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Adsorption efficiency of Congo red dye on modified and unmodified *Cassia fistula* shells

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ABSTRACT

Colour waste from the dyeing, paper, pulp, textile, plastics, leather, cosmetics, and food sectors causes a variety of hazards and environmental problems. Dye persistence and the difficulties of biodegradation motivate researchers to investigate the use of adsorption techniques in dye mopping up. Adsorption of Congo red dye from aqueous solution was performed using modified and unmodified *Cassia fistula* shells. Prior to the application of adsorption, *Cassia fistula* shells were carbonized, treated with oxalic acid and EDTA. All the modified *Cassia fistula* shells had good adsorption parameters, isotherms, and kinetics. The experimental data were in agreement with the pseudo second order kinetic model. According to the Freundlich isotherm, *Cassia fistula* shells EDTA sample (CFSED) has a maximum adsorption capacity of 70.24 mg/g, which means that 1 gram of CFSED will adsorb 70.24 mg of Congo red dyes. CFSED fits best into Freundlich isotherms and pseudo second order kinetic models. CFSED has the highest Freundlich isotherms (R^2 value of 0.8628) compared R^2 values of other modified and unmodified *Cassia fistula*, indicating that good surface area, a physio-sorption adsorption mechanism, and a multi-layer adsorption system dominate the adsorption process. Pseudo second order kinetics also suggests that CFSED adsorption is caused by both physio-sorption and chemisorption. *Cassia fistula* shell treated with EDTA has the best potential for adsorption of Congo red dye compared to other modified and unmodified *Cassia fistula* and well reliable to be a new class of adsorbent for Congo red dye mop up.

Keywords: Carbonized Congo red, EDTA, Shell, Oxalic acid

INTRODUCTION

Dyeing, paper and pulp, textiles, plastics, leather, cosmetics, and food industries have all employed dyes [1]. Colour waste discharged from these sectors cause a number of dangers and environmental issues. Dyes have complex aromatic molecular structures, making them more durable and difficult to biodegrade [2, 3]. Dyes and pigments are used in the textile industry to colour their products. Over 100,000 commercially accessible dyes are available, with over 7105 tonnes of dyestuff produced annually [4]. The majority of these dyes are harmful and carcinogenic to the ecological system [2, 5, 6]. In textile waste water, 72 hazardous chemicals have been found. About 30 of which may be difficult to remove using standard procedures. This is an environmental issue for apparel and textile manufacturers. [7, 8].

Adsorption has been discovered to be an efficient and cost-effective method of eliminating dyes, pigments, and other colourants from wastewater. When compared to other traditional methods, this process has an advantage due to its sludge-free clean operation, full removal of colours even from weak solutions [9], and adsorption of a significant number of dyes [10]. Adsorption is the accumulation of a gas or liquid solute (adsorbate) on the surface of a solid or liquid. This is distinct from absorption, which occurs when a material diffuses into a liquid or solid to form a solution [11].

Numerous studies on the adsorption capabilities of low-cost materials have been conducted in the last decade with the goal of remediating industrial waste waters. Oladele *et al.*, [12] adsorbed simulated wastewater methylene blue dye onto modified and unmodified cassis fistula pods. Tella *et al*., [1] synthesized and used a crystal structure of a Cd-based metal-organic framework to remove methyl orange dye. At a temperature of 300 K, Langmuir calculated the maximal adsorption capacity for methyl orange absorption to be 166 mg/g. Olawale *et al*., [10] also synthesized and characterized a lead-based polymeric molecule utilised for aqueous methyl red dye adsorption. The polymeric material adsorbed 118.89 mg of the methyl red dye under the testing conditions.

This study looks into the efficacy of modified and unmodified *Cassia fistula* shells in the adsorption of Congo red aqueous solution using EDTA and Oxalic acid as modifiers.

MATERIALS AND METHODS

Chemical and solvent used were purchased from Sigma Aldrich Company without modification. The *Cassia fistula* shells were collected from a *Cassia fistula* tree at Joseph Ayo Babalola University, Arakeji, Osun State, Nigeria.

Treatment of *Cassia fistula* pods

The shells were thoroughly cleansed in running tap water to eliminate dirt before being rinsed twice with distilled water. The shells were cracked to remove the seed before being dried in an oven at 120 °C for 24 hours. Dried shells were ground in a domestic mixer grinder and then pulverised to a particle size of 250 µm using a pulverising equipment. The fraction with a mesh size of 100 µm was sieved with a Tyler sieve and identified as Cassia fistula shells raw sample (CFSR).

