COMPARATIVE KINETIC AND ISOTHERM STUDIES ON ADSORPTIVE REMOVAL OF MALACHITE GREEN AND CONGO RED FROM WASTEWATER BY CORN STALK AND CORN HUSK

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ABSTRACT

Adsorption is considered to be one of the most effective technologies widely used in global environmental protection areas. Modeling of experimental adsorption isotherm data and kinetics data were essential ways for predicting the mechanisms of adsorption, which will lead to an improvement in the area of adsorption science. In this paper, we employed two isotherms model, namely: Langmuir and Freundlich, to correlate four sets of experimental adsorption isotherm data, which were obtained by batch tests in lab. Linear regression analysis was used to evaluate and to determine the best fit isotherm model; the correlation coefficient (R^2) was used to evaluate the data. The modeling results showed that linear Freundlich model could fit the data better than Langmuir model, with relatively higher R^2 values. The kinetics model of adsorpbents was tested by the pseudo-first order kinetics and pseudo-second order kinetics models. The result showed that the adsorptions of the adsorbates on adsorbents strongly followed pseudo-second order kinetics model which revealed that the experimental equilibrium adsorption capacity $q_{e(exp)}$ (mg/g) and calculated equilibrium capacity $q_{e(cal)}$ (mg/g) for the adsorbates adsorption were in agreement with high values of the correlation coefficient R^2. The pseudo- first order kinetics had high values for their correlation coefficient R^2, however, the experimental equilibrium adsorption capacity $q_{e(exp)}$ (mg/g) and calculated equilibrium adsorption capacity $q_{e(cal)}$ (mg/g) were not in agreement and therefore, the adsorption did not follow pseudo-first order kinetics.

KEYWORDS

Modeling; isotherm data; linear; kinetics data; congo red; malachite green; corn stalk; corn husk.

INTRODUCTION

One of the most common water pollutants is colour. They are release into the water by the discharge of dyes from paper and pulp industries, textile industries, tanning industries and many other industries [1]. Dyes are widely used

by several industries like plastics, textile, and paper, to color their final products [2]. Thus using of dyes contaminated water without any treatment may cause adverse effect on human health, domestic animals, wildlife and on the environment. So, it is necessary to treat or remove colour from the industrial effluent before discharge [3]. This could be achieved through adsorption process. Adsorption process involves three steps. First of all, the substance which has to be adsorbed i.e. adsorbate enters to the outer surface of substance which adsorbs it i.e. adsorbent. After that, the adsorbate move into the openings/pores of the adsorbent particles. The higher the surface area of the pores, the higher will be the adsorption. And finally the molecules get attached to the surface area of adsorbents. Thus adsorption is a surface phenomenon. It occurs because of the interparticle forces of attraction between molecules or ions of adsorbate and adsorbent [4]. Among a numbers of strategies, the adsorption-based process is considered to be efficient to remove various pollutants in water [5]. In this regard, a great deal of interest has been focused on the use of different types of materials as adsorbents for dye removal, such as activated carbon fiber [6], Fe-Zr binary oxide [7], pillared bentonites [8], hydrous zirconium oxide [9], and ferric oxides [10], *etc.* However, the cost implication of activated carbon has necessitated the need for low cost adsorbents. A research reported that locally available low cost bio-adsorbents like neem leaves, orange peels, peanut hulls and coconut coir pith powders were used to remove colour from textile industry waste water [11]. By batch adsorption studies observing the effect of experimental parameters such as adsorbent dose, dye concentration and contact time. A maximum removal of 90-95% was obtained for an adsorbent dose of 0.3g [12]. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms e.t.c. The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists onto an adsorbent [13]. The adsorption process and mechanism depends on the physical and/or chemical characteristics of the adsorbent, mass transfer of dye molecules to adsorbent surfaces, diffusion of dye molecules into the interior pores of adsorbent and equilibrium dye attachment [14]. The kinetics of malachite green and congo red adsorption process was investigated using the pseudo-first order kinetics and pseudo-second order kinetics models [15]. This model is based on the assumption that the rate of change of adsorbed solute with time is directly proportional to the difference in equilibrium adsorption capacity and the adsorbed amount [16].

