Utilisation of Unmodified and Acid Modified Snail Shells as Low-cost Adsorbents for the Removal of Congo Red

Abimbola A. Ogundiran[1], Obanla Bilikis Ololade[1], Olusegun O. Ogundiran[2] and *Edwin A. Ofudje[3]

[1]Department of Chemical Sciences, Tai Solarin University of Education, Ijagun, Ogun-State, Nigeria
[2]Department of Chemistry, Tai Solarin College of Education, Omu-Ijebu, Ogun-State, Nigeria.
[3]Department of Chemical Sciences, Mountain Top University, Ibafo, Ogun State, Nigeria

ABSTRACT

This study focussed on the utilisation of both unmodified and acid modified snail shells as low cost adsorbents for the removal of Congo Red (CR) from aqueous solution using batch adsorption process. Different parameters such as pH, Contact time, temperature and adsorbent dose were varied. The kinetic studies using pseudo first order and pseudo second order of the adsorption were carried out. The adsorption of Congo Red (CR) was found to be dependent on the varied parameters. The optimum time for the uptake was 60 min, adsorbent dosage of 2 g and pH was found to be 2.0. The amount of CR removed (q_e) rose from 2.445 to 19.230 mg/g when the contact time progressed from 5 to 60 min for unmodified snail shell and from 5.540 to 26.170 mg/g when treated snail shell was used. Pseudo-first-order model better described the kinetic of the adsorption process. The value of ΔH obtained was 42.20 kJ/mol with ΔS value of 20.30 kJ/mol) and this is an indication that the process of adsorption to be endothermic reaction. FT-IR characterization of the adsorbent before and after adsorption process revealed the probable functional groups present on the surface of the adsorbent to be –OH, C=O and C-H. Thus, snail shells can be deployed as low cost adsorbent for Congo Red removal from effluents.

Keywords*: Adsorption, adsorbate, adsorbent, kinetics, snail shells*

1. Introduction

Environmental pollutions have increased due to the growth of the industrial world. Water pollution is the most common being faced currently worldwide. Many industries, such as food, textile, paint, printing ink, pharmaceutical make use of dyes. Wastewater containing dyes usually have high Biological Oxygen Demand and Chemical Oxygen Demand. At low concentration dye containing wastewater are hazardous to the environmental and human health. Therefore, in order to alleviate the negative effect, the removal become paramount before wastewater is being discharged into the environment. Diverse physical, chemical and biological methods, have been employed for the treatment of wastewater containing dyes which include adsorption, coagulation and flocculation, advanced oxidation, ozonation, membrane filtration and liquid–liquid extraction (Yao *et al.,* 2009; El-Lateef *et al.,* 2010; Ghaedi *et al.,* 2011). Adsorption in literatures is a very effective separation technique and is considered to be better than other techniques for water treatment considering its cost, simplicity of design, ease of operation and resilience to toxic substances (Mohammad *et al*., 2010).

Snail is a popular food in the western and southern part of Nigeria. The snail shell after snail processing are directly disposed into the environment thereby causing foul smell which pollute the air thereby affecting human healthy living. The shell of snails is very rich in calcium carbonates, it can be utilised as biosorbent in the industries. It has a potential to be used for the removal of pollutants from wastewater. Its preparation and processing are economical and it is readily available.

Several adsorbents had been examined for the removal of pollutants from contaminated environment and such adsorbents includes scale of croaker fish (Nkiko *et al*., 2013), modified phosphate dolomite (Ivanets *et al*., 2014), clay (Veli and Alyüz, 2007), fish scale (Ofudje *et al*., 2021), peanut (Witek-Krowiak *et al*., 2011), eggshells derived calcium oxide nanoparticles (Ofudje *et al*., 2022), Modified Irish Potato Leaf (Ogundiran *et al*., 2021) and hydroxyapatite (Ofudje *et al*., 2018).

Due to the need to further increase the knowledge of other adsorbents, this present is aimed at investigating the potency of unmodified and acid modified snail shells as low cost adsorbents for the removal of Congo Red (CR) from aqueous solution using batch adsorption process. The effects of time, initial concentration of metal, solution pH and adsorbent dosage on the adsorption process were examined, while data obtained were evaluated using kinetic modeling. The morphology of the adsorbent was examined with Fourier transform infrared (FT-IR).

