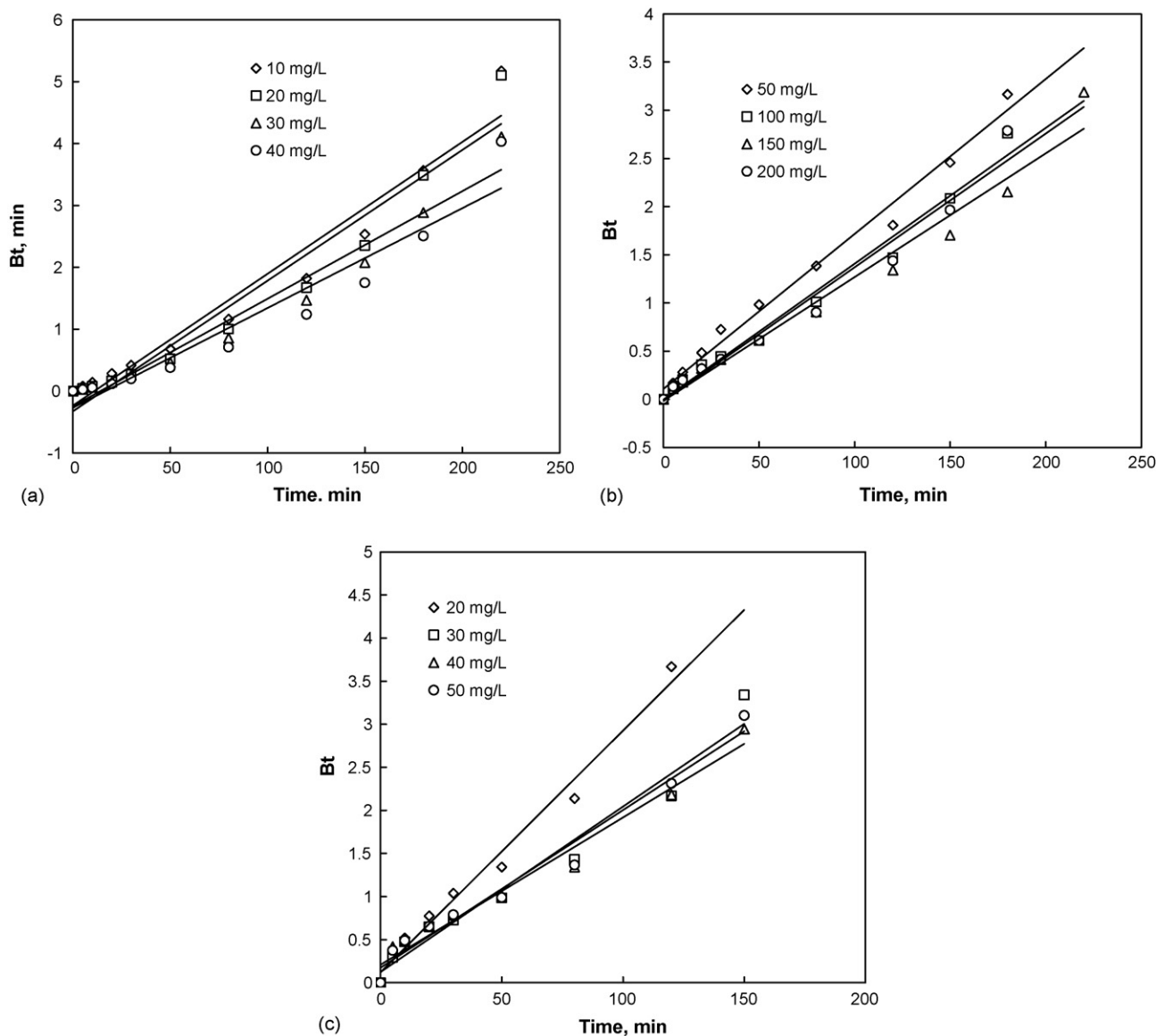| Dye/JFC system		
x	y	r^2
Eosin yellow/JFC		
1.03	8.32×10^{-4}	0.993
Malachite green/JFC		
1.18	7.18×10^{-4}	0.982
Crystal violet/JFC		
1.07	1.95×10^{-4}	0.952

Fig. 13. (a) Boyd plot for eosin yellow onto jute fiber carbon. (b) Boyd plot for malachite green onto jute fiber carbon. (c) Boyd plot for malachite green onto jute fiber carbon.

