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Kinetics of Adsorptive Removal of Congo Red using Activated Kola Nut Pod

Abdurrahman, M. A. and *Muhammad, A. S.
Department of Pure and Industrial Chemistry, Bayero University, Kano. P.M.B 3011, BUK, Kano, Nigeria.
***Correspondence Email:** asmuhammed.chm@buk.edu.ng

ABSTRACT
The objectives of this study is to evaluate the kinetics for the adsorption of Congo red (CR) onto activated kola nut pod (AKP) from aqueous solutions using a batch adsorption process. The effect of contact time (10 min to 180 min) and initial concentration (5 mg/l to150 mg/l) of the adsorption of CR onto AKP were optimized. Characterization of the adsorbent was undergone using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), and the result obtained showed shifting and disappearance of peaks after adsorption. The results of the adsorption kinetics revealed that Congo red (CR) was adsorbed according to the pseudo second-order kinetic model, the data showed the highest correlation coefficient for pseudo Second-order (0.997) and an agreement between the amount adsorbed experimentally (1.907 mg/g) and the calculated amount (1.839 mg/g).

Keywords: Activation, Adsorption, Congo red, Dye, Kinetics

INTRODUCTION

Textile, cosmetics, Paper, food, pharmaceutical plastic and ternary industries releases effluents which content are mostly highly colored dyes, they are marked as one of the major causes of environmental pollution (Vidyadhar, 2019). Another report of the World Bank estimates that nearly 20% of all global industrial water pollution comes from the treatment and dying of textiles (Seema, 2017). Approximately 60% of the dyes used in the textile industries are azo dyes which includes Congo red (Fathi *et al*. 2015). Congo red (CR) dye [1-naphthalenesulfonic acid, 3,3′-(4,4′-biphenylenebis(azo))-bis(4-amino) disodium salt] is a benzidine-based anionic diazo dye, which is known to metabolize the 1,1'-biphenyl-4,4'-diamine (benzidine), a known carcinogen that effects humans (Shu *et al*. 2015). Low concentration of CR dye can affects the aquatic habitat which therefore leads to hazardous health symptoms in humans such as difficulty in breathing, vomiting, diarrhea and nausea (Naba and Sumana, 2018). As a result, control measures have been taking over the years, using several processes that includes, flocculation, coagulation, chemical oxidation, biological degradation and photochemical degradation for wastewater treatment except that all the aforementioned methods have limitations and unsuccessful in removing the color completely from wastewater (Sumanjit and Mahajan 2012). In recent years adsorption have become one of the most popular treatment process for the removal of dye from wastewater due to its cheap cost, simple to use and its possibly reuse (Naba and Sumana, 2018).

Samuel and Oladipupo (2014) studied chemically treated kola nut pod for the removal of 2,4-dinitrophenol from synthetic wastewater using batch process, the percentage removal decreases with increase in concentration of the adsorbent and increase with increase in contact time, they also reported the kinetics of the adsorption obeying the pseudo first-order kinetic model with a very good correlation coefficient there by suggesting the biosorption process to be physisoption.

Olugbenga *et al*. (2016) reported adsorption process using activated agro-west which include kola nut pod and coconut husk, it was acid-activated and characterized using FTIR, SEM, energy dispersive x-ray (EDX), determination of oxygen containing functional groups, the data obtained suggest a well-developed pores on the surface of the precursor yielding product with high carbon content, as well as the acidic surfaced adsorbent indicates a promising ability to remove dye, metal ion, and other organic pollutant.

Kola nut pod (*cola acumlata* known as abata and *cola nitida* known as Goro in Hausa language) is the seed kernel of an African tree, commercially grown around the world. It has its origin from the Congo and West African, it has gained cultivation in places like Jamaica, Indonesia, South America (Brazil) and West Indian island (Taiwo *et al*., 2017. Samuel and Oladipupo, 2014). A good amount of kola nut is exported from Nigeria to other African countries, Europe as well

as North America (Taiwo *et al*., 2017). Kola nut pod as a west can be utilize for adsorption.

In this study, the kinetics of the adsorption of Congo red (CR) onto Activated kola nut pod (AKP) using batch adsorption process was investigated.

MATERIALS AND METHOD

Chemicals used in the work were of analytical reagent (AR) grade therefore, they were not subjected to any further purification. The chemicals used includes Congo Red (CR) with 98% purity, hydrochloric acid (37% purity), sodium hydroxide (≥ 99% purity). Routine laboratory apparatus were used.