2. Materials and Methods

2.1 Preparation of the Adsorbent

Waste snail shells were obtained from Itoku market in Abeokuta, Ogun State, Nigeria and cleaned with hot water to get rid of any organic material stocked on the surface as well as the odour. Thereafter, the samples were crushed and treated with 0.1 M of HCl on a hot plate for deproteinization and then washed using distilled water. The acid-heat treated samples were dried at 100°C in an oven for 8 hours and pulverized to small pieces and filtered to obtained the required particle size and referred to as acid modified snail shell (AMSS), while the other sample was referred to as unmodified snail shell (UMSS).

2.2 Characterization of Adsorbent

Functional group determination was obtained using Fourier transform infrared spectroscopy (FT-IR) model 8400S (Shimadzu, Japan).

2.3 Batch Adsorption Study

Different concentrations (10 to 100 mg/L) of Congo red dye were placed in a series of separate 100 mL beakers. 2 g of the prepared sorbents were introduced into the respective flask and left to agitate for specific contact time (10 to 120 min) on orbital shaker at a speed of 150 rpm and temperature of (35 ± 1 °C). Adjustment of the solution pH was done using 0.1 M NaOH or HCl in the range of pH 2 to 10. After attaining equilibrium, the flask content was centrifuged at a speed of 2500 rpm for 10 min and the concentrations of the Congo red dye in the filtrate were estimated using UV-vis spectrophotometer respectively. The amounts adsorbed as well as the removal percentage of Congo red were computed using the equations below respectively:

$$Q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

$$\% \mathrm{Re}\,moval = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

Q_e stands for the amount of CR adsorbed in mg/g, C_o and C_e are the initial and equilibrium concentrations of CR in mg/L respectively, 'm' represents the mass of the sorbent, and 'V' is the volume of the adsorbate used in litre.

2.4 Kinetics Studies

The adsorption process of Congo red by unmodified and modified snail shell was subjected to Pseudo-first-order and Pseudo-second-order models. The linear form of the Pseudo-first-order model is given as (Qaiser *et al.*, 2009; Qaiser *et al.*, 2007):

$$In(q_e - q_t) = Inq_e - k_1 t \tag{3}$$

Where q_e is the amount adsorbed at equilibrium and q_t is amount adsorbed at time t. The slope $k_1$and the intercept Inq_e from the linear plots of In (q_e –q_t) against t were used to evaluate the constants shown in figure 6 and their physical parameters are presented in Table 1. The rate expression for the Ho's-pseudo-second-order equation is given as (Jirekara and Mazahar, 2008):

$$\frac{d_{qt}}{d_t} = k(q_e - q_t)^2 \tag{4}$$

Integrating between boundary conditions and on rearrangement we obtained:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{5}$$

where

$$h = k_2 q_e^2 \tag{6}$$

Where k_2 is the equilibrium rate constant of the pseudo-second-order model in g/mg/ mins, h is the initial sorption rate, q_e is the amount of CR adsorbed at equilibrium in mg/g, q_t is the amount of CR adsorbed at time t in mg/g. The corresponding values of q_e and h were evaluated from the slopes $1/q_e$ and intercepts $1/h$ of the plots of t/q_t against t .

3.0 Results and Discussion

3.1 Characterization of Adsorbent

FT–IR spectra (Fig.1) of the adsorbent before and after biosorption showed vibration bands at 714, 885, 1106 and 1465 cm^{-1} which may be assigned to the CO_3^{2-} polymorph. Also, the bands noticed at around 1780 cm^{-1} was allotted to C=O, bands at 2867, and 2959 cm^{-1} to C-H strech while the broad bands at around 3300 and 3486 cm^{-1} are due to O-H of carboxylic acids. The sharp peak observed at around 1216 cm^{-1} was assigned to C–O. Differences in peaks were noted after the adsorption process. This suggests that the adsorption of Congo red dye by snail shell could be due to the functional groups of the sorbents. Thus, the main probable functional groups present on the surface of the adsorbent were -CH –OH, C=O and C-O. It was also noticed that there is no change in the spectra pattern before and after adsorption, this may be due to that the adsorption of Congo red onto the adsorbent is by physical forces.