MATERIALS AND METHODS

ADSORBENTS PREPARATION

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Fresh Corn stalks and Corn husks were collected from a local Corn/Maize Mill in Rimi Local Government Area, Katsina State. The stalks and husks were washed thoroughly with tap water to remove the dust and other adhering particles followed by distilled water. The washed corn stalks and corn husks were sun-dried followed by oven-drying at 105°C for 24 hours. The dried stalk and husk were pounded with a mortar and sieved to mesh sizes of 106µm, 250µm, 500µm, 750µm and 1000µm and stored in a plastic container labeled as CS (Corn stalk) and CH (Corn husk) for further analysis. The analytical grade Adsorbates (Malachite Green and Congo red) were obtained from the laboratory without any further treatment. Approximately 1g of each Adsorbate was dissolved in distilled water (1000 ml) to make 1000 mg/L stock solution. The Congo red solution was labeled as CR and Malachite Green as MG. All other experimental MG and CR solutions of desired concentrations were prepared from the stock solution by serial dilution using the formula: $M_1 V_1 = M_2 V_2$

Where; M_1 = Concentration of stock solution

M_2 = Concentration of dilute solution

V_1 = Volume extracted from stock solution

V_2 = Final volume of dilute solution

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BATCH ADSORPTION EXPERIMENTS

Adsorption experiments on MG and CR by Corn stalks and Corn husks were carried out by batch adsorption method. Various parameters such as contact time, initial dye concentration, adsorbent dosage, initial dye pH and adsorbent particle size were studied at constant agitation rate of 300rpm, and room temperature (25°C) in triplicates, only the average is taken. The adsorption measurements were conducted by mixing various amounts of adsorbent in Erlenmeyer conical flasks (250cm^3) containing dye solutions of known concentrations (50cm^3). The solutions were agitated using an orbital shaker for a predetermined time to attain equilibrium after which the samples were taken out and the supernatant solutions were separated from the adsorbent by filtration using Whatman No. 41 filter paper and centrifugation using a centrifuge at 100rpm for 20 minutes. The filtrates were analyzed using UV-Visible Spectrophotometer at maximum adsorption (λmax) of 615 nm for MG and 500 nm for CR dye solutions. Each

reported data represents an average value of triplicate readings and the percentage adsorption and equilibrium adsorption capacity, qe (mg/g) were evaluated using equation 1 and 2 respectively.

$$\% \text{ adsorbed} = \frac{C_o - C_e}{C_o} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$q_e = \frac{C_o - C_e V}{w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where C_o and C_e are the concentrations (mg/L) of the dye initially and at equilibrium time, *w* is the weight of the adsorbent (g), q_e is the amount of the dye adsorbed (mg/g) while v is the volume of the solution in litre. [17].

RESULTS AND DISCUSSION

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LANGMUIR ADSORPTION ISOTHERM

Langmuir isotherm is used to determine whether the adsorption process occurs through monolayer formation. Langmuir isotherm model was tested on the adsorption of MG and CR on CS and CH and the results were presented on Figure 1,2,3,4 and Table 1. The results showed that the adsorption of MG and CR on CS and CH having lower values of R^2 in comparison with R^2 value for freundlich isotherm. The R^2 values for the adsorption process from Langmuir's model plot decreases in the order CS-CR (0.991), CH-MG (0.984), CS-MG (0.952) and CH-CR (0.906). Higher values of the regression coefficient, R^2 confirms that the adsorptions followed the Langmuir model. The maximum adsorptive capacity q_m were found to increase in the order CS-MG (4.092), CH-MG (3.774), CS-CR (3.329) and CH-CR (3.078) which are generally lower than values 149.35mg/g for the removal of malachite green from aqueous medium onto oil palm fiber [18], 77.5mg/g for MG adsorption onto dead tree leaves [19], 80.645mg/g for the removal of malachite green by wood apple shell and 66.7mg/g adsorption of congo red onto Eucalyptus wood [20]. But higher than 0.36mg/g onto neem bark for the malachite green adsorption and 0.5mg/g onto mango bark for the removal of MG [21] and 2.6 coipith for removal congo red [22]. The dimensionless separation factor R_L which is the measure of favorability of adsorption. The R_L values for the adsorption of MG dye on CS and CH were found to be 0.7891 and 0.789 respectively which indicated that the adsorptions were favorable.

