

## Kinetic and equilibrium studies of Congo red dye adsorption on cabbage waste powder

Joan N. Wekoye, Wycliffe C. Wanyonyi<sup>\*</sup>, Phanice T. Wangila, Mathew K. Tonui

Department of Physical Sciences, School of Science and Technology, University of Kabianga, P.O. Box 2030-20200-Kericho, Kenya

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### ABSTRACT

In this work, the potential of utilizing of dried Cabbage Waste Powder (CWP) as an agro-waste biosorbent for the removal of noxious Congo Red (CR) dye was successfully investigated. FTIR spectroscopic analysis found multiple functional groups on CWP and their interactive effects played important roles in dye removal. Batch experiments were carried out to determine adsorption kinetics and isotherms. Experimental results showed that the rate of adsorption increased with increase in adsorbent weight, dye concentration, pH and decrease in particle size. However, the CR dye removal declined with increased in temperature indicating an endothermic process. Adsorption equilibrium was achieved within 3 h with efficiency of up to 91% at equilibrium. Langmuir adsorption isotherm model, Elovich equation and pseudo-second-order kinetics gave a good fit to the experimental data. Results furnish evidence that CWP is an efficacious, eco-friendly, bio renewable and affordable biomaterial for dye removal from industrial effluents.

### 1. Introduction

Synthetic dyes are vital component in textile industries for dyeing of fabric to impart colors. Chemical groups such as nitroso (NO), xanthene, thiocarbonyl (CS), carbonyl (CO), quinoid, azoxy, azoamino (NNNH) and auxochrome groups are responsible for different shades of colors [1]. About  $1.0 \times 10^5$  different kinds of synthetic dyes and pigments are used on an industrial scale and almost  $7.0 \times 10^5$  tons are utilized per year [2]. Inefficiency in dyeing process results in discharge of colored wastewater that adversely contaminating surface and groundwater resources. Approximately 10 to 15% of organic dyes consumed in textile and other industries are release into environment, provoking acute aquatic pollution [3]. Diseases associated to contaminated freshwater, unhygienic food, insufficient excreta disposal and uncleanness household environments constitute a major health burden in developing countries [4].

Effluents from textile industries are characterized by severe variations in many parameters such as BOD, turbidity, color, COD, pH, odor and salinity [5]. Azo dyes like Congo red, Direct Blue15 and Direct Red 2, are known for their health hazards due to their toxicity, mutagenicity, and

carcinogenicity [6,7]. Congo red dye in particular has a strong attraction to cellulose fibers and thus employed extensively in textile industries. Effluent contaminated with dye damage aquatic biota by reducing oxygen levels in water, negatively affecting aquatic plants photosynthesis leading to suffocating aquatic flora and fauna [8]. For instance, exposure of *Chlorella vulgaris* to Congo red dye adversely diminished its growth rate and photosynthetic efficiency [9]. Treatment of wastewater contaminated with organic dyes has become critical due to dwindling freshwater sources, increased treatment costs and firm governments' disposal rules that have lowered acceptable contaminant levels in industrial effluents.

Textile dye effluent treatment is an essential, but difficult process due to complex aromatic structure which makes them unsusceptible to conventional treatments methods. Currently, there are a number of approaches deployed in treatment of textile effluent contaminated with dyes namely adsorption [10], biological [11], membrane filtration [12], photo degradation [13], ion exchange [14], biodegradation [15], catalytic ozonation [16] and electrochemical oxidation [17]. Lately, adsorption is deemed as one of the most promising technique because of its efficacy, easy operation, non-toxicity, simplicity and mild reaction condition. Adsorption is commonly applied to decolorize, separate, detoxify, deodorize, purify and pre-concentrate to enable removal and recovery of toxic products from liquid and gaseous mixtures [18].

Commercial activated carbon is extensively utilized as an adsorbent because of its high efficiency and capacity to adsorb contaminants [19]. However, its initial cost, rapid saturation and difficult in regeneration make it less attractive as an adsorbent. For these reasons, diverse studies have

<sup>\*</sup> Corresponding author.

E-mail address: [wwanyonyi@kabianga.ac.ke](mailto:wwanyonyi@kabianga.ac.ke). (W.C. Wanyonyi).



been carried out to search for affordable, eco-friendly and efficient substitute adsorbent materials. Various low-cost adsorbent like *Eichhornia crassipes* [8], waste furnace slag [20], activated sludge [21], Chitin [22], copper-doped zinc sulfide nanoparticles [23], activated macadamia nutshell [24], cerium zirconium oxide nanocomposites [25], macadamia seed husks [26], Fe<sub>3</sub>O<sub>4</sub> nanoparticles coupled with flower-like MoSe<sub>2</sub> nano-sheets [27] and natural clays [28] have been investigated.

