

Use of Low Cost Nano-porous Materials of Pomelo Fruit Peel Wastes in Removal of Textile Dye

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ABSTRACT

The aim of the present study is to discover the effect of nano-porous adsorbent of Pomelo fruit peel wastes for removing Congo red dye (CR) from aqueous solution. In batch equilibrium experiments, the CR dye solutions were prepared by dissolving dye in deionized water to the required concentrations. The effect of adsorption isotherm were calculated by carryout a series of isotherm at different adsorbent dosages (1.0, 2.0, 3.0 g L⁻¹), temperatures (30, 40 and 60°C) and pH (5.99, 6.72, 8.73), respectively. The adsorption equilibrium data were analyzed by using various adsorption isotherm models and the results have shown that adsorption behavior of the dye could be described reasonably well by Langmuir and Freundlich models. The characteristic parameters for each isotherm have been determined. The monolayer adsorption capacity determined was reasonably high (g L⁻¹) at adsorbent dosage 1.049 (g L⁻¹), Temperature 1.081 (g L⁻¹) and pH 1.270 (g L⁻¹) for adsorption of CR dye respectively. The monolayer adsorption capacity was determined to be 1.08 to 0.75 mg g⁻¹. We concluded based on these results that Pomelo peel nano-porous adsorbent was an attractive candidate for removing CR dye from the wastewater. The present study suggests that the modified Pomelo peel nano-adsorbent was a cost-effective and attractive candidate for dyestuff removal from industrial wastewater.

Key words: Pomelo peel waste, congo red dye, adsorption, aqueous solution, Langmuir and Freundlich model

INTRODUCTION

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber (Arunachalam and Annadurai, 2011; Azhar *et al.*, 2005; Grag *et al.*, 2004). The textile dye colored effluents has mainly the complex nature and most of them are toxic to aquatic life, mutagenic and carcinogenic and can cause some health problems. Color that inherently occurs in water bodies receiving dye contaminated effluents can significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, chlorides, etc., in them (Bayramoglu and Arica, 2007; Bayramoglu *et al.*, 2006; Ozer *et al.*, 2006). Having usually synthetic origin and complex aromatic molecular structures, dye components are hardly degradable (Fu and Viraraghavan, 2002; Radha *et al.*, 2005). The removal of color effluents come from textile dyes are one of the main problems because of the difficulty in treating such wastewaters by using traditional treatment methods including coagulation, ultrafiltration,

ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, etc., due to the economic reasons (Gercel *et al.*, 2007; Orfao *et al.*, 2006; Banat *et al.*, 1996).

However, high cost, formation of hazardous by-products, intensive energy requirements and inefficient reusability of adsorbents are still limitations commonly countered during the application of these techniques (Arica and Bayramoglu, 2005; Arica *et al.*, 2004). Among treatment technologies, adsorption has been shown to be the most promising option for the removal of non-biodegradable organics from aqueous effluents, activated carbons being the most common adsorbent for this process due to its effectiveness and versatility (Bayramoglu and Arica, 2007; Aksu, 2005). Today, there is numerous numbers of low cost, commercially available adsorbents coal, fly ash, wood, silica gel, clay materials (bentonite, montmorillonite, etc.), agricultural wastes (bagasse pith, maize cob, coconut shell, rice husk, etc.), cotton wastes and cellulose based wastes such as orange, lemon, banana and lychee (Arunachalam and Annadurai, 2011; Bhatnagar and Minocha, 2010; Thirumavalavan *et al.*, 2010; Bhatnagar *et al.*, 2010; Memon *et al.*, 2009; Achak *et al.*, 2009) which had been used for the dye removal (Azhar *et al.*, 2005; Annadurai *et al.*, 2002; Juang *et al.*, 1997; Theng and Wells, 1995; Singh and Rawat, 1994). Thereby, the present investigation was made on low cost wastes of Pomelo peel for adsorption of Congo red dye from aqueous solution. The amounts of equilibrium adsorption were also investigated.