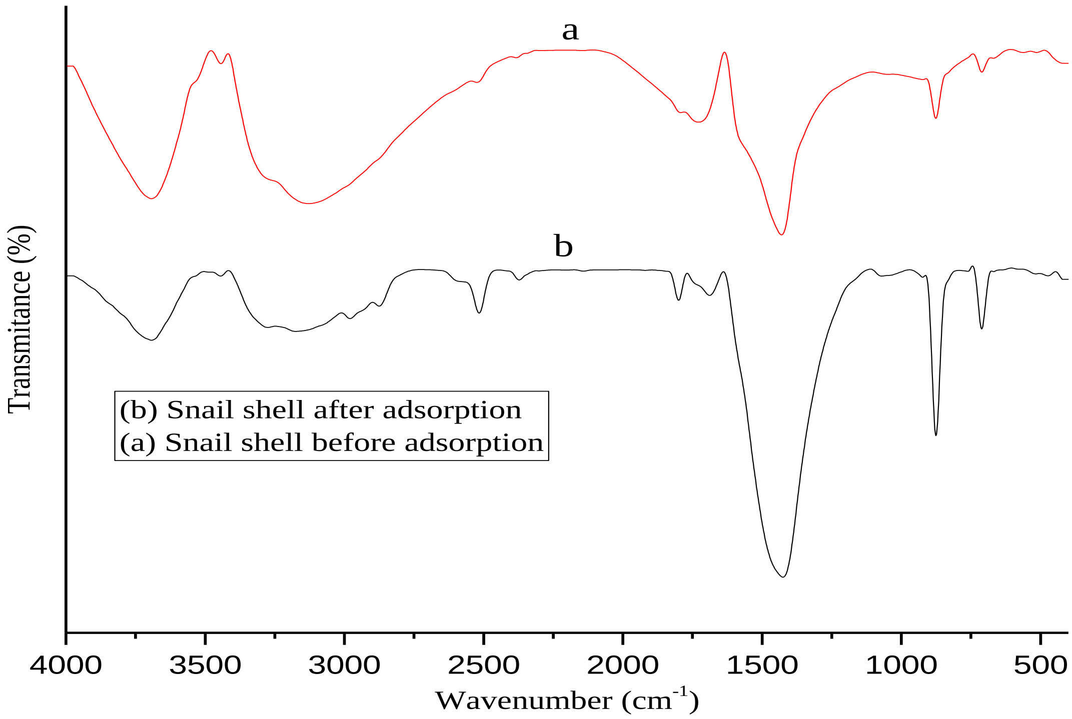

Fig. 1: FT-IR spectra of snail shells before and after adsorption process

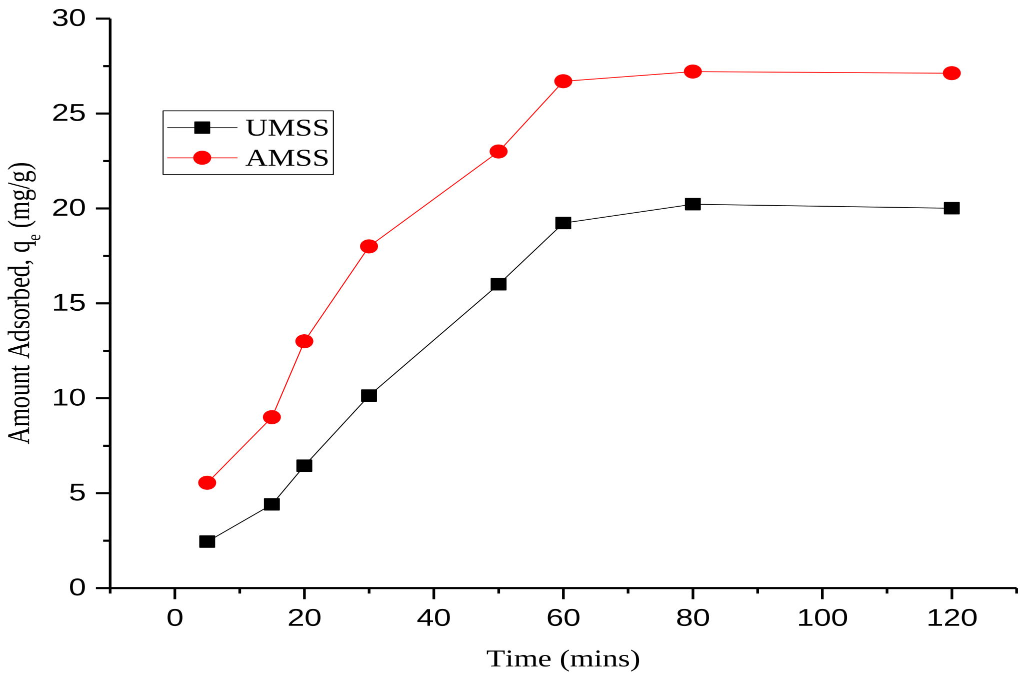

Fig. 2: Effect of contact time on the removal of Congo red

3.2. Effect of Contact Time

Figure 2 shows the results of the adsorption of Congo red (CR) onto unmodified and modified snail shells at various contact time. It was observed that the amount of CR removed increases with increase in the contact time. The amount of CR removed (q_e) rose from 2.445 to 19.230 mg/g when the contact time progressed from 5 to 60 min for unmodified snail shell and from 5.540 to 26.170 mg/g when treated snail shell was used. Vacant sites which were present at the biomass surface at the beginning of the reaction process enhance the adsorption capacity. However, as the reaction progress, the vacant sites are being occupied by the CR molecules and this reduces the adsorption capacity of the adsorbent (Aravind *et al.*, 2014). When the contact time was further increased the rate of uptake of the dye became lower.