On the other hand, the R_L values for the adsorption of CR on CS and CH were found to be 1.9596 and 1.9596 respectively which indicated that the adsorptions were unfavorable.

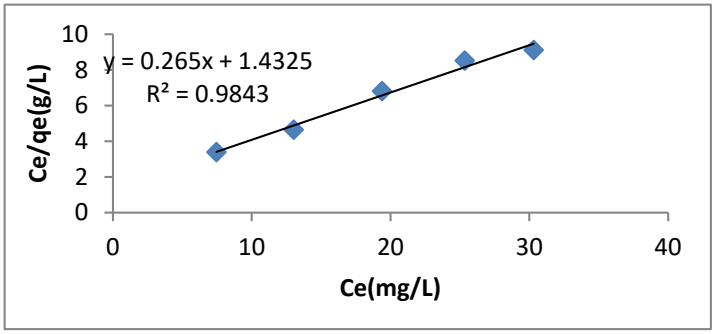

Fig.1 Langmuir Isotherm Plot of CH-MG

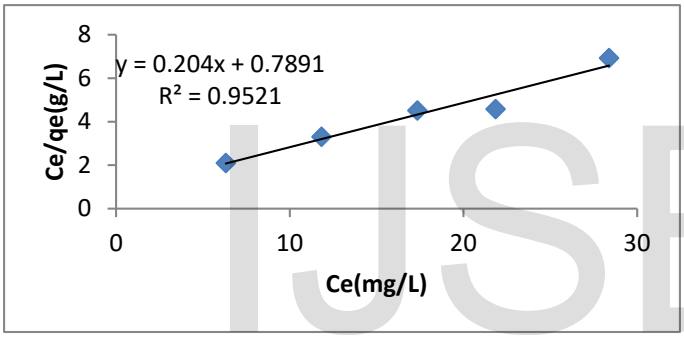

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Fig.2 Langmuir Isotherm Plot of CS-MG