MATERIALS AND METHODS

Fruit peel preparation: Pomelo fruit peels were obtained from a local fruit market at Nagercoil, India on January, 2010. The peels were cut into small pieces, crushed and washed thoroughly with deionized water to remove the adhering dirt. They were air dried in an oven at 40°C for 48 h, before being ball-milled to form particles approximately 0.840 m m⁻¹ in size. Congo red dye was purchased from Merck Co. The concentrations of dyes were measured with an UV/visible spectrophotometer (Hitachi Model U-2000). The solution pH was adjusted by adding a small amount of 0.1 M HCl or NaOH.

Adsorption studies: In batch equilibrium experiments, the CR dye solutions were prepared by dissolving dye in deionized water to the required concentrations. A portion of adsorbent material Pomelo sorbent of known (1 g) and varied concentration of initial dye concentration 20-120 mg L⁻¹ was poured into the reaction conical flask. The time required to reach equilibrium as determined in equilibrium studies was 24 h. The effect of adsorption isotherm was studied by carrying out a series of isotherm at different temperatures (30, 40 and 60°C) and adsorbent dosages (1.0, 2.0 and 3.0 g L⁻¹) and pH (5.99, 6.72 and 8.73) respectively. The concentrations of dyes were measured with an UV/visible spectrophotometer (Hitachi Model U-2000). The amount of dye absorbed onto the peels, q_e (mg g⁻¹), was calculated by a mass balance relationship (Eq. 1). The aqueous samples were taken at preset time intervals, and the concentrations of dyes were similarly measured.

The amount of adsorption at time t, q_t (mg g⁻¹), was obtained as follows:

$$q_t = (C_0 - C_t) \times V / M \quad (1)$$

where, C₀ (mg L⁻¹) and C_t (mg g⁻¹) are the liquid-phase concentrations of solutes at initial and any time t, respectively, V is volume of the solution, M is the dosage of adsorbent in the solution (g L⁻¹).

To find the relation between the mass of dye adsorbed at a particular dosage, temperature and pH and liquid phase of dye concentration, the Langmuir (1918) and Freundlich (1906) isotherm model have been used.

RESULTS AND DISCUSSION

Effect of dosage, temperature and pH: Figure 1A-C had shown the adsorption of dye at different adsorbent dosage, temperature and pH by using environmental nano-porous material of Pomelo peel. The adsorbent rate variation may be due to the number of positive charges on the sorbent surface which leads to the no rejection of the negatively charged dye molecule, and thereby increasing the adsorption. The adsorption of dye increased with the increases of adsorbent dosage (Fig. 1A). The maximum percentage removal of 32.1 g L^{-1} was obtained for adsorbent dosage of 3.0 g L^{-1} for CR dye at 100 mg L^{-1} concentration. The increase in adsorption of dye with adsorbent dosage was due to the availability of more surface area of the adsorbent for adsorption. The result is similar to the observation of Namasivayam *et al.* (1996).

Temperature is an important parameter for the adsorption process. A plot of the CR dye uptake as a function of temperature (30, 40 and 60°C) is shown in Fig. 1B. The maximum percentage removal of 30.1 g L^{-1} was obtained for the temperature of 60°C for CR dye at 100 mg L^{-1} concentration. The adsorption of dye at higher temperature was found to be greater compared to that at a lower temperature. The curves indicate the strong tendency of the process for monolayer formation (Lucarelli *et al.*, 2000; Poots *et al.*, 1976; Ho and McKay, 1998, 1999; McKay *et al.*, 1987; Namasivayam *et al.*, 1998, 2001). The increase in temperature would increase the mobility of the large dye ion and also produces a swelling effect with in the internal structure of the nano-porous material, thus enabling the large dye molecule to penetrate further (Namasivayam *et al.*, 2001; Namasivayam and Kavitha, 2002; Ho and McKay, 1999). Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate and should increase with temperature rising. The adsorption of dye at higher temperature was found in the present investigation is similar to results of Namasivayam *et al.* (2001), Namasivayam and Kavitha (2002) and Ho and McKay (1999).

The maximum percentage removal of 29.1 g L^{-1} was obtained in pH of 8.73 for CR dye at 100 mg L^{-1} concentration. The dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions. This explanation is conflict with our data on pH effect (Fig. 1C). It can be seen that the pH of aqueous solution plays an important role in the adsorption of CR dye onto environmental nanomaterial. The present results conflict with the results of Namasivayam *et al.* (1996) and parallel to the results of Habib *et al.* (2006).