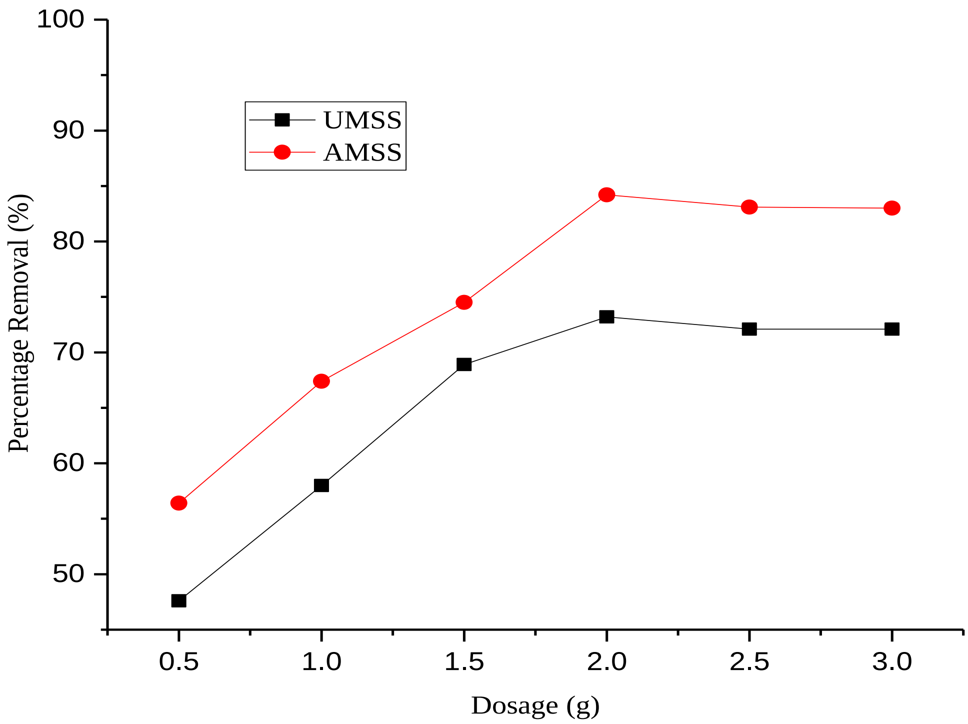

Fig. 4.3: Percentage Removal against adsorbent dosage

3.3. Effect of Adsorbent Dose

The result of varying the dosage of UMSS and AMSS is as presented in Figure 3. It can be seen that the removal percentage of the dye increased when the dosage of the adsorbent was increased from 0.5 to 2 g and became almostt constant at a dosage above 2 g. The percentage of the dye removed increased from 47.6 to 73.2 % for UMSS and from 56.4 to 84.2 % when AMSS was used. The parentage removed may have been due to more available sites for adsorption as the mass of adsorbent increased. However, there is formation of aggregate of adsorbent on the active sites of adsorption at higher dosage caused by the deposition of the CR molecules on the adsorbent surface which resulted in the reduction of the adsorption eefficiency of the biomass (Qaiser *et al.*, 2009; Zvezdelina and Nedyalka, 2012).

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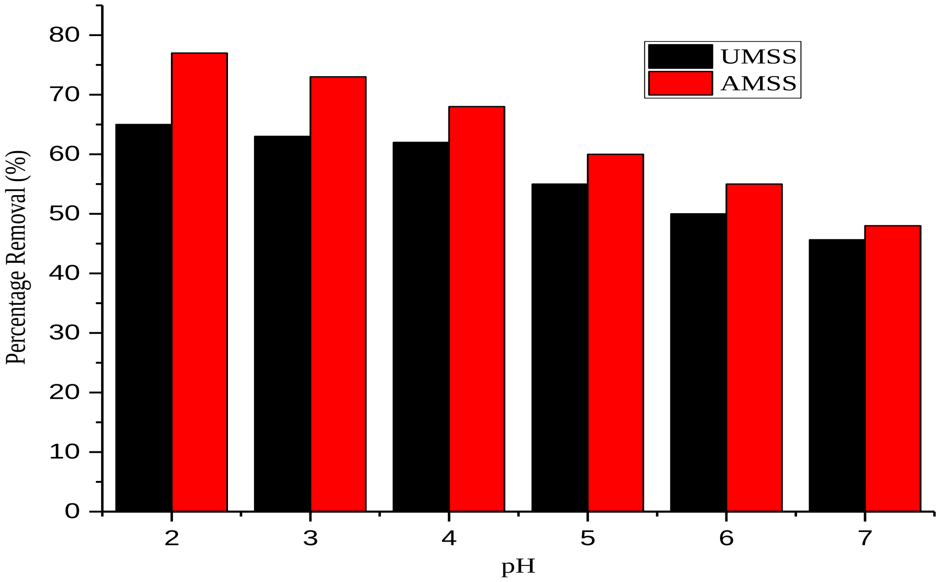

Fig. 4: Effect of solution pH

3.4 Effect of Solution pH

Figure 4 present the study on the effect of solution pH on the uptake of CR by unmodified and modified snail shell. The study showed that maximum uptake of CR was at a pH of 2.0 with percentage removal 65 % and 77 % for UMSS and AMSS respectively. This proved that adsorption is dependent on solution pH. Solution pH is vital in adsorption process since it can affect the chemistry of both the adsorbate and adsorbent. From the results, the various functional groups responsible for the uptake of CR are positively charged at lower pH and negatively charged at higher pH. Congo red is an anionic dye which exists as negatively charged species at lower pH and this will be better adsorbed at lower pH. However, at elevated pH, the surface becomes more negatively charged and adsorption of anionic dye decreases due to deprotonation on the surface of the biomass. Similar reports had it in literature by Fathy *et al.,* (2013) and Mahmoud *et al*., (2012).