Sample Collection

Approximately 100 kola nut pods and its content were collected from Osun state, southwest of Nigeria from a village called Ikoromoja in Atakunmosa east local government.

Sample Preparation

The kola nut pods were cracked and emptied, the empty kola nut pod were chopped into smaller pieces to hasten the drying process and the debris were washed. The rinsing of the samples were carried out with deionized water and air dried for two weeks and then subsequently washed repeatedly with deionized water to remove all the viscos liquid and finally air dried for a week and stored at room temperature prior to use. (Samuel and Oladipupo, 2014).

Preparation of the Activated Kola nut Pod

The dried kola nut sample was mixed with concentrated sulphuric acid (97% purity, 1.84 specific gravity) in the ratio 1:1 and confined in a Muffle furnace at 300 ^{o}C for 3 h for activation. The material was taken out and washed severally with deionized water till the pH is neutral. It was then sieved through the mesh size of 0.5 mm and then stored in plastic containers with the label AKP. Activation is based on the work reported by Yamun and Kamaraj (2016) with slight modification.

Adsorbate Preparation

A stock solution 1 g/L of CR was prepared by dissolving 1g of the dye in 1litre volumetric flask containing 0.2 L distilled water and then made up to the mark. Experimental solutions of the desired concentrations were obtained by dilution from the stock solution thereafter to produce 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 mg/L which were used for calibration curve and 10 mg/L for adsorption studies.

Characterization and Analysis

The various functional groups present on the AKP surface were determined using Fourier Transform Infrared Spectroscopy Analysis (FTIR). The concentration of CR in the solution was measured by PerkinElmer UV-visible spectrophotometer at a predetermined maximum wavelength of 495 nm. The solution pH was determined by pH meter and the surface morphology was revealed through the use of scanning electron microscopy at 2000 magnification.

Batch Adsorption Experiment

The batch adsorption process was carried out in a 120 ml stoppered bottle which contains 50 ml of 10 mg/L CR. 0.2 g of AKP was added into the solution. The dye solution was made to undergo adsorption by agitating using an electric agitator at 200 rpm for 180 min at ambient temperature (31.5^{0}C). Samples were taking out and filtered after intervals of 10, 20, 30, 60, 90, 120, 150, 180 min after which concentrations were determined using PerkinElmer UV-spectrophotometer at an absorbance wavelength of 495 nm. The optimum contact time was obtained by calculating the highest percentage removal using Equation 1 and highest adsorption capacity using Equation 2;

$$\%removal = \frac{C_0 - C_1}{C_0} \text{X } 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \text{X } 100 \quad (2)$$

Where C_0 (mg/L) is the initial dye concentration, C_e (mg/L) is the equilibrium dye concentration, m (g) is the sorbent mass, and V (L) is the volume of the dye solution.

The optimum concentration was calculated at intervals of 5, 10, 20, 30, 50, 70, 100, 120 and 150 mg/L, (Samusolomon and Martin, 2011).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy is an important analytical tool which can be used to describe important functional groups associated with the adsorbent surface (Mondal and Roy 2018). The properties of the adsorbent, such as physical structure, chemical nature and functional groups, controls the adsorption performance. The FTIR spectra of AKP before and after CR adsorption are presented in Figs. 1and 2, respectively, while Table 1 presents peaks and frequencies of IR absorption.

The FTIR spectra in Figures 1 and 2 shows the bands of AKP before and after adsorption of CR and the functional groups assigned are highlighted in Table1, the spectra were measured within 4000 – 400 cm^{-1}, the band around 3387-3327 cm^{-1}, represent he OH stretching vibration in carboxylic acid groups, the band at around 2877-2836 cm^{-1} corresponds to carboxylic acid groups stretching vibration, the peak at 1719 generally indicates the presence of C=O group stretching vibration, while 1547 cm^{-1} band indicates the presence of NO_2 in aliphatic nitro

compounds due to antisymmetric stretching, the peak at 1424 cm^{-1} represents in-plane OH bending in carboxylic acid group, the peak around 1127-1160 cm^{-1} corresponds to C-N stretching vibration in amines, 676-665 cm^{-1} indicates O-C=O in carboxylic acid groups due to O-C=O bending and aldehyde compounds due to C-C-CHO bending (Olubgenga *et al.*, 2016; sumanjit *et al.*, 2013). FTIR spectra of AKP peaks around 2877-1547 cm^{-1} which are present in the adsorbent before loading and are not observed in the dye loaded adsorbent because of the adsorption of CR on the AKP surface (sumanjit *et al.*, 2013). Shifting and disappearance of peaks, and the functional groups assigned describes the natures of the surface and the type of functional groups attached to it (Mondal and Roy 2018).