Cabbage (*Brassica oleracea*) is a traditional leafy vegetable grown and consumed in many parts of the world because it is regarded as a cheap source of essential minerals, protein, vitamins macro and micro nutrients for human [29]. Currently, consumption of cabbage has been on an increase in urban areas in East Africa and as a result, huge quantities of waste are generated every day. Cabbage waste is generated during harvesting, transportation, at the wholesale markets and trimming process [30]. Because of high moisture content, the waste readily decomposes, when discarded in fields or near factories causing unpleasant environmental consequences. The decomposing wastes in landfills are blamed for being health hazard by providing favorable condition for breeding of pathogens, snails, mosquitoes and snakes. This research provides a suitable prospect to establish an alternative technology for utilizing abundant cabbage waste in solving environmental problems in our sustained efforts to exploit for inexpensive biomaterials for removal of pollutants in wastewaters. The efficacy of dried cabbage waste powder in adsorption of Congo red dye was analyzed and factors affecting dye removal optimized.

## 2. Materials and methods

### 2.1. Material

Fresh cabbage waste was collected from Kericho town dumpsite. The wastes were washed with running tap water before sun drying for two week to eliminate moisture. The dried cabbage wastes were pulverized using a ball mill machine and soaked in 10% hydrogen peroxide for 24 h at 25 °C to remove soluble impurities. Fine and homogeneous CWP was washed severally with double distilled water and dried at 60 °C in an oven for 36 h. The powdered CWP were sieved using standard sieves to get different particle sizes which were later used in the batch experiments. Congo red dye is a red crystalline powder with a molecular weight of 696.68 g/mol and  $\lambda_{\max} = 497$  (nm) was procured from sigma-aldrich limited and used without any further purification.

### 2.2. FTIR analysis

Identification of functional groups on CWP was carried out using Fourier Transform Infrared Spectrophotometer, (IRAffinity-1S FTIR-Shimadzu model). Specimens were first mixed with KBr and then ground in an agate mortar at an approximate ratio of 1/200 for the preparation of pellets. The resulting mixture was pressed with a pressure of 10 ton for 3 min. The pellet was placed on the disk holder in the spectrometer for analysis. The background was automatically subtracted from the sample spectra.

### 2.3. Batch adsorption experiments

The batch sorption experiments were carried out in 100 mL conical flask with 50 mL CR dye solution and 1.0 g of cabbage waste. The mixture was then put on a mechanical oscillator and shaken at 140 rpm for 6 h. Residual dye concentration for each experiment was measured at intervals of 30 min using a UV-Vis spectrophotometer at  $\lambda_{\max} = 497$ . Effect of contact time was investigated using 2.0 g cabbage waste powder in 50 mL of 48.76 mg/L CR dye in 100 mL conical flask. Adsorbent dose was investigated using the adsorbent masses of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g in 100 mL conical flask added to 50 ml of 48.76 mg/L of CR. Aliquot were drawn from the dye mixture at different time intervals and residuary dye concentration measured. The quantity of CR dye removed ( $Q_e$ ) was

determined using Eq. (1).

$$Q_e = \left( \frac{C_0 - C_e}{W} \right) \times V \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium CR dye concentration (mg/L),  $V$  is the volume of the CR dye (L) and  $W$  is the weight of CWP (g). The percent dye adsorbed was calculated using Eq. (2).

$$\%CR \text{ adsorbed} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (2)$$

The kinetics of dye removal was evaluated using different CR dye concentration at 25 °C. 1.0 g of CWP of particle size 150–300 nm was added to 50 mL CR dye solution in 100 mL conical flasks shaking at 140 rpm. 3 mL of dye solution was drawn from the flask at different time and residual CR dye concentration determined.

## 3. Results and discussions

### 3.1. Structural characterization by FTIR

FTIR analysis was undertaken to identify the main functional group present on the surface of CWP responsible for dye binding. Fig. 1 shows the FTIR spectrum of WCP and the bands assigned summarized in Table 1. The results shows that CWP poses some functional groups namely OH, CO, CH, CH<sub>3</sub>, C-O-H, NH and CO that might have been involved adsorption process. Most of the absorption bands can be associated with the presence of lignocellulosic components, i.e. lignin, hemicelluloses, and cellulose present in CWP.

### 3.2. Effect of contact time

Contact time is a significant factor in industrial set up since it helps determine the maximum treatment time and the cost effective of the method. Contact time effect on CR dye removal was investigated and results displayed in Fig. 2(a). It is evident that rate of dye removal was fast at the beginning of the experiment before gradually slowing down till equilibrium. The observation can be attributed to availability of unoccupied sites on the adsorbent which decreased with time until all were occupied at equilibrium. Similar findings have been observed in the removal of CR dye using roots of *Eichhornia crassipes* [8].