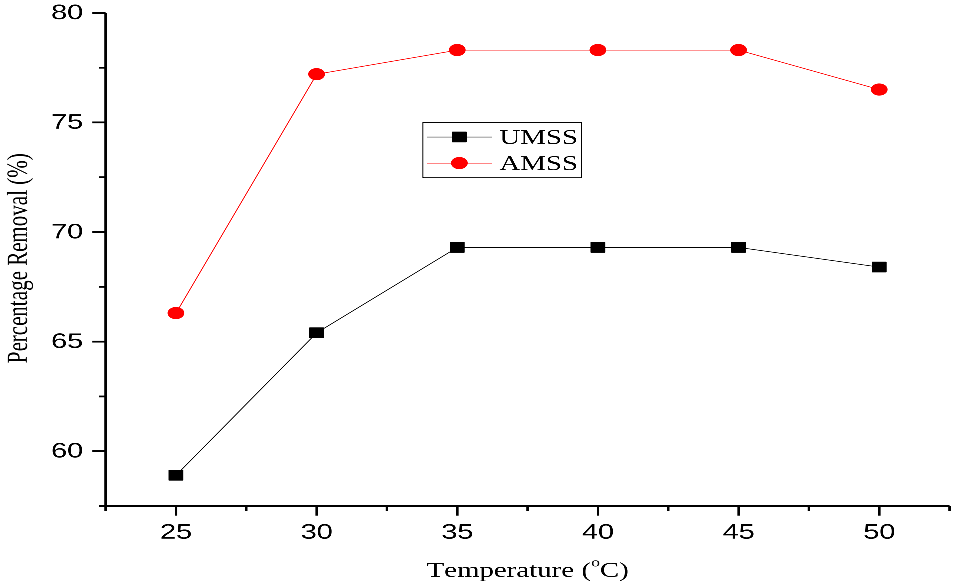

Fig.5: Effect of Temperature

3.5 Effect of Temperature

Figure 5 shows the effects of temperature on the uptake of CR by UMSS and AMSS in the temperature range of 25 to 50°C. The results showed that the percentage removal of CR increased from 58.9 % to 69.3 % for UMSS and from 66.3 % to 78.5 % when AMSS was used when the temperature was raised from 25 to 40°C. Above a temperature higher than 40°C, there was no further appreciable uptake of CR. When the temperature was increased, there is an increase in diffusion process of the CR molecules from the aqueous solution onto the surface of the adsorbent which enhances the adsorption process. However, at a much higher temperature, desorption of the CR molecules from the surface as well as rupture of bonds might lead to a reduction in the adsorption process. (Qaiser *et al.*, 2009; Qaiser *et al.*, 2007; Namasivayam and Kavitha, 2002).

3.6 Kinetic studies

Pseudo-first- order and Pseudo-second-order kinetics models (Figures 6 and 7) were used to study the adsorption of the Congo red dye by UMSS and AMSS. However, a plot of t/qt against t, for pseudo-first order model adequately gave a good fit as presented in Fig. 6. The pseudo-first -order model suggests that the biosorption process follows a pseudo first-order mechanism, which assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites (Salam, 2013). The correlation coefficient values (R^2) are 99%. And 98% for the two adsorbents respectively. However, the physical parameters are presented in Table 1.

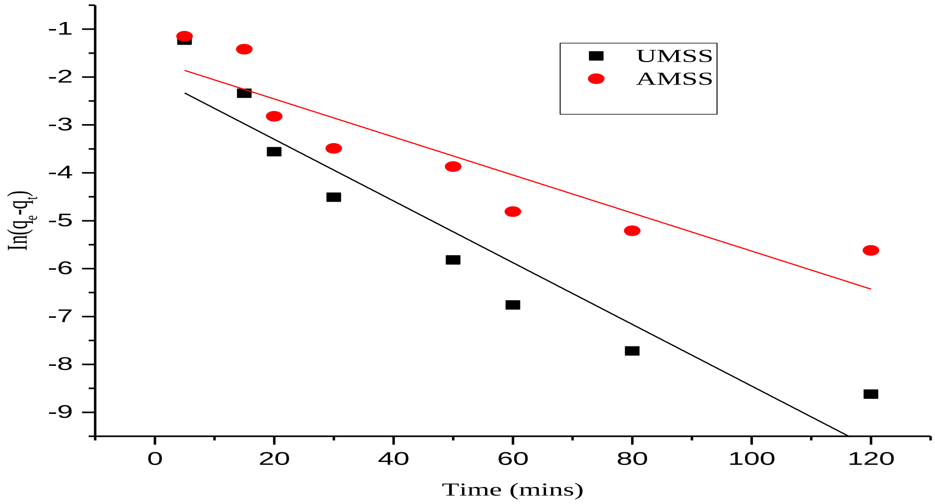

Fig. 6: Plots of Pseudo-first-order for the adsorption CR by UMSS and AMSS.