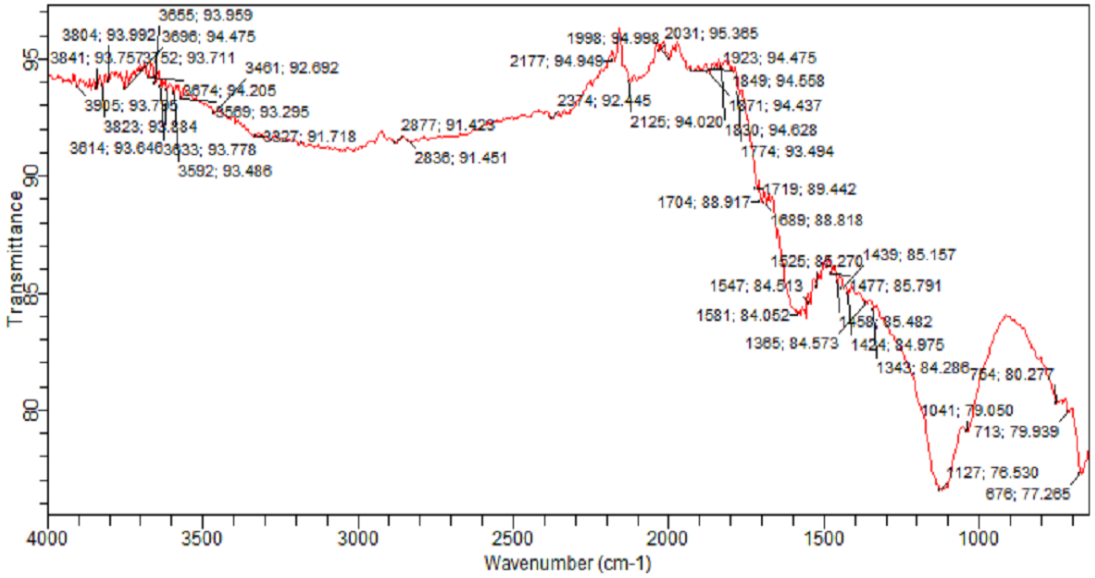


Figure 1: FTIR spectrum of AKP before adsorption

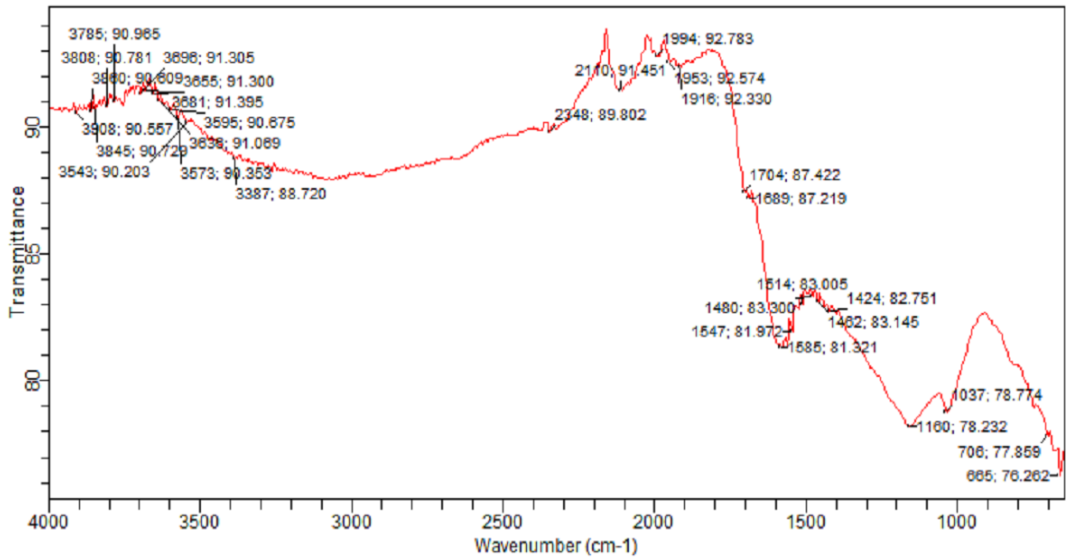


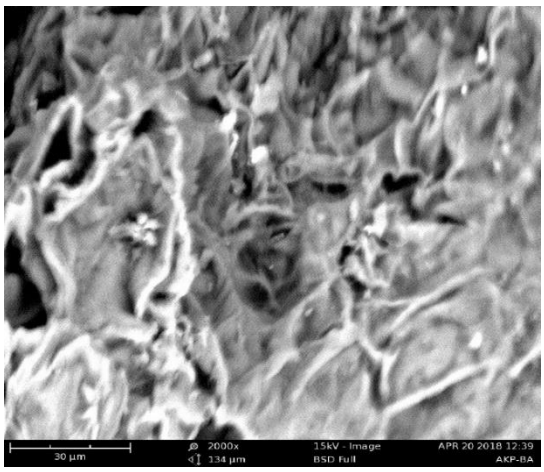
Figure 2: FTIR spectrum of AKP after adsorption of CR

Table 1: FTIR Spectral Data of AKP Before and After Adsorption by CR and MB

Before Adsorption	After Adsorption	Assignment
AKP (cm^{-1})	AKP-CR(cm^{-1}) Loade	
3327	3387(+60)	O-H stretching vibration in carboxylic acid groups (3500-2500 cm^{-1})
2877	-	O-H stretching vibration in carboxylic acid groups (3500-2500 cm^{-1})
2836	-	O-H stretching vibration in carboxylic acid groups (3500-2500 cm^{-1})
1719	-	General presence of C=O groups stretching vibrations (1800-1650 cm^{-1})
1547	-	NO_2 in aliphatic nitro compounds due to antisymmetric stretching (1575-1545 cm^{-1})
1424	1424(+0)	OH in carboxylic acid groups due to in-plane OH bending (1440-1400 cm^{-1})
1127	1160(+33)	C-N stretching vibration in amines (1330-1030 cm^{-1})
676	665(-11)	O-C=O in carboxylic acid groups due to O-C=O bending (700-590 cm^{-1}); C-C-CHO in aldehyde compounds due to C-C-CHO bending (695-635 cm^{-1})

The surface morphology of the adsorbent can be described using the scanning electron microscopy (SEM). Figures 3 and 4 is the micrographs of AKP before and after adsorption of CR respectively.