EDTA *Cassia fistula* Sample

Excess ethanoic acid was used to cure 100 g of the pulverised samples for 24 hours. The residues were rinsed with de-ionized water multiple times before being oven-dried. After being oven dried, the Cassia shells were equilibrated in 0.1 mol/dm^3 EDTA solution. After 24 hours, the materials were filtered, oven dried, marked *Cassia fistula* shells EDTA sample (CFSED), and stored in sealed containers for the adsorption experiment.

Cassia fistula Oxalic Acid Sample

About 100 g of the pulverized sample was cured with excess concentrated ammonia solution for 24 hours. The residue of the mixture was severally washed with de-ionized water and oven dried. The oven dried Cassia shells powder was then equilibrated in 0.1 mol/dm^3 of oxalic acid solution. After 24 hours, samples were filtered, oven dried and kept for adsorption experiment. These samples were labelled as *Cassia fistula* Shells Oxalic (CFSO)

Carbonized *Cassia fistula* Sample

About 120 g of the dried material was placed in a muffle furnace under oxygen-deficient environment, at a heat rate of 400 °C for 2 hours. Thermal decomposition of the sample resulted in porous carbonaceous compounds. After the activated samples were cooled to room temperature, they were rinsed with distilled water until a consistent pH of 7 was achieved. The washed activated sample was then dried to constant weight in an oven at 105 °C. The finished product, called *Cassia fistula* shells Carbonised sample (CFSC), was stored in an airtight plastic bag.

Congo red dye solution preparation

The Congo red dyes stock solution concentration was created by weighing 0.999 g of Congo red dye (molar mass = 697 g/mol) and dissolving it in approximately 10 ml of distilled water, which was then put into a 1itre volumetric flask, agitated, and brought up to mark. The adsorption studies were conducted in a batch procedure using an aqueous solution of Congo red dye. Distilled water was used to dilute the stock solution, and the standard solutions included 20, 40, 60, 80, and 100 mg/l of Congo red dye. The calibration curve was derived using the standard solution spectra. After obtaining the UV spectra of the solution with a spectrophotometer, the concentration of Congo red dye was measured using the absorbance (at MAX = 510 nm) of the solutions [1]. The dye concentration was determined using a UV-visible spectrophotometer (SHIMADZU UV-1650pc UV-vis spectrophotometer).

Adsorption experiments of Congo red dye on *Cassia fistula* Shells

A 50 ml dye solution was measured into glass vials and stirred at room temperature with a known weight of pulverised *Cassia fistula* shells in a shaker set at 150 rpm for 60 minutes. For the full equilibrium test, a contact time of 180 minutes [13, 14], was chosen. The pH of the solution was carefully adjusted by adding a little amount of HCl and NaOH solutions (0.1 M) and measuring it using a pH metre. The mass balance equation was used to compute the amounts of adsorbed dye at equilibrium and dye removal efficiency [15,16].

$$\%E = \frac{(C_O - C_e)}{C_O} \times 100 \qquad (1)$$

$$Lq_e = \frac{(C_O - C_e)V}{m} \qquad (2)$$

Where:

C_e and C_0 are the equilibrium and initial dye concentrations (mg/l), respectively; q_e is the adsorbent equilibrium dye concentration (mg/g). V denotes the volume of dye solution in litres, M the adsorbent mass in grams, and E the removal efficiency [17, 18]. The effect of adsorbent dose was investigated by varying the amount of powdered Cassia shell from (0.2-3.0 g). To optimise adsorption efficiency, the effect of pH, contact time, optimal concentration, and temperature were investigated. The acquired data was subjected to adsorption isotherms and kinetic analysis.

RESULTS AND DISCUSSION

Effect of *Cassia fistula* Adsorbent Dose

The Congo red dose was held constant at 50 mL while the adsorbent amount was changed. 50 ml of the concentration was combined with CFSR, CFSO, CFSC, and CFSED doses of 0.2, 0.4, 0.6, 0.8, 1.0, and 3.0 g. The contact period was 180 minutes, the pH was 7, the agitation speed was 150 rpm, the temperature was 50 $^{\circ}$C, and the particle size was 100 micro mesh.