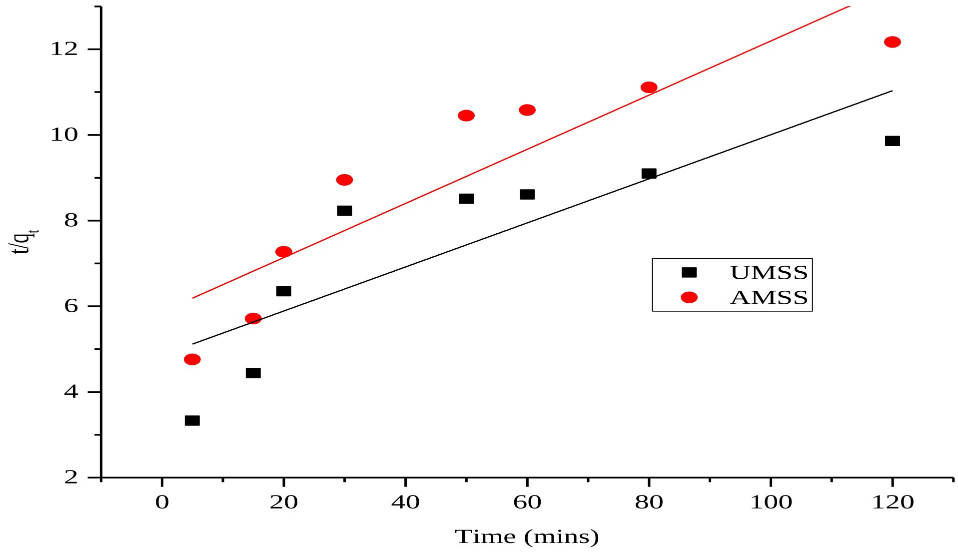

Fig. 7: Plot of Ho's-pseudo-second-order model for the adsorption of CR by UMSS and AMSS.

Table 1: Kinetic Model Parameters for the Adsorption of CR by UMSS and AMSS.

Parameter	UMSS	AMSS

Pseudo First Order	C_o (mg/L)	100	100
	Q_{eexp}(mg/g)	2.55	5.66
	K_1 (mg/g/mins)	0.02	0.01
	q_{ecal}(mg/g)	2.45	5.33
	R^2	0.99	0.98
Pseudo Second Order	C_o (mg/L)	100	100
	k (mg/g/mins)	0.17	0.12
	hmg/g)	0.21	0.34
	q_{ecal}(mg/g)	4.25	8.87
	R^2	0.97	0.97

Thermodynamics Studies

The change in free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) were evaluated as follows:

$$\Delta G^\circ = -RTInK_d \qquad (7)$$

$$InK_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (8)$$

The equilibrium constant, K_C, was obtained using the relation of Q_e/C_e. The plots of InK_C versu $1/T$ with slope and intercept of $\Delta H^o/R$ and $\Delta S^o/R$ respectively as showed in Figure 8, while the thermodynamic parameters are listed in Table 2. The activation energy (Ea) is obtained as 23.40 kJ/mol. The value of ΔH obtained was 42.20 kJ/mol with ΔS value of 20.30 kJ/mol) and this is an indication that the process of adsorption to be endothermic reaction. The values of ΔG calculated were negative which increases with temperature, thus inferred that the adsorption process is spontaneous nature.