In the present study, the micrograph of AKP before and after adsorption of CR showed a heterogeneous, rough and porous nature. However, after adsorption of CR, the surface of AKP is almost smooth and homogeneous in nature as can be seen in Fig 3 and 4.this indicates adsorption has taken place on the adsorben. Similar result was obtained by Naba and Sumana (2018).



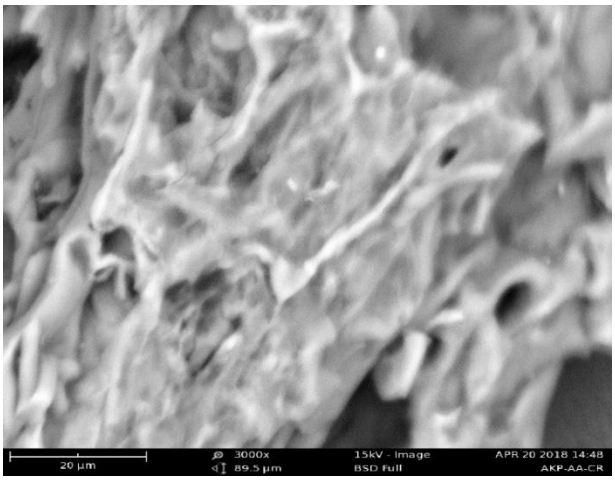


Figure 3 and 4: SEM micrograph of AKP before and after adsorption of CR respectively

Effect of Contact Time

Figure 5 present the result of effect of contact time for the adsorption of CR onto AKP. From the figure the percentage removal increased from 62.67 to 72.71% as the contact time changed from 10 to 150 min and no further improvement was recorded. Moreover, the results also revealed that the adsorption capacity was very fast within the first 10 min. This is perhaps due to the initial availability of maximum number of active sites which gets saturated as the contact time increases. These results to difficulty in occupying the remaining vacant surface sites due to the formation of repulsive force between the CR dye compounds that was recently adsorbed on the solid surface and the bulk phase (Srivastava *et al.* 2006).