#### Effect of Cabbage Waste Powder (CWP) dose

Adsorbent dose and the size of pore tremendously affect the rate of adsorption and quantity of dye removed [37]. Effect of CWP dose on sorption of CR dye was evaluated at different CWP dosage and results displayed in Fig. 2b. The percent dye adsorbed improved with increase in the amount of CWP. For example, percent dye adsorbed increased from 29.75 to 90.95% when CWP dosages was increased from 0.50 g to 2.50 g respectively. The rate of dye uptake for all CWP dose tested followed a similar pattern. This results has been rationalized by Cao et al. [38] that as the adsorbent dose increase, there was a considerable increase in adsorption sites accessible by the dye resulting in higher percent of adsorption. Similar trend was described in adsorption of acid red 97 dye using walnut shell where increase in walnut shell dose resulted in an increase dye removal [39].

### 3.3. Effect of initial dye concentration

The effect CR dye concentration was examined at different concentrations and results presented in Fig. 3a. The quantity of CR adsorbed at equilibrium improved when initial CR dye concentration increased. For instance the amount of CR adsorbed at equilibrium increased from 0.25 to 1.78 mg/g when CR concentration increased from 4.88 to 48.76 mg/L. The observation can be expounded by the fact that high concentration presents a higher concentration slope or a stronger driving force between

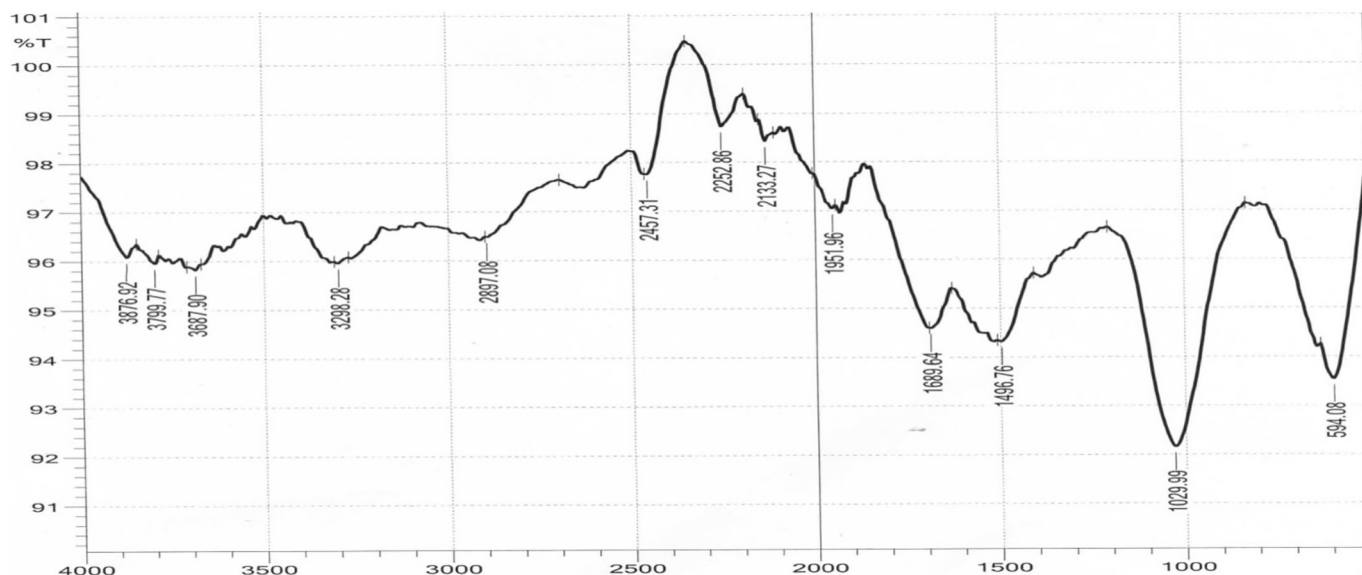


Fig. 1. Infrared spectra of Cabbage waste powder.

adsorbent and liquid phases and hence increasing the adsorption rate [40]. However, adsorption efficiency dropped with rise in dye concentration due to faster saturation of the adsorption sites on CWP. Similar output has been reported in the adsorption of crystal violet dye using coffee husks [41].

### 3.4. Effect of pH

pH plays an critical role in adsorption process because it regulates the ionization of the dye molecules and charges on the adsorbent material [10]. It related directly to the capability of hydrogen ions to compete with dye molecules for the active sites on adsorbent surface [42]. Effect of pH on adsorption of CR dye using CWP was determined and the results given in Fig. 3b. Effect of pH results revealed that percent removal of CR at equilibrium improved with rise in pH. These findings can be attributed to the positive charge density on CWP surface resulting in electrostatic attraction between negatively charged CR dye molecule and CWP. Similar findings were observed in the removal of Basic Yellow 28 (BY28) and onto smectite rich natural clays [28].