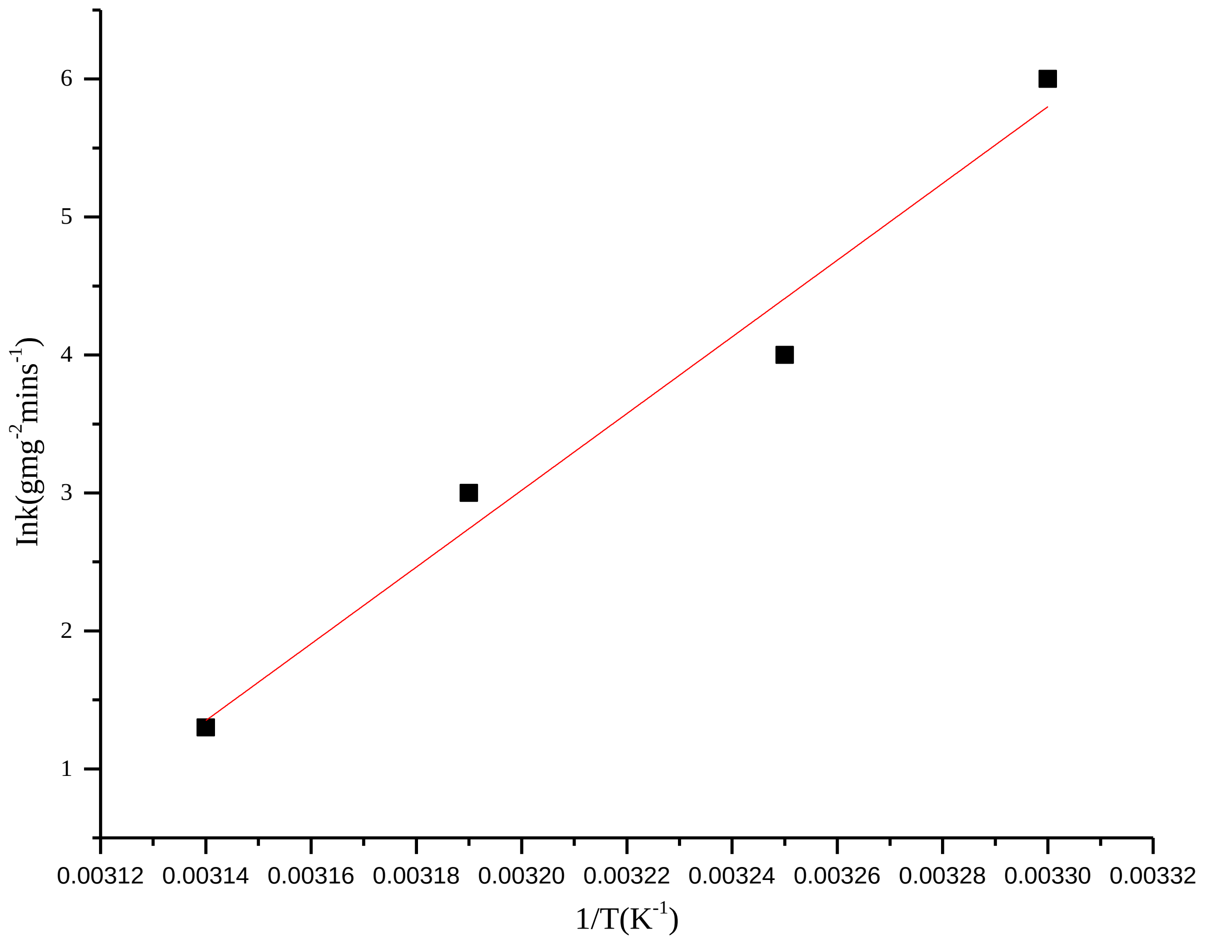

Fig. 8: Thermodynamic plots of the adsorption of CR by eggshells

Table 2: Thermodynamic parameters of the adsorption of CR dye by eggshell powder

Cu(II)						
T (K)	**Kc**	**ΔG (kJ/mol)**	**Ea kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (kJ/mol)**	**R^2**
303	1.56	-14.49	23.40	42.20	20.30	0.975
308	1.33	-35.71				
313	1.77	-63.10				
318	1.89	-83.40				

4. Conclusion

This present work examined the application of unmodified and modified agricultural waste of snail shell as adsorbents for the removal of Congo red from aqueous solution in batch adsorption process. The adsorption potency of the adsorbent was found to depend on solution pH, contact time, adsorbent dosage and temperature. The modification of the adsorbent greatly enhanced the adsorption capacity. The value of ΔH obtained was 42.20 kJ/mol with ΔS value of 20.30 kJ/mol) and this is an indication that the process of adsorption to be endothermic reaction. Thus, unmodified and modified snail shell can be utilized as effective adsorbents for the sorption of congo red from aqueous solutions.

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