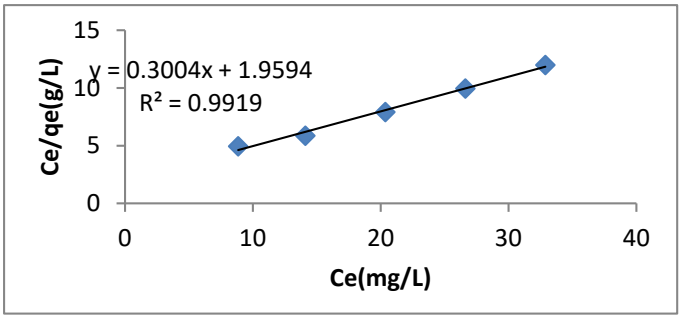

Fig.3 Langmuir Isotherm Plot of CS-CR

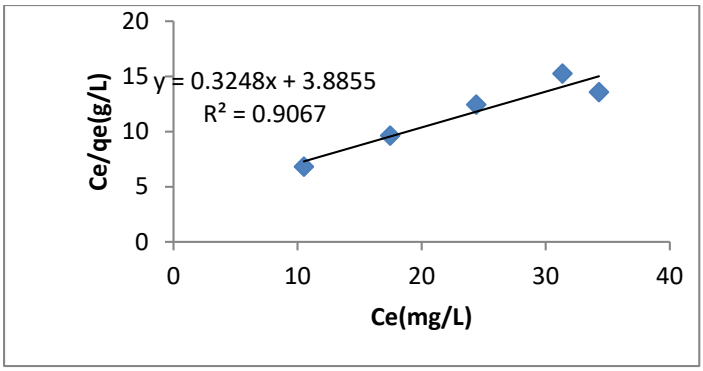

Fig.4 Langmuir Isotherm Plot of CH-CR

FREUNDLICH ISOTHERM

The Freundlich isotherm model was tested on the adsorption of MG and CR on CS and CH and the results were presented on Figure 5,6,7,8. The Freundlich Isotherm assumes that dye uptake occurs on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase in solute concentration. Table 1 show that the adsorption of MG and CR on CS and CH follows Freundlich isotherm for having high values of R^2. The R^2 values for the adsorption of MG on CS and CH were 0.998 and 0.997 respectively. While the R^2 values for the adsorption of CR on CS and CH were found to be 0.990 and 0.994 respectively. The K_F value for MG adsorption on CS was found to be highest with the value of 0.5623 mg/g, followed by the adsorption of MG on CH with the value of 0.4083 mg/g, followed by the adsorption of CR on CS with the value of 0.2655, and then followed by CR-CH with value 0.1374mg/g. But higher K_F value indicates an easy uptake of dye from solution [23]. n is an empirical constant related to the magnitude of the adsorption driving force. The n values were found to increase in the order CS-MG (0.9107), CH-MG (0.8643), CS-CR (0.7911) and CH-CR (0.7133). The adsorption process is said to be favorable when the value of nF satisfies the condition /1/ < nF < /10/, otherwise it is unfavorable [24].

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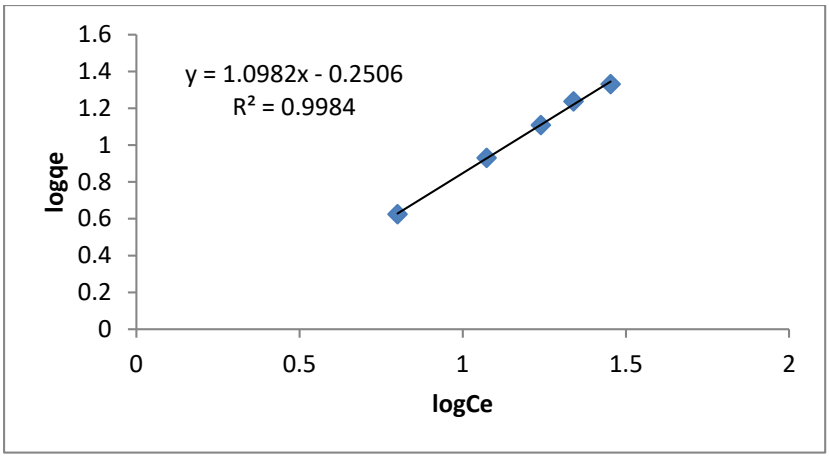

Fig.5 Freundlich Isotherm Plot for MG on CS

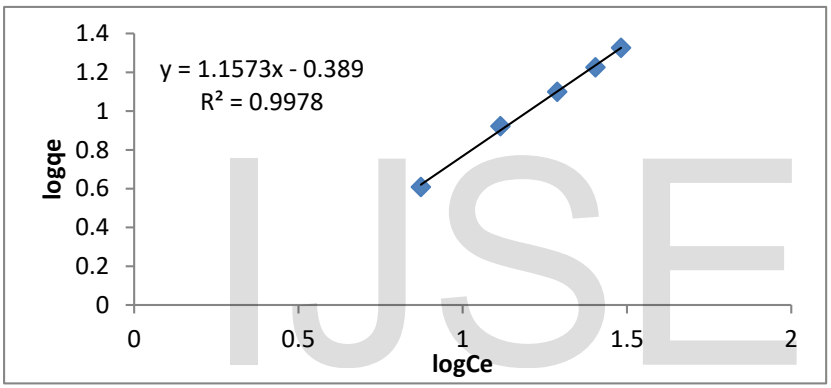

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Fig.6 Freundlich Isotherm Plot for MG on CH