### 3.5. Effect of temperature

Temperature is known to influence the viscosity of the solution as well as controlling the rate of diffusion of the dye molecules over the external boundary layer and in the internal pores of the adsorbent [43]. Fig. 4a shows effect of temperature on percent removal of CR. The percent CR dye removal rose from 64.81% to 85.21% when the temperatures increased from 25 °C to 75 °C. This is because at elevated temperatures, the kinetic energy of adsorbate molecules increase which in turn increases the collision

rate of the dye and CWP. Moreover, at higher temperatures there is also a possibility of the inner pores of CWP opening up increasing the sorption sites hence high adsorption rate. The results further imply that adsorption of CR on CWP is an endothermic process. Adsorption of methylene blue on FA-HNO<sub>3</sub> and RM [43] showed similar trend.

### 3.6. Effect of particle size

Adsorption process is highly controlled by surface area available for adsorption [44]. The percent dye removal dropped when CWP particle size increased (Fig. 4b). The maximum percentage dye removal for smaller particles (150–300 μm) was 75.95% while that of the large particles (2360–4750 μm) was 8.03%. This is attributed to the smaller surface area to volume ratio of the large particles hence adsorb lower while the small particles have a large surface area exposed to adsorption hence high adsorption.

### 3.7. Adsorption isotherms

Adsorption isotherms are of significant in the designing an effective wastewater treatment system. Langmuir and Freundlich adsorption isotherms were applied to evaluate the practicability of adsorption as a technique of removing CR dye from aqueous solution. Langmuir adsorption isotherm [45] assumes that the adsorptions occur on uniform, homogeneous surface with sites of identical nature on the adsorbent and is used to describe monolayer adsorption processes. The nonlinear and linearized forms of Langmuir isotherm equation is given as following equations:

$$q_e = \frac{(Q_m b C_e)}{1 + b C_e} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \left( \frac{1}{Q_m b} \right) \frac{1}{C_e} \quad (4)$$

where  $q_e$  is the adsorption density mg/g of Congo red dye at equilibrium,  $C_e$  is the equilibrium concentration of Congo red dye,  $Q_m$  is the mono layer adsorption capacity mg/g and  $b$  is the Langmuir constant (L/mg).  $Q_m$  and  $b$  are determined from the intercepts and slopes of the plots  $1/q_e$  vs  $1/C_e$ . A dimensionless constant termed separation factor ( $R_L$ ) was applied to assess

Table 1

Functional groups as assigned to particular wave numbers for CWP FTIR analysis.

Wavenumber (cm <sup>-1</sup> )	Vibrational mode	Functional groups	Assigned species
594	bend	OH	Alcohols, ketones, acids and aldehydes [31]
1029	Stretch	COH, CO,	Alcohols, ethers, phenols [32]
1496	Bends	CH, CH <sub>3</sub> ,	Carboxylic [33]
1689	Stretch	CO	Carboxylic [34]
2855–2925	Stretch	CH	Alkyl, aliphatic hydrocarbons [32], lignocellulosic components [33]
3298	Stretch	OH, NH	Cellulose [31]
3799	Stretch	OH, NH	Monomeric alcohols, alcohols, phenols, amine stretches [35,36]