Langmuir and Freundlich isotherm: The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption systems. The isotherm expresses the relation between the mass of dye adsorbed at a particular dosage, temperature and pH and liquid phase of dye concentration. For any adsorption investigation one of the most important parameters required to understand the behavior of the adsorption process in the adsorption isotherm. The shape of an isotherm not only provides information about the affinity of the dye molecule for adsorption, but it also reflects the possible mode of adsorbing dye molecule. The most common way of obtaining an adsorption isotherm, is to determine the concentration of dye solution before and after the adsorption experiments, although several attempts have been made to find the adsorbed amount. A basic assumption of the Langmuir theory (Langmuir, 1918) is that sorption takes place at specific sites within the adsorbent (Chen *et al.*, 2008; Asfour *et al.*, 1985; Poots *et al.*, 1976).

The data obtained from the adsorption experiment conducted in the present investigation was fitted in different adsorbent dosage, temperature and pH in isotherm equation as shown in Fig. 1A-C. The saturation monolayer can be represented by the expression.

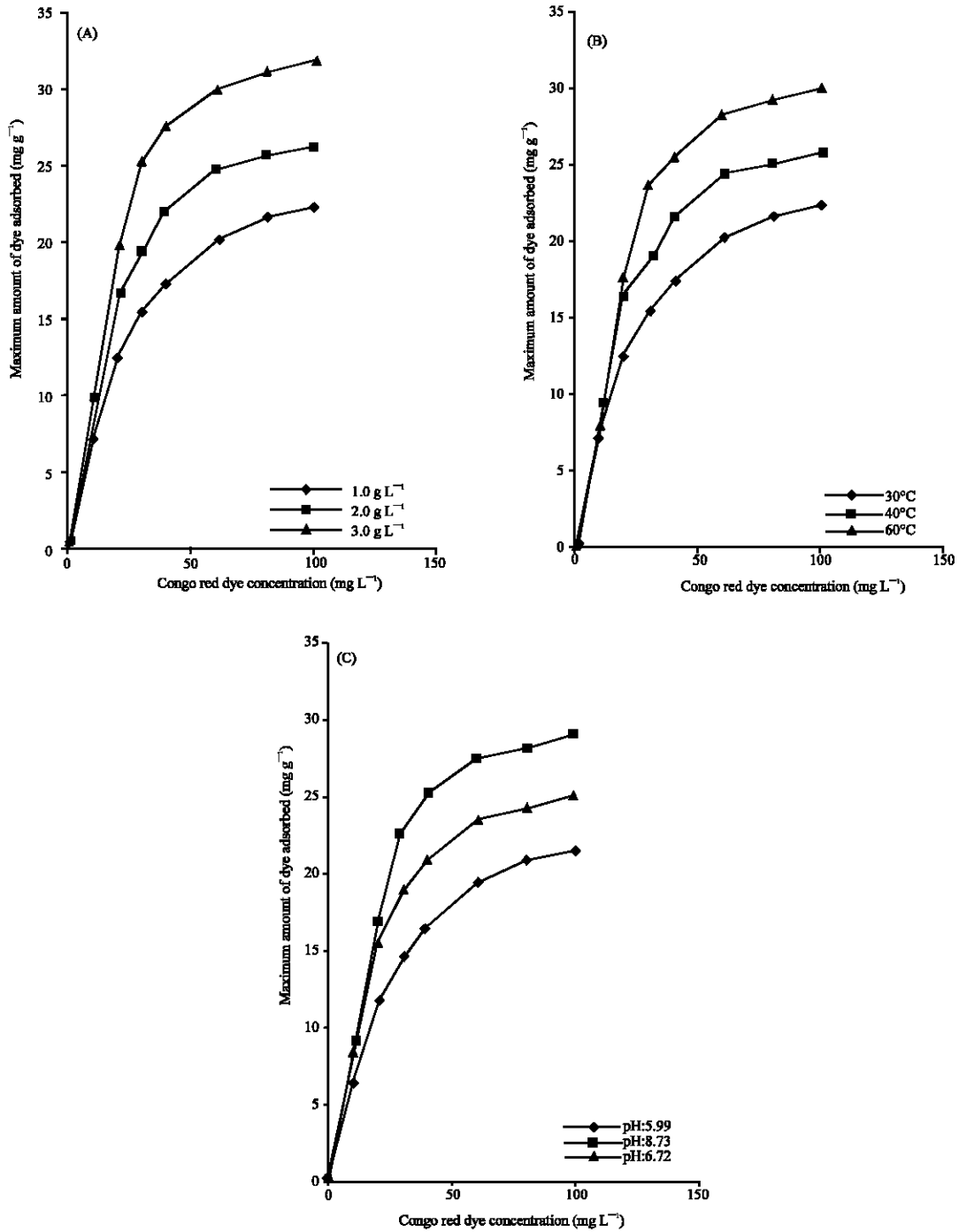


Fig. 1: Effect of specific dye uptakes (A) at different dosages with dye concentration; (B) at different temperatures dye concentration and (C) at different pH with dye concentration

$$q_e = \frac{KbC_e}{(1 + bC_e)} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{K} + \frac{1}{KbC_e} \quad (3)$$