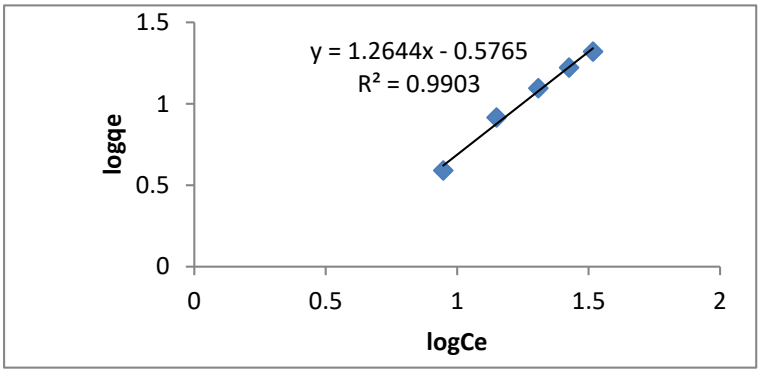

Fig.7 Freundlich Isotherm Plot for CR on CS

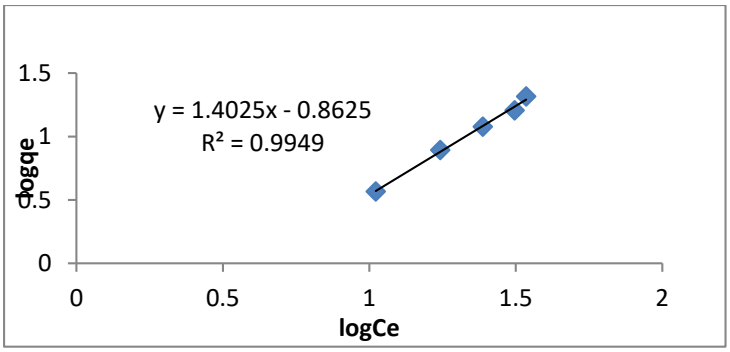

Fig.8 Freundlich Isotherm Plot for CR on CH

Table 1.Adsorption Isotherms

Adsorbent-Dye Interactions	**Langamuir Isotherm**				**Freundlich Isotherm**		
	q_m (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g)	N (g/L)	R^2
CS-MG	4.092	0.2585	0.952	0.7891	0.5623	0.9107	0.998
CS-CR	3.329	0.1533	0.991	1.9596	0.2655	0.7911	0.990
CH-MG	3.774	0.185	0.984	0.7891	0.4083	0.8643	0.997
CH-CR	3.078	0.084	0.906	1.9596	0.1374	0.7133	0.994

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PSEUDO FIRST ORDER KINETIC MODEL

The pseudo first order kinetics was tested for Malachite Green and Congo red adsorption onto corn stalk and corn husk as shown on Figure 9, 10, 11, and 12. As presented on Table 2. the adsorption of MG on CS and CH gave high values of R^2 of 0.912 and 0.818 respectively, While the adsorption of CR on CS and CH gave high values of R^2 of 0.824 and 0.858 respectively. The adsorption of MG and CR dyes on CS and CH did not follow pseudo first order kinetics since the experimental equilibrium adsorption capacity $q_{e(exp)}$ (mg/g), and calculated equilibrium adsorption capacity $q_{e(cal)}$ (mg/g), ware not in agreement, despite high values for their correlation coefficients R^2, and therefore the kinetic model cannot satisfactorily be used to interpret the adsorption of MG and CR by both CS and CH.