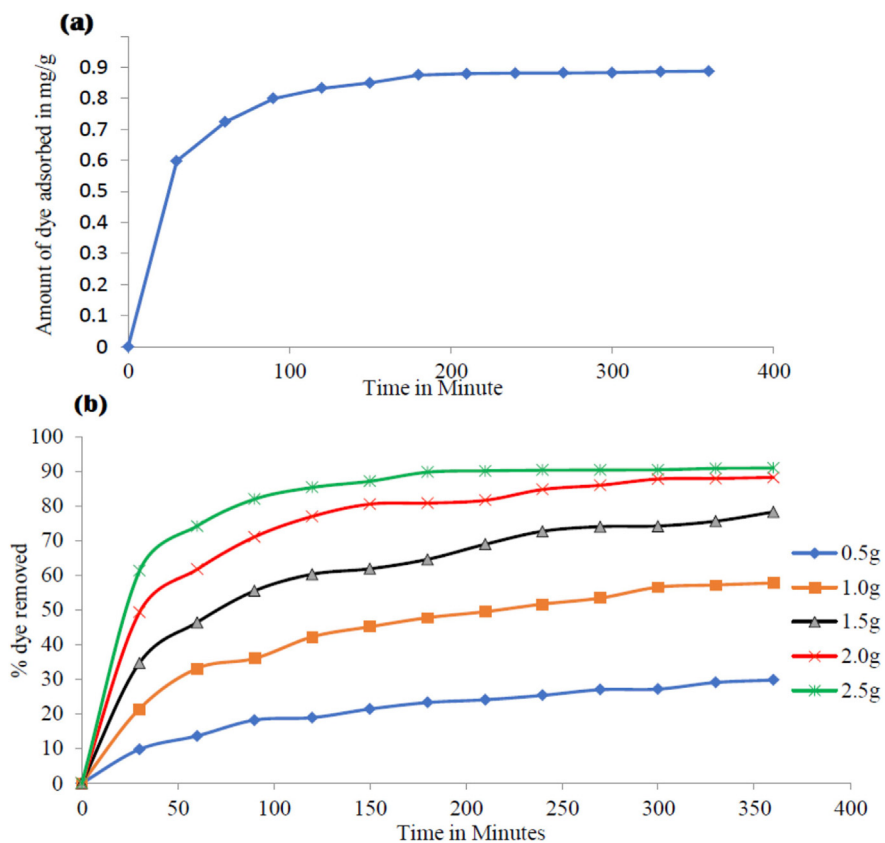


Fig. 2. (a) Effect of contact time on adsorption of CR dye (48.76 mg/L) by CWP (2.0 g), pH 8.0 and at 25 °C, (b) Effect of adsorbent dose on adsorption of CR dye (48.76 mg/L CR; 50 ml at 25 °C, pH 8.0).

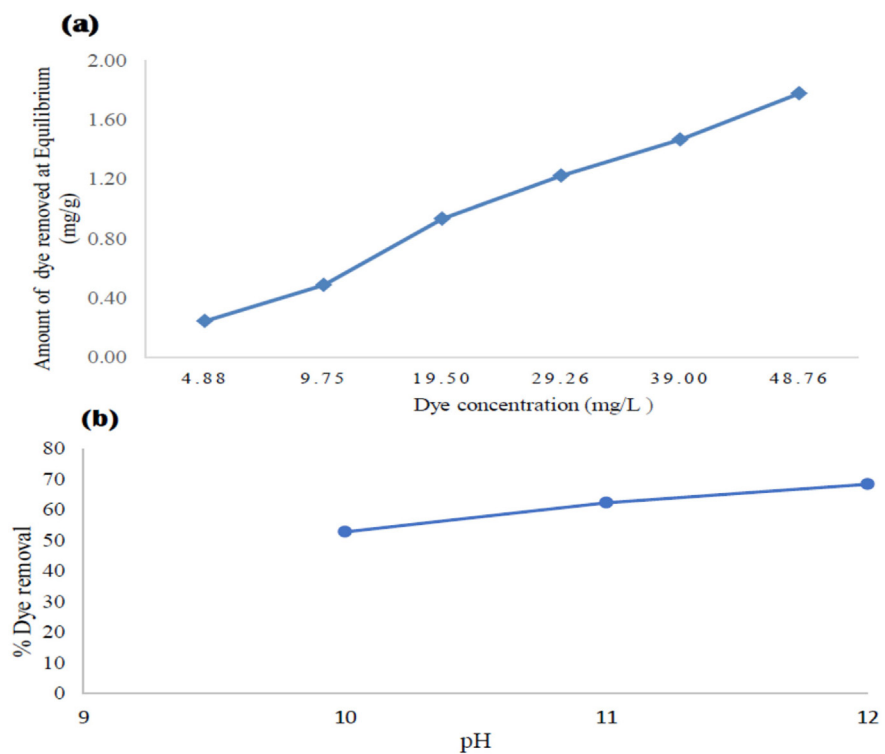


Fig. 3. (a). Effect CR dye concentration on amount of dye adsorbed (1.0 g CWP at 25 °C, pH 8.0), (b) Effect of pH on % removal of CR. (48.76 mg/L CR, 1.0 g CWP at 25 °C).