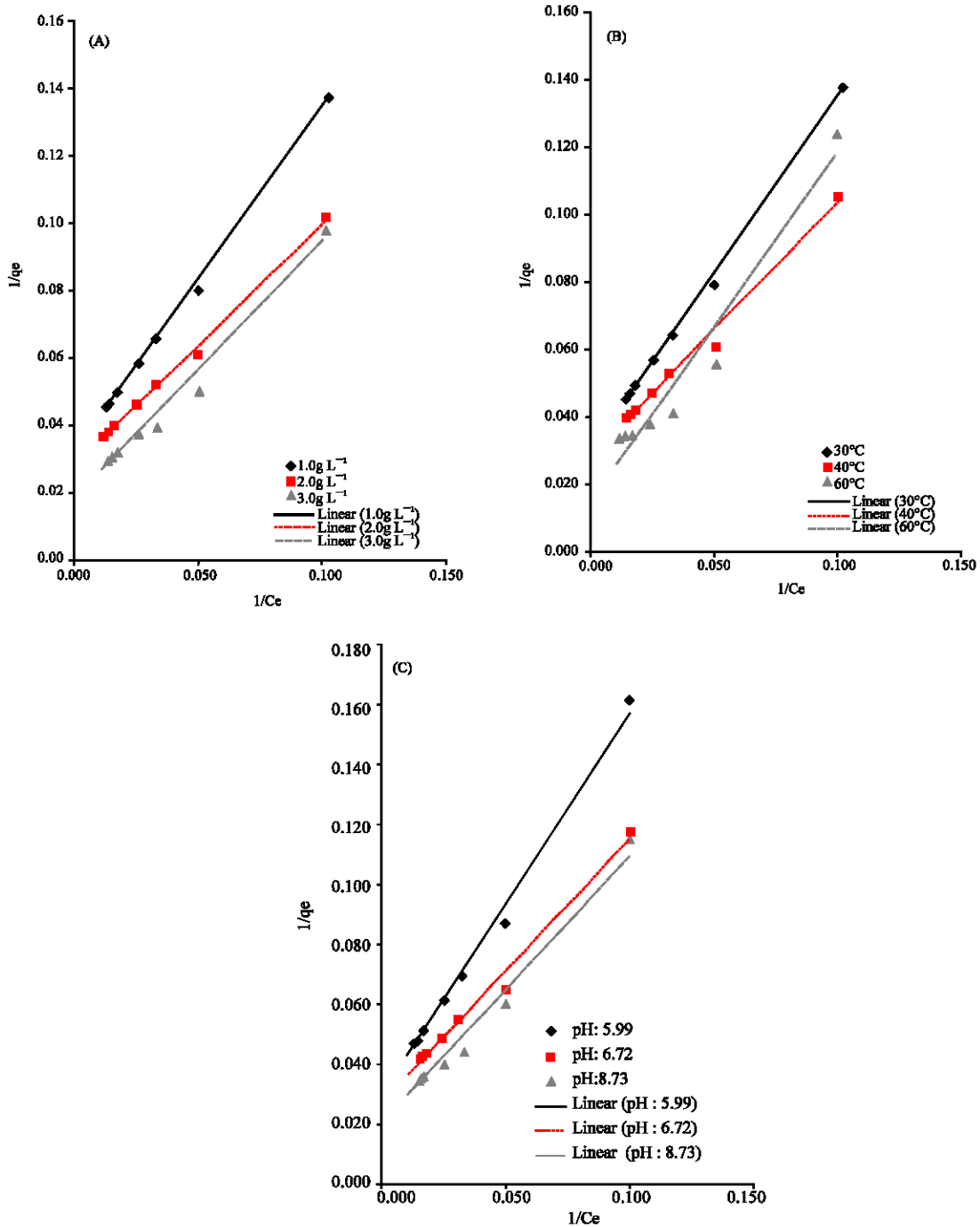


Fig. 2: Langmuir isotherm for the adsorption of dye using Pomelo peels (A) at different adsorbent dosages with dye concentration; (B) at different temperatures dye concentration and (C) at different pH with dye concentration

A plot of $(1/q_e$ vs $1/C_e)$ resulted in a linear graphical relation indicating the applicability of the above model as shown in Fig. 2A-C. The values are calculated from the slope and intercept of different straight line representing the different adsorbent dosage, temperature and pH (b)