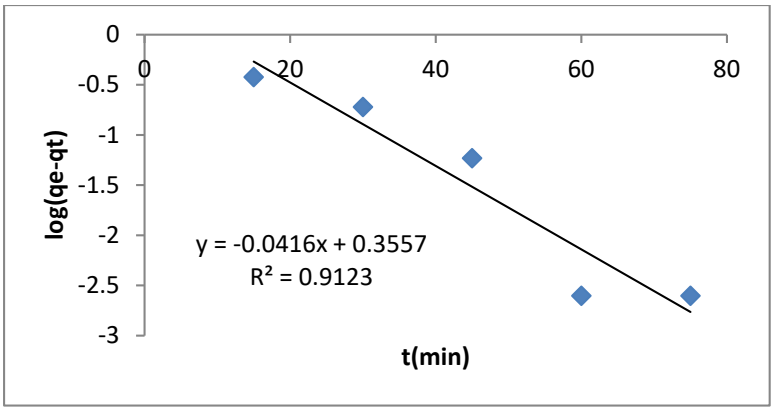

Fig.9 Pseudo First Order Kinetic of MG on CS

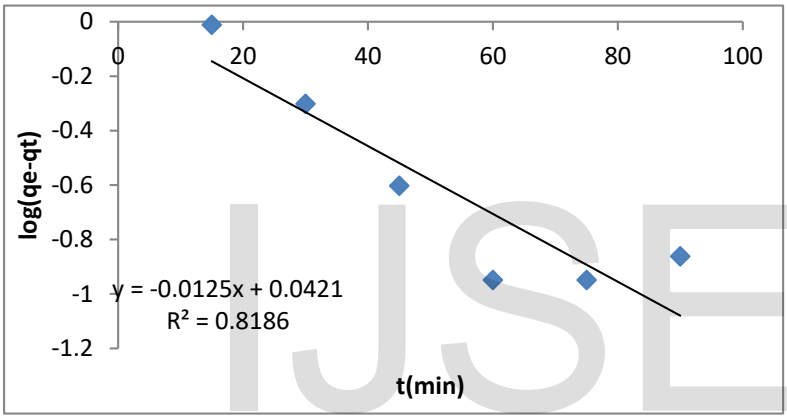

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Fig.10 Pseudo First Order Kinetic of MG on CH