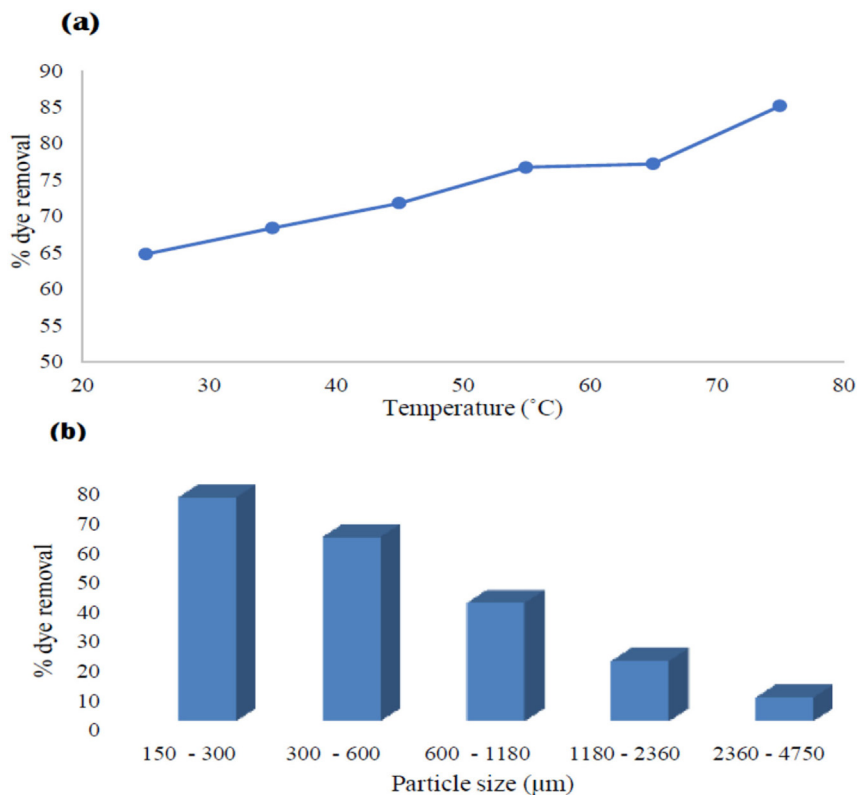


Fig. 4. (a) Effect of temperature on % removal of CR, (b) Effect of particle size on % removal of CR. (48.76 mg/L CR, 1.0 g CWP, pH 8.0).

the appropriateness of an adsorption process.  $R_L$  given by:

$$R_L = \frac{1}{1 + b(C_0)} \quad (5)$$

The values of  $R_L$  shows that the isotherms are either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) and irreversible ( $R_L = 0$ ). Fig. 5 shows a plot of  $1/q_e$  versus  $1/C_e$  for CR adsorption onto CWP. From the plot, the corresponding Langmuir isotherm constants were determined. The result reveals that mono layer adsorption capacity ( $Q_m$ ) of 2.313 mg/g was achieved with Langmuir constant (b) of 2.355 L mg and  $R^2$  values of 0.992.

Freundlich isotherm [46] is valid for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The nonlinear and linearized form of the equation is expressed as:

$$q_e = K_f \cdot C_e^{1/n} \quad (6)$$

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (7)$$

where  $k_f$  and  $n$  are Freundlich constant related to adsorption capacity and adsorption intensity of adsorbent. Values of  $k_f$  and  $n$  are obtained from the intercepts ( $\ln k_f$ ) and slopes ( $1/n$ ) of the plot of  $\ln q_e$  against  $\ln C_e$ .  $1/n$  shows how favorable the adsorption process and values of  $n > 1$  indicates favorable adsorption conditions. A plot of  $\ln q_e$  versus  $\ln C_e$  for the adsorption of CR dye on CWP is shown in Fig. 6. The corresponding Freundlich constants were determined. The results showed that Freundlich constant related to adsorption capacity ( $k_f$ ) of 1.814 (mg/g) ( $L/mg^{1/n}$ ) was achieved with adsorption intensity ( $n$ ) value of 1.568 and  $R^2$  value of 0.978. Considering high values of  $R^2$ , for both Langmuir and Freundlich adsorption isotherm model, it can be conclude that both monolayer and multilayer adsorption processes occurred at 25 °C. The  $R_L$  value ranges between zero and one ( $0 < R_L < 1$ ) indicating that adsorption process was favorable. Previous results from arsenic removal from drinking water by iron-enriched aluminosilicate experiments followed Langmuir model suggested monolayer adsorption [47].

### 3.8. Adsorption kinetics

Pseudo-first, pseudo-second order kinetic models and Elovich equation was used to study the reaction pathways and the potential rate limiting

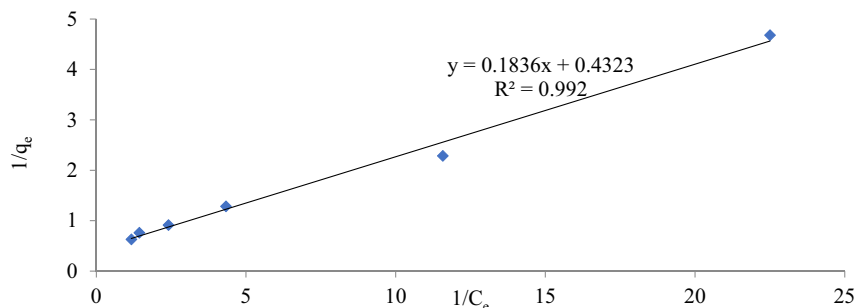


Fig. 5. Langmuir isotherm plot for CR on CWP.