where D_{AB} represents the diffusivity of dyes in solvent (water) and can be calculated using Wilke Chang expression [31]:

$$D_{AB} = \frac{7.4 \times 10^{-8} (\Phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \qquad (31)$$

Present study showed the presence of both external and intra-particle diffusion in the actual process. However from the design aspect it is important to determine the actual rate limiting step involved in the process. Thus to determine the actual rate controlling step involved in the process, the equation provided by Boyd, Adamson and Myers was used [32]. In 1947, Boyd et al. [32] proposed a particle diffusion mode to explain the diffusion mechanism in ion exchange resin. Adsorption and ion exchange share so many common features in regard to application in batch and fixed-bed processes that they can be grouped together as sorption for a unified treatment [33]. These processes involve the transfer and resulting equilibrium distribution of one or more solutes between a fluid phase and particles. Boyd et al. [32] proposed the pore diffusion model based on the solid phase concentration and not based on the solute concentration which helps to apply this model to understand the mechanism or to predict the rate limiting step in any solid/liquid adsorption systems which are normally a pseudo process. A pseudo process indicates that the sorption depends only on the solid phase concentration irrespective of the solute concentration in the liquid. Recently Boyd et al. [32] kinetic expression was successfully applied to explain the kinetics of several solid liquid sorption systems which includes the sorption of methylene blue onto fly ash [34], methylene blue onto mango seed kernel [35], methylene blue onto rice husk [36], malachite green sorption by bottom ash [37], phenol (hydroxybenzene) on fly ash [38], o-hydroxyphenol (1,2-dihydroxybenzene) on fly ash [38],

m-hydroxyphenol (1,3-dihydroxybenzene) on fly ash [38], and 4-nitrophenol (1-hydroxy-4-nitrobenzene) on fly ash [38]. The Boyd's kinetic expression was given by the Eq. (32) as follows [32]:

$$F = \frac{q}{qe} = 1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2} \tag{32}$$

where B is given by

$$B = \frac{\Pi^2 D_i}{r^2} \tag{33}$$

where D_i is the effective diffusion coefficient.

Eq. (32) was proposed based on the assumption of particle diffusion as the sole rate controlling process. Some of the significance of Eq. (32) is as follows:

(1) F is a mathematical function of Bt and vice versa. The plot between Bt versus experimental t with a straight line (of slope B) passing through the origin represents the particle diffusion process. Thus indicating that the diffusion coefficient D_i does not vary with F over the range of values.

(2) For a given value of t, F will be dependent only on D_i/r^2 and is independent of concentration of solute ions.

(3) The Boyd's constant B is inversely proportional to the square of particle radius for a given value of F and dF/dt and dQ/dt are proportional to B. The rate of solute transfer will be proportional to the square of the particle radius for all values of F under condition of particle diffusion.

The solution of Eq. (32) for lower range of values of F was given by

$$F = \sum_{n=1}^{\infty} e^{-n^2(Bt)} = -\frac{1}{2} + \sqrt{\frac{\Pi}{Bt}} \left[\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\Pi^2 n^2 / Bt} \right] \tag{34}$$

Integrating Eq. (34) with respect to (Bt) and rearranging:

$$F = \frac{6}{\Pi^{3/2}} Bt - \frac{3}{\Pi^2} Bt + \frac{6}{\Pi^{3/2}} \int_0^{Bt} \frac{\sum_{n=1}^{\infty} e^{-\Pi^2 n^2 / Bt}}{\sqrt{Bt}} \tag{35}$$

Considering the first two terms alone, the simplified equation is given by

$$F = \frac{6}{\Pi^{3/2}} Bt - \frac{3}{\Pi^2} Bt \tag{36}$$

The last term in Eq. (35) is zero when $F = 0$ and increases as F increases. For any value of F, Eq. (35) gives a very high value of Bt, the error being zero when $F = 0$. Previously Riechenberg [39] reported that Eq. (32) can be used for a higher value of F ($F > 0.85$) and also Riechenberg [39] proposed a simple solution with added assumptions to the Boyd's assumptions given by Eq. (37):

$$Bt = 2\Pi - \frac{\Pi^2 F}{3} - 2\Pi \left(1 - \frac{\Pi F}{3} \right)^{1/2} \tag{37}$$

Eq. (37) can be simplified to:

$$Bt = 6.28318 - 3.2899 F - 6.28318(1 - 1.0470 F)^{1/2} \tag{38}$$

Table 9
Constants 'x_1' and 'y_1' in Eq. (39)