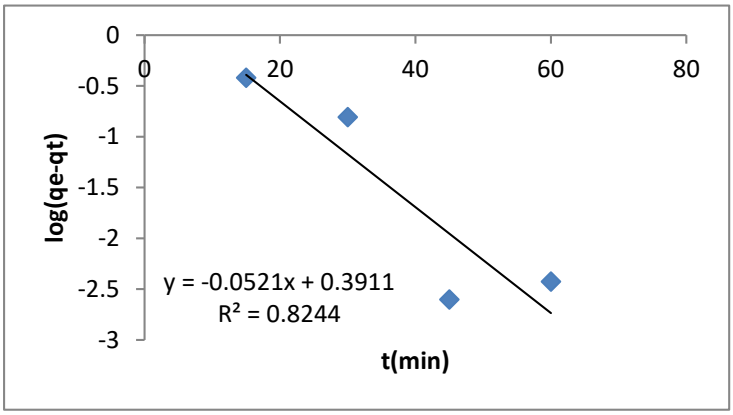

Fig. 11 Pseudo First Order Kinetic of CR on CS

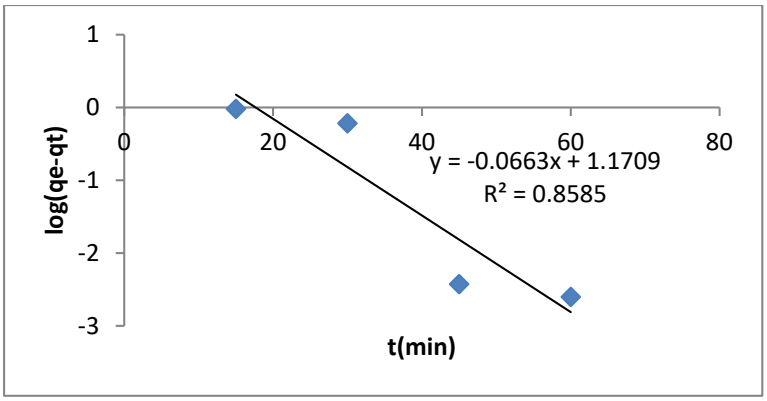

Fig.12 Pseudo First Order Kinetic of CR on CH

PSEUDO SECOND ORDER KINETIC MODEL

The pseudo-second order kinetic was modeled for Malachite Green and adsorption onto corn stalk and corn husk as presented on Table 2. The calculated pseudo-second order kinetic parameters for MG and CR on CS and CH obtained from Figures 13, 14, 15 and 16. The experimental equilibrium adsorption capacity $q_{e(exp)}$. (mg/g), and calculated equilibrium adsorption capacity $q_{e(cal)}$. (mg/g), for both the MG and CR adsorptions on CS and CH were in agreement with high values of the correlation coefficient R^2. Therefore the adsorptions of MG and CR dye on CS and CH strongly followed pseudo-second order kinetics. The adsorption of MG and CR according to pseudo-second order kinetics implied that the rate limiting step during adsorption was based on chemisorptions [25]. Therefore the rate of MG and CR adsorptions were dependent on both concentration of dye molecules and surface characteristics of the adsorbent.