Fig. 1 depicts the influence of adsorbent dose on the equilibrium adsorption of Congo red dye onto CFSR, CFSC, CFSO, and CFSED. The results show that Congo red adsorption reduces with increasing adsorbent dosage mass of 0.2, 0.4, 0.6, 0.8, and 1.0 g in each case. The highest amount of Congo red adsorption was seen for all *Cassia fistula*adsorbent dosages of 0.2 g. When compared to unmodified Cassia fistula adsorbent (CFSR), every chemically treated *Cassia fistula* adsorbent demonstrated higher Congo red adsorption. The increase in adsorption is most likely due to the chemical treatment applied to the *Cassia fistula*, which is thought to boost the adsorbent's adsorption ability. Increased adsorbent dose, on the other hand, reduces the number of adsorbent active sites, which may be related to a decrease in adsorbent surface area and the availability of few adsorption sites. Furthermore, increasing adsorbent concentration may cause adsorbent overlapping, limiting dye molecules' access to accessible surface-active sites and so lowering adsorption capability. Oladele *et al.*, [12] made a similar observation. CFSED gave the most desired adsorption quantity signifying that the EDTA treatment exposed the surface area of the *Cassia fistula* to adsorption.

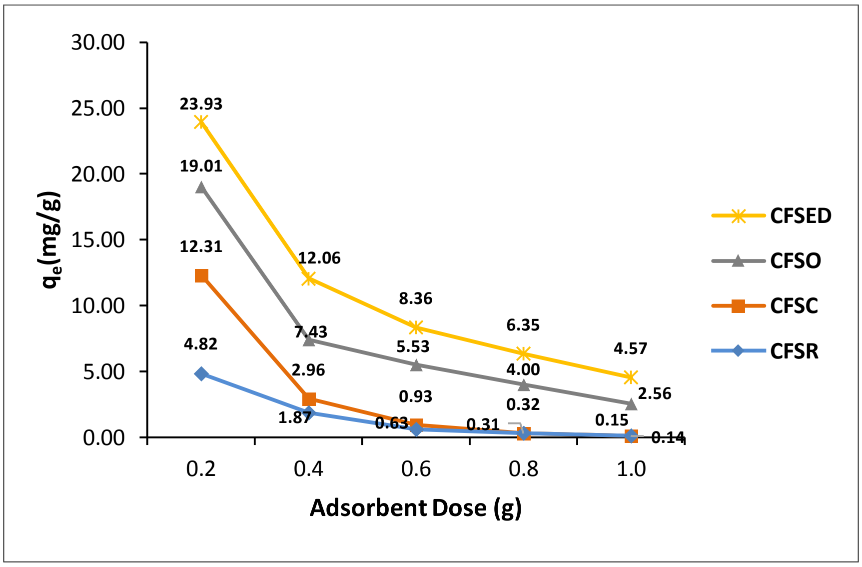

Fig 1: Effect of adsorbent dosage on Congo red adsorption by *Cassia fistula* shells

Initial Congo red dye concentration investigation on *Cassia fistula* shells

The effect of Congo red dye concentration on adsorption performance was also investigated in the initial Congo red dye concentration range of 20-100 mg/L, as shown in Fig. 2. For all varieties of *Cassia fistula* shells adsorbents, the adsorption capacity of powdered *Cassia fistula* shells appear to increase with increasing concentration of the dye concentration. This pattern could be explained by the dye's high concentration. Furthermore, as the dye concentration in the solution increases, the active sites of the *Cassia fistula* shells will have more dye molecules to adsorb, resulting in more effective adsorption. The chemically treated *Cassia fistula* shells performed better in terms of adsorption than the unmodified *Cassia* *fistula* adsorbent (CFSR), indicating the importance of the chemical treatment. Furthermore, CFSED provided the greatest desirable adsorption quantity, indicating that EDTA considerably affected the *Cassia fistula* shell surface area, resulting in adsorption.