Dye/JFC system	
x_1	y_1
Eosin yellow/JFC	
1407	2951.1
Malachite green/JFC	
8201.5	29524
Crystal violet/JFC	
2264.6	6083.9

Reichenberg suggested the Eq. (38) to calculate Bt value for F value ranging from 0 to 0.85 and Eq. (32) for F values from 0.86 to 1. The calculated Bt values were plotted against time t as shown in Fig. 13(a)–(c) for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon. Fig. 13(a)–(c) are used to identify whether the external mass transfer or the internal mass transfer controls the rate of sorption process. From these figures it was observed that the plots of Bt versus t were linear but does not pass through origin. Thus for the studied initial dye concentration external mass transfer controls the sorption process. The calculated B values were represented in the form of:

$$B = \frac{C_0}{x_1 \ln C_0 - y_1} \tag{39}$$

where x_1 and y_1 are the constants in Eq. (39). The calculated x_1 and y_1 value for the sorption of eosin yellow, malachite green and crystal violet sorption onto jute fiber carbon was given in Table 9. Based on the calculated x_1 and y_1 values, the effective diffusion coefficient, D_i (cm^2/s) at different initial dye concentration was calculated using Eq. (33). The effect of initial dye concentration on the effective diffusion coefficient, D_i (cm^2/s) was shown in Fig. 14(a)–(c) for eosin yellow, malachite green and crystal violet sorption onto jute fiber carbon. The average effective
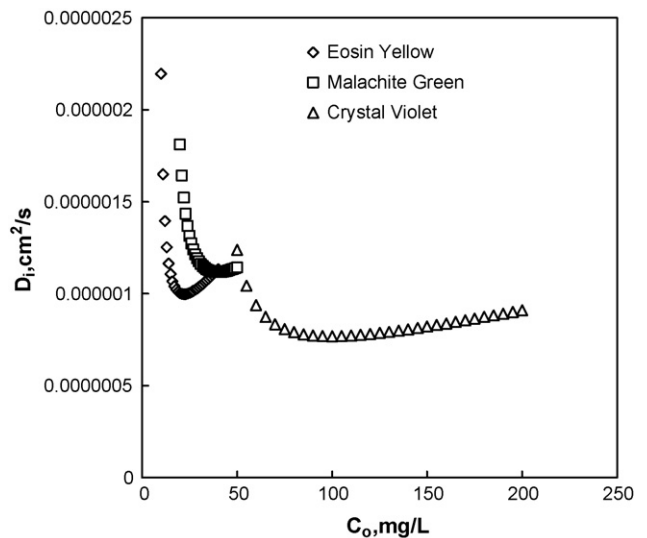
Fig. 14. Effect of initial dye concentration on the effective diffusivity of dyes onto jute fiber carbon.

diffusion coefficient, D_i (cm^2/s) for the sorption of eosin yellow, malachite green and crystal violet onto jute fiber carbon were calculated to be 1.125×10^{-6} cm^2/s, 8.46×10^{-9} cm^2/s, 1.22×10^{-6} cm^2/s, respectively.

4. Conclusions

The present study shows that the jute fiber carbon can be used as a potential adsorbent for the removal of both acid (eosin yellow) and basic (malachite green, crystal violet) dyes from their aqueous solutions. The amount of dye sorbed was found to vary with increasing initial solution pH for the sorption of malachite green and crystal violet onto jute fiber carbon. In the case of eosin yellow, lower pH favors the dye uptake process. The amount of dye uptake (mg/g) was found to increase with increase in dye concentration and contact time and found to decrease with increase in jute fiber carbon dosage. The kinetics of eosin yellow, malachite green and crystal violet was found to follow a pseudo second order kinetic expression. A generalized pseudo second order expression was derived and was found to be successful in simulating the kinetics of eosin yellow, malachite green and crystal violet onto jute fiber carbon. Equilibrium data of eosin yellow onto jute fiber carbon was found to follow Langmuir isotherm thus suggesting the monolayer sorption of dye ions. Freundlich isotherm was found to be the optimum isotherm for the sorption of malachite green and crystal violet onto jute fiber carbon. The dye uptake process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages. The effect of initial dye concentration on the external mass transfer was represented in the form of dimensionless mass transfer numbers ($Sh/Sc^{0.33}$). A Boyd plot confirms the external mass transfer as the slowest step involved in the sorption process.

Acknowledgments

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