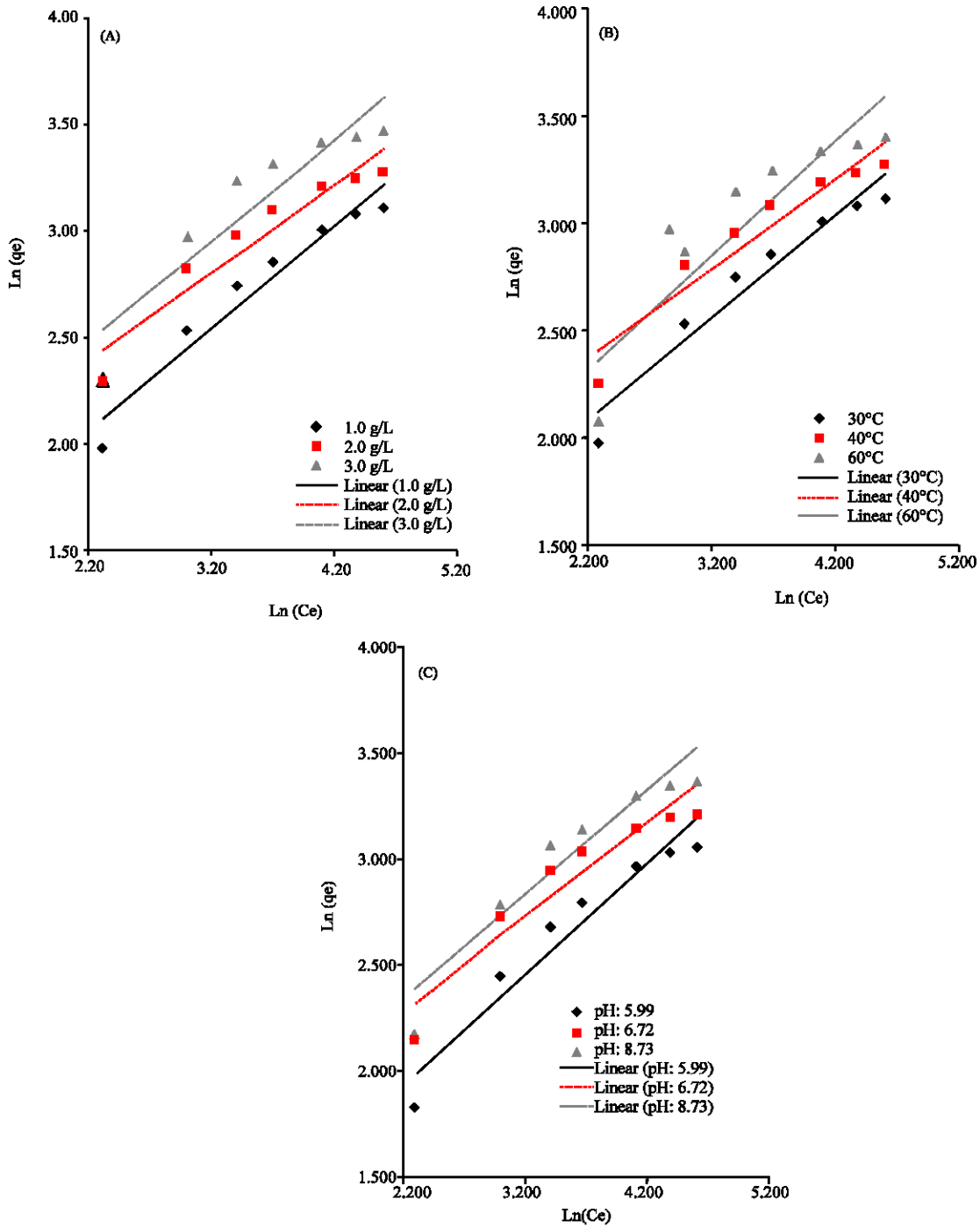


Fig. 3: Freundlich isotherm for the adsorption of dye using Pomelo peels (A) at different adsorbent dosages with dye concentration; (B) at different temperatures dye concentration and (C) at different pH with dye concentration

energy of adsorption and (k) adsorption capacity and Q_0 is represented by (K). The Langmuir isotherm constant (Q_0) in Eq. 2 is a measure of the amount of dye adsorbed, when the monolayer is completed. Monolayer capacity (Q_0) of the adsorbent for the dye is comparable obtained from

adsorption isotherm. The observed statistically significant (at the 95% confidence level) linear relationship as evidenced of these by the R^2 values (close to unity) indicate the applicability of the isotherm (Langmuir isotherm) and surface. The Langmuir isotherm constants along with correction coefficients are reported on Fig. 2 and 3 it is also clear from the shape of the adsorption isotherm, that it belongs to the L_2 category of isotherm, which indicates of the normal (or) Langmuir type of adsorption (Mohanty *et al.*, 2006).

Freundlich isotherm (Freundlich, 1906) is used for heterogeneous surface energies system. The sorption isotherm is the most convenient form of representing the experimental data at different adsorbent dosage, temperature and pH as shown in Fig. 3A-C. Moreover the figures show the batch isothermal data fitted to the linear form of the Freundlich isotherm (Poots *et al.*, 1976; Ho and McKay, 1998; McKay *et al.*, 1987; Namasivayam *et al.*, 1998).

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$\ln q_e = \ln K_F / (1/n) \ln C_e \quad (5)$$

The various constants, associated with the isotherm are the intercept, which is roughly on indicator of sorption capacity (k_p) and the slope ($1/n$) sorption intensity values are recorded in Fig. 2 and 3. Freundlich of isotherm has been illustrated to be a special case of heterogeneous surface energies and it can be easily extended to this case. It has been stated by Poots *et al.