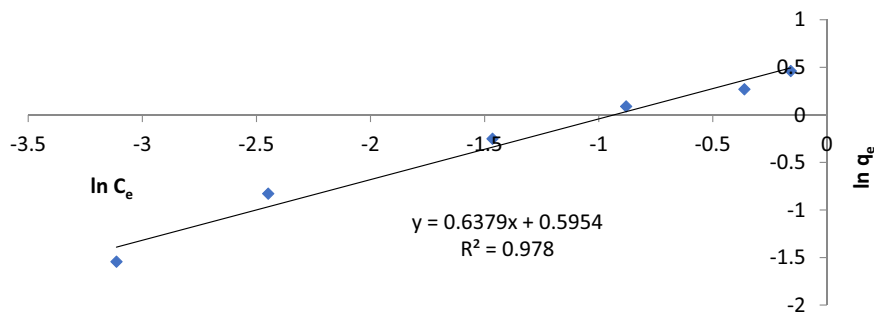


Fig. 6. Freundlich isotherm plot for CR on CWP.

**Table 2**  
Kinetics data for adsorption of Congo Red dye by Cabbage Waste powder.

C <sub>0</sub> (mg/L)	q <sub>e, exp</sub> (mg/g)	Pseudo - First - order			Pseudo - Second - order			Elovich equation		
		q <sub>e, cal</sub> (mg/g)	k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e, cal</sub> (mg/g)	k <sub>2</sub> (g/mg min)	R <sup>2</sup>	α(mg/(g min))	β(g/mg)	R <sup>2</sup>
4.876	0.2135	1.2382	2.8788 × 10 <sup>-2</sup>	0.546	0.2500	6.128 × 10 <sup>-2</sup>	0.945	0.7126	16.181	0.970
9.752	0.4370	1.1384	2.0497 × 10 <sup>-2</sup>	0.621	0.4530	7.606 × 10 <sup>-2</sup>	0.971	0.1553	15.798	0.962
19.504	0.7777	2.0725	2.3951 × 10 <sup>-2</sup>	0.560	0.8273	4.135 × 10 <sup>-2</sup>	0.989	0.5131	5.914	0.969
29.256	1.0924	3.4316	2.3951 × 10 <sup>-2</sup>	0.586	1.1800	2.218 × 10 <sup>-2</sup>	0.980	1.1850	3.897	0.984
39.008	1.3097	4.2491	2.3721 × 10 <sup>-2</sup>	0.533	1.4184	1736 × 10 <sup>-2</sup>	0.981	1.7462	3.128	0.996
48.761	1.5850	5.8023	2.4412 × 10 <sup>-2</sup>	0.479	1.7337	1.276 × 10 <sup>-2</sup>	0.975	2.6344	2.480	0.987

steps for adsorption of CR on CWP. The linearized integral form of the pseudo-first-order model [48] is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

where q<sub>e</sub> and q<sub>t</sub> are quantities of adsorbed dye (mg/g) at equilibrium and at any moment of time (min) respectively, while k<sub>1</sub> is the rate constant of pseudo-first-order adsorption (min<sup>-1</sup>). The values of k<sub>1</sub> and q<sub>e, cal</sub> are calculated from the gradient and intercepts of log (q<sub>e</sub> - q<sub>t</sub>) versus t (not shown). The pseudo-first order kinetic model gave a poor fit to the experimental data with low R<sup>2</sup> values (R<sup>2</sup> < 0.621). The theoretical and experimental adsorption capacities differed widely (Table 2.) depicting the deficiency of the model in describing adsorption of CR on CWP.

Pseudo-second order model was also used to study adsorption of CR dye on to CWP. The differential equation is generally described as [49]:

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

Integrating Eq. (9) above when q<sub>t</sub> = 0 at t = 0, gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k<sub>2</sub> is the rate constant of adsorption (g/mg min), q<sub>e</sub> and q<sub>t</sub> are the dye adsorbed at equilibrium and time t(mg/g) respectively. Values of k<sub>2</sub> and q<sub>e</sub> are calculated from the intercepts and gradient of t/q<sub>e</sub> vs t. Fig. 7 displays the plot of pseudo-second order kinetics for adsorption of CR dye onto CWP at different concentrations. The experimental data gave a good fit the model. Values of k<sub>2</sub>, q<sub>e</sub> and R<sup>2</sup> were calculated and summarized in Table 2. The R<sup>2</sup> values for the studied concentrations were high (R<sup>2</sup> > 0.94) while the theoretical q<sub>e, cal</sub> values and experimental q<sub>e, exp</sub> values were comparable. The result shows that the adsorption of CR dye by CWP followed pseudo-second order kinetic model. This further implies that adsorption process was enhanced by chemisorption involving exchange or sharing of electrons between the adsorbent and adsorbate [50].