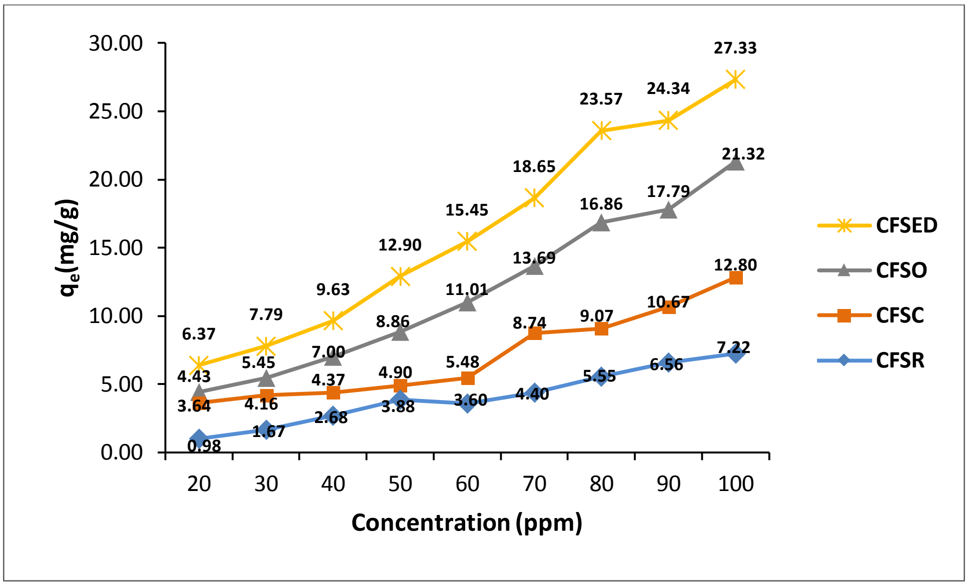

Fig. 2: Effect of initial Congo red dye concentration adsorption on *Cassia fistula* shell

The pH effect of Congo red dye concentration adsorption on *Cassia fistula* shell

A gram of each CFSR, CFSO, CFSC, and CFSED was weighed, and the experiment was conducted at room temperature, pH range (3- 10), and agitation time of 240 minutes. 50 mL of the 100 mg/L Congo red dye solution was distributed into 5 distinct conical flasks, each of which was adjusted to the various pH indicated above using either 0.1 M NaOH or HCl.

The influence of pH variation on the amount of Congo red dye solution adsorbed by *Cassia fistula* shells sample is shown in Fig. 3. The Congo red dye adsorption capability is quite good in acidic medium for all kinds of *Cassia fistula* shells adsorbents and decreases at pH greater than 3. This suggests that the Congo red dye molecules ionise in acidic media, resulting in interactions between the positively charged dye cations and the surface functional groups found in *Cassia fistula* shells. Adsorption reduces at higher pH values, which may be due to the production of soluble hydroxyl complexes. This is consistent with the use of Bagasse fly ash and coir pith as adsorbents [17].

All the chemically treated *Cassia fistula* shells outperformed the unmodified *Cassia fistula* adsorbent (CFSR) in acidic media, demonstrating the significance of the chemical treatment. Furthermore, CFSED gave the highest ideal adsorption quantity, indicating that EDTA significantly changed the surface area of the *Cassia fistula* shell, resulting in adsorption.