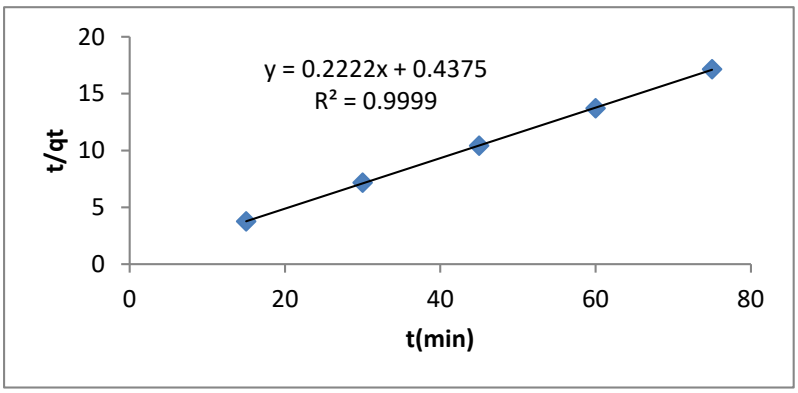

Fig.13 Pseudo Second Order Kinetics for MG on CS

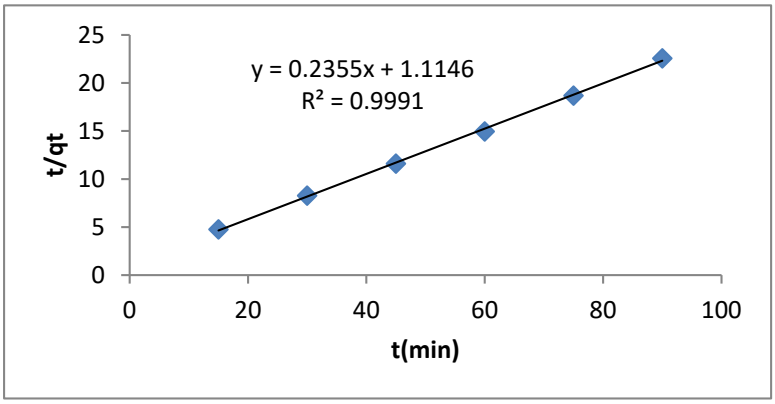

Fig.14 Pseudo Second Order Kinetic for MG on CH

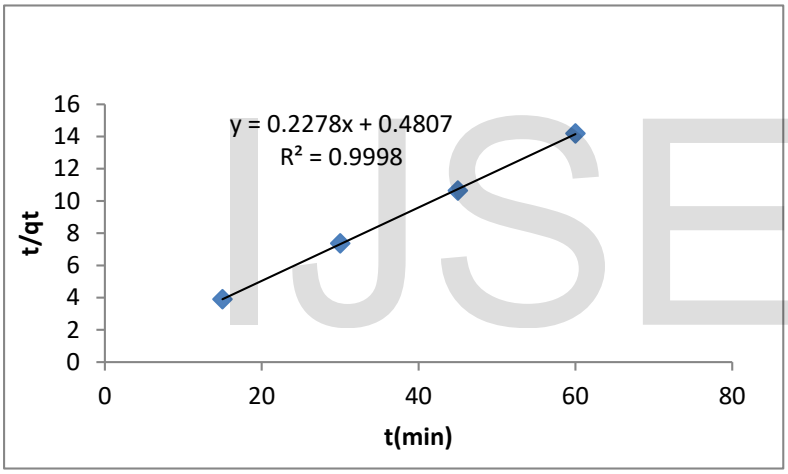

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Fig.15 Pseudo Second Order Kinetic for CR on CS

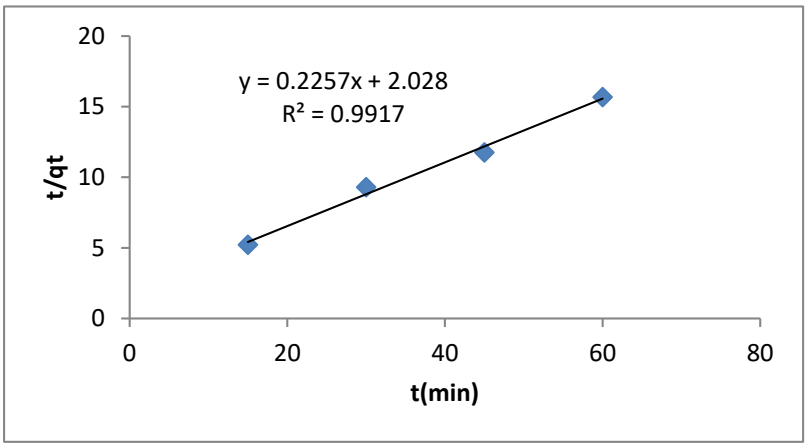

Fig.16 Pseudo Second Order Kinetics for CR on CH

Table 2. Kinetic Models

Adsorbent-Dye Interactions	**pseudo first order kinetic**				**pseudo second order kinetic**			
	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	K_1 min^{-1}	R^2	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	K_2 $gmin^{-1}mg^{-1}$	R^2
CS-MG	4.375	2.2646	0.0944	0.912	4.375	4.5050	0.1128	0.999
CS-CR	4.228	2.4604	0.1198	0.824	4.228	4.4053	0.1074	0.999
CH-MG	4.013	1.1015	0.0280	0.818	4.0125	4.2550	0.0500	0.999
CH-CR	3.825	14.7911	0.1520	0.858	3.8250	4.4440	0.0250	0.991

CONCLUSION

The equilibrium data for both MG and CR dyes fits well to the Freundlich isotherm model as evidenced by high regression coefficient values (R^2) 0.998, 0.990, 0.997 and 0.994 for CS-MG, CH-MG, CS-CR and CH-CR respectively. Therefore the adsorption of MG and CR onto CS and CH occurs through multilayer formation on the adsorbent surfaces. While the values of the Langmuir's separation factor R_L suggest that all the adsorption processes are unfavorable. The Freundlich isotherm constant n_F for the adsorption of MG and CR on CS and CH indicated adsorptions on heterogeneous surfaces. The adsorption of MG and CR dyes follows pseudo-second order kinetics implying chemisorption. Hence rate of dye removal from aqueous solution was dependent on electrostatic interactions between dye molecules and adsorbent surfaces.

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