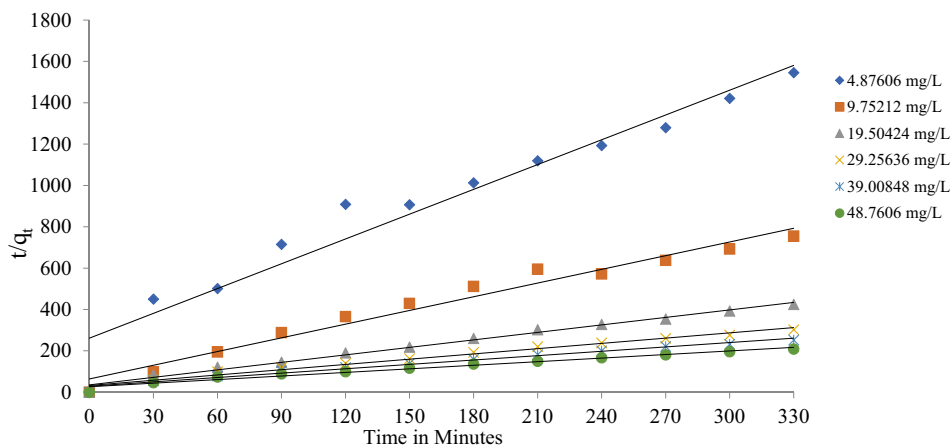


Fig. 7. Pseudo-second order model plots for adsorption of CR dye on cabbage waste powder.

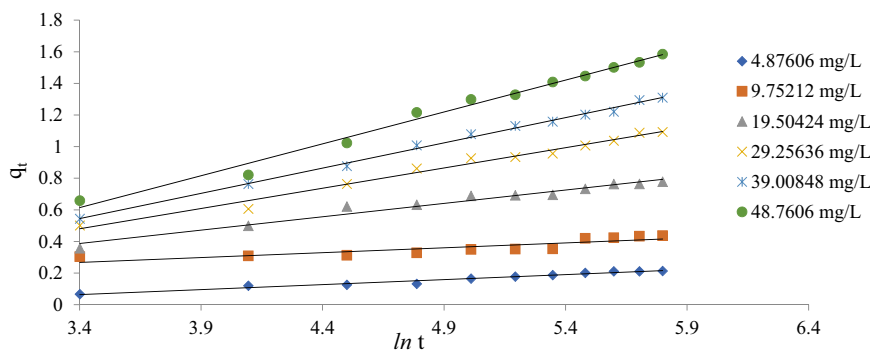


Fig. 8. Elovich equation plots for adsorption of CR dye on cabbage waste powder.

Adsorption of CR dye by CWP was further evaluated by Elovich equation [51] given as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (11)$$

where  $\alpha$  is the initial adsorption rate (mg/(g min)), and  $\beta$  is the desorption constant related to the extent of surface coverage and activation energy for chemisorption (g/mg). The values of  $\alpha$  and  $\beta$  are obtained from the plot of  $q_t$  vs  $\ln t$ , (Fig. 8). The values of  $\alpha$ ,  $\beta$  and their respective  $R^2$  are summarized in Table 2. The experimental data fitted well on the Elovich equation with high  $R^2$  values indicating that the equation can be applied in predicting adsorption of CR dye on CWP. The values of  $\beta$  reduced with initial concentration because fewer surfaces available for CR dye. Appropriateness of the Elovich equation further suggests that adsorption of CR was a chemisorption [52].

#### 4. Conclusion

Recent enthusiasm in developing affordable biomaterials for removal of organic dyes from wastewaters led us to investigate adsorption of CR dye by Cabbage waste powder. To do this, we studied adsorption mechanism, isotherms and kinetics for adsorption of CR dye onto CWP. Adsorption process was greatly controlled by, adsorbent dose, time, temperature, pH, size of particles and dye concentration. Percent removal of CR dye increased with increase in contact time, temperature, dosage and pH but dropped when particle sizes were increased. Experimental data fitted to both Langmuir and Freundlich adsorption isotherm model implying monolayer and multilayer adsorption processes occurred at 25 °C. The pseudo-second order model and Elovich equation best fitted the kinetics data indicating that chemisorption is the rate limiting step. Basing on these results, large scale practical application of the CWP along with the already existing procedure in industrial wastewater treatment might be interesting in terms of efficacy, eco-friendly and cost effectiveness.

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