* (1976), Ho and McKay (1998, 1999), McKay *et al.* (1987) and Namasivayam *et al.* (1998) that magnitude of the exponent $1/n$ gives an indication of the favorability and capacity of the adsorbent system. The values $n > 1$ represents favorable adsorption conditions. Most of the cases the exponent between $1 < n < 10$ shows the beneficial adsorption.

CONCLUSION

The adsorption of Congo red dye form aqueous solution using nano-porous material of Pomelo fruit peels wastes has been investigated under different reaction conditions in batch and equilibrium mode. The fitness of Langmuir model in the present system shows the formation of monolayer coverage of the adsorbate at the outer space of the adsorbent. Freundlich model isotherm was analyzed. It was determined that the monolayer adsorption capacity was reasonably high (g/L) at adsorbent dosage 1.049 (g L⁻¹), Temperature 1.081 (g L⁻¹) and pH 1.270 (g L⁻¹) for adsorption of CR dye respectively. Moreover, the monolayer adsorption capacity was found to be 1.08-0.75 mg g⁻¹.

The values of dimensionless equilibrium parameter like separation factor (R_L) at different particle size and temperature indicates the favorability of the process described in the present study. Langmuir and Freundlich models could be used to describe dye sorption on environmental nanomaterial at equilibrium gave a better fit. It's revealed that the agricultural waste of Pomelo fruit peels were used as low-cost alternatives in wastewater treatment and the data reported here should be useful for the design and fabrication of an economically viable treatment process using batch (or) stirred tank reactors. Further studies may be needed for the removal of hazardous materials such as heavy metal ions and other textile dyes present in textile effluents.

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