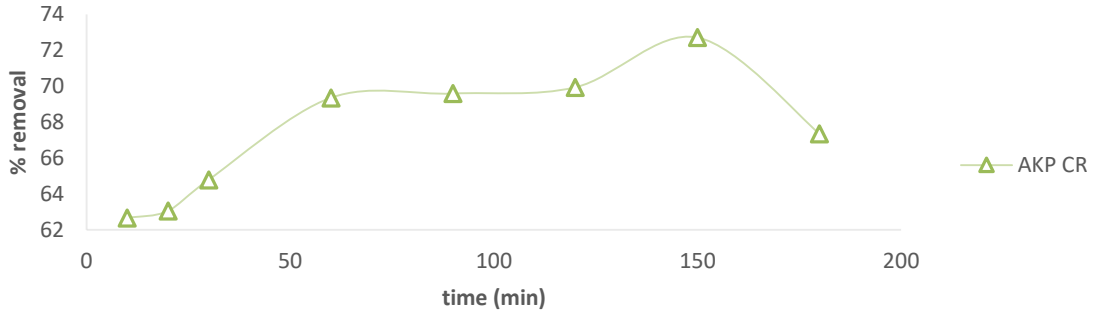


Figure 5: Effect of Contact Time on the Adsorption of CR onto the AKP

Effect of Initial Concentration

Figure 6 presents the result of the effect of initial dye concentration for the adsorption CR onto AKP. The percentage removal of CR increases as the initial dye concentration increases from 5 to 20 mg/L. This is because the active sites on the adsorbent surface are less occupied and the AKP will continue adsorbing the dye until it fully reaches its maximum (Kannan and Sundaram, 2001). However, on reaching 20 mg/L the percentage removal decreases, this is due to the limited vacant sites on the surface of the adsorbent (Salleh et *al*., 2011).

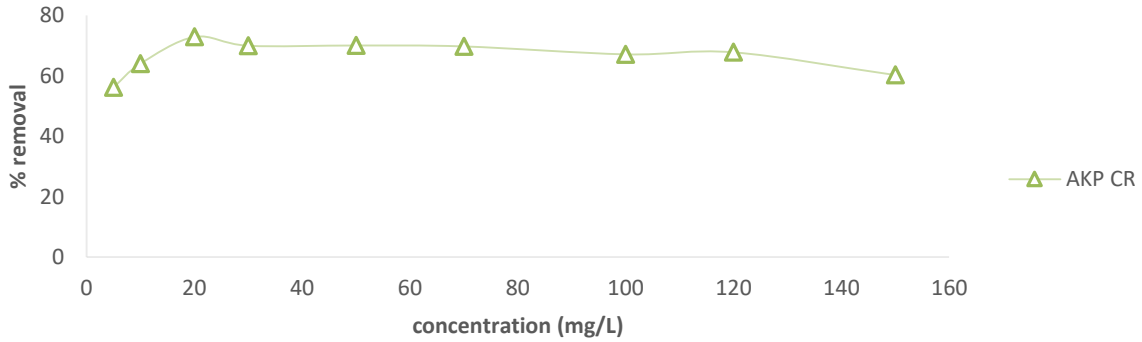


Figure 6: Effect of Initial CR Concentration.

Kinetic Studies

The kinetics of the adsorption CR onto AKP was investigated using the Pseudo first-order (PFO), Pseudo second-order (PSO) and Elovich models represented by equations 3, 4 and 5 respectively whose plot are presented in Figures 7, 8 and 9 respectively and the results are shown in Table 2. The adsorption kinetics was calculated at optimum conditions of contact time (150 min), initial concentration (20 mg/L), ambient temperature (31.5 ^{o}C), and adsorbent dosage of 0.2 g.

The slopes of Figures 7, 8 and 9 that gave a linear relationship and have the correlation coefficient that is closest to unity indicates the best model that fits the adsorption process.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where q_e is the mount of adsorbent adsorbed at equilibrium (mg/g), q_t is the amount of adsorbent adsorbed at equilibrium at a specific time interval (mg/g), k_1 is the Lagergren rate constant (1/min), and t is the Contact time (min). Plotting $\ln(q_e - q_t)$ against t gives a straight line that passes through the origin with a slope k_1 for systems that fits this model.

The PSO model assumes that the uptake rate is second order with respect to the available surface sites (Ho and McKay, 2000).

$$\frac{t}{q} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad (4)$$

Where k_2 is the pseudo-second-order (PSO) rate constant. Other Symbols have same meanings as in the PFO model.

A plot of $\frac{t}{q}$ against t gives a straight line for PSO-compliant kinetics. The slope is $\frac{1}{q_e}$, and the intercept is $\frac{1}{k_2 q_e^{\,2}}$ (Ho and McKay, 2000)

The Elovich equation is expressed as

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (5)$$

Kinetics that obeys Elovich equation should produce a straight line on the plot of q against lnt. The slope is 1/β, and the intercept is (ln (αβ))/β. α Stands for the initial adsorption rate (mg/g·min), and β is a desorption constant related

to the extent of surface coverage and activation energy for chemisorption.

The adsorption parameters derived from the application of the pseudo-first-order equation (K_1 and q_e), the pseudo-second-order equation (K_2, q_e) and Elovich's equation were calculated and are listed in Table 2. The low correlation coefficients, R^2, of the PFO and Elovich suggest that the experimental data do not fit the two models. The correlation coefficients of the pseudo-second-order model of AKP for the adsorption is 0.997, which indicates the suitability of the pseudo second-order equation for the adsorption process. In addition, the percentage removal values of AKP in the adsorption is 72.915%, These results shows that the adsorption of CR from aqueous solution onto AKP obeys the PSO kinetic model and could be used to determine the equilibrium adsorption capacity and rate constant. Similar result was obtained by Zhou *et al.* (2018), Naba and Sumana (2018) and Sumanjit *et al.* (2013).

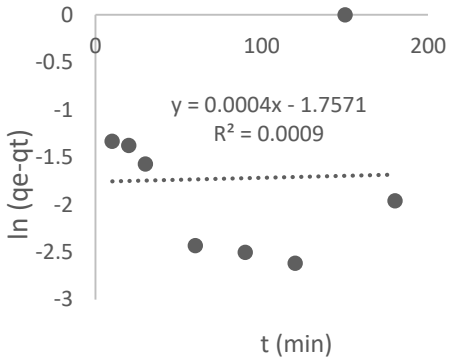


Figure 7: PFO kinetic model

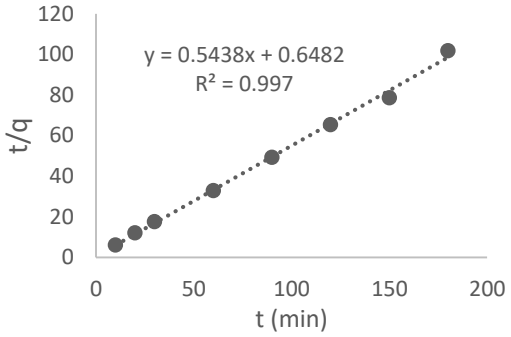


Figure 8: PSO kinetic model

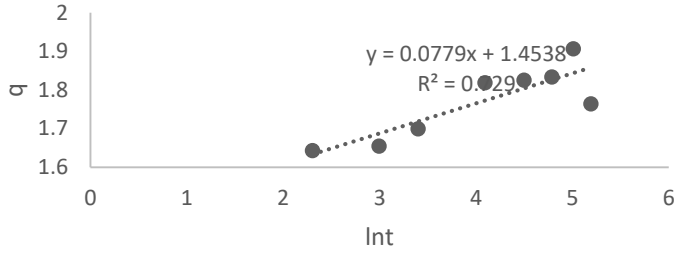


Figure 9: Elovich kinetic model

Table 2: Kinetic Parameters for the Removal of CR from Aqueous Solution onto AKP

Model	Kinetic parameter	Adsorbents
		AKP
	$q_{e,exp.}$(mg/g)	1.907
PFO	$q_{e,cal.}$(mg/g)	0.173
	k_1(min^{-1})	0.0004
	R^2	0.0009
PSO	$q_{e,cal.}$(mg/g)	1.839
	k_2(g/mg.min)	2.192
	R^2	0.997
Elovich	α(mg/g.min)	$9x10^6$
	β(mg/g)	12.788
	R^2	0.7365

AKP (C_o = 10mg/L, m = 0.2 g, T = 304.5 K).

CONCLUSION

The present study shows that AKP is an important agricultural waste that could be used for the removal of CR from aqueous solution with a percentage removal of 72.915%. From kinetic studies, the adsorption of CR onto AKP was found to be best fitted to pseudo second-order model with correlation coefficient of 0.997 and also there is an agreement between the experimental and the calculated amount adsorbed which were found to be 1.907 and 1.839 respectively.

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