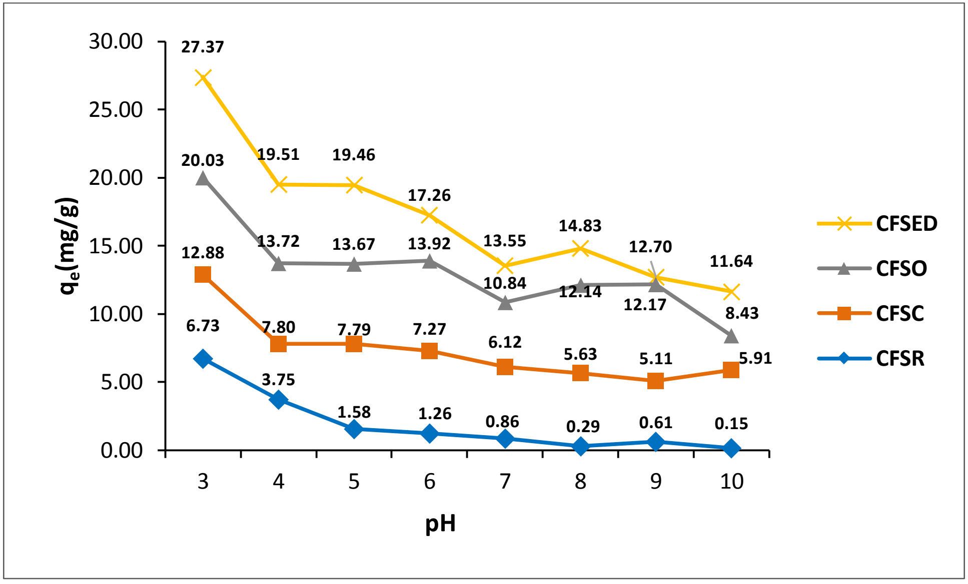

Fig. 3: Effect of Congo red dye pH variation on adsorption by *Cassia fistula* shells

Congo red dye concentration contact time effect investigation on *Cassia fistula* shells

Each gramme of CFSR, CFSO, CFSC, and CFSED was weighed into a 250 mL conical flask, and 50 mL of the 100 mg/L dye solution was added before agitation commenced for 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, and 240 min. Figure 4 depicts the effect of contact time on Congo red dye adsorption. The figure clearly shows that the rate of adsorption is very high at first, but later on, the rate of adsorption drops in CFSR and CFSC and increases in both CFSED and CFSO. After 180 minutes, the dye concentration is practically constant. It is mostly due to the saturation of these active sites on the *Cassia fistula* shells powder, which prevents further adsorption. This can be explained by the fact that the number of sites on the surface is initially relatively enormous, allowing adsorption to occur very easily. However, as time passes, the active sites get saturated, lowering the rate of adsorption. CFSED also had the maximum ideal adsorption quantity, showing that EDTA greatly increased the surface area of the Cassia fistula shell, resulting in adsorption.

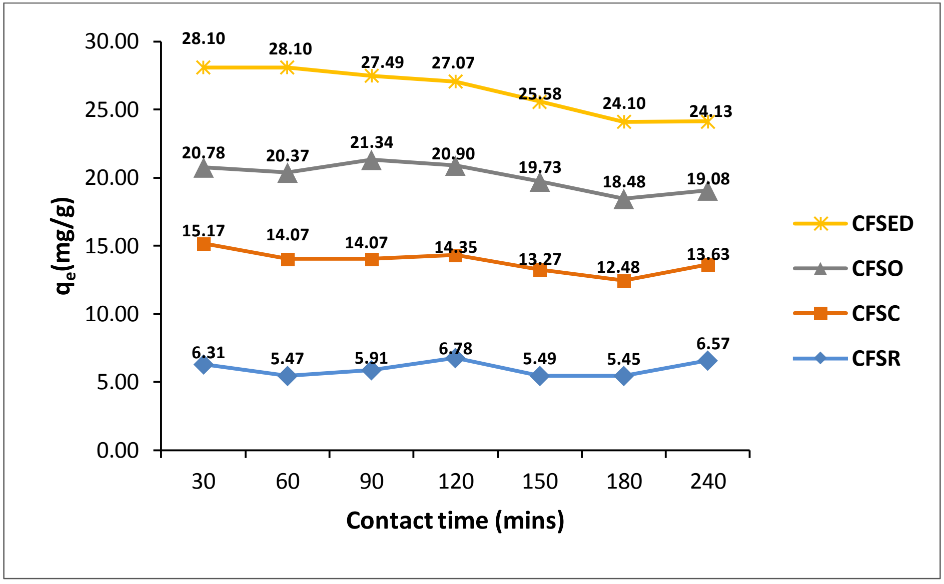

Fig 4: Effect of contact time on adsorption of Congo red by *Cassia fistula* shells

Effect of temperatureadsorption of Congo red by *Cassia fistula* shells

A gram each of CFSR, CFSO, CFSC, CFSED was weighed and this was carried out as described in adsorbent dosage using varying temperatures of 30 °C, 35 °C, 40 °C, 45 °C and 50 °C, 60 °C respectively.

Temperature is also a notable controlling factor in the real applications of adsorbent for the dye removal process. Fig. 5 represents the adsorption of Congo red by Cassia fistula shells at different temperatures. The temperature affects the dye adsorption capacity positively with CFSC and CFSO which means that the removal of dye increases with the increase in temperature of the system from 30 to 60 °C. While adsorption capacity of CFSR and CFSED is temperature independent and the maximum adsorption capacity was recorded at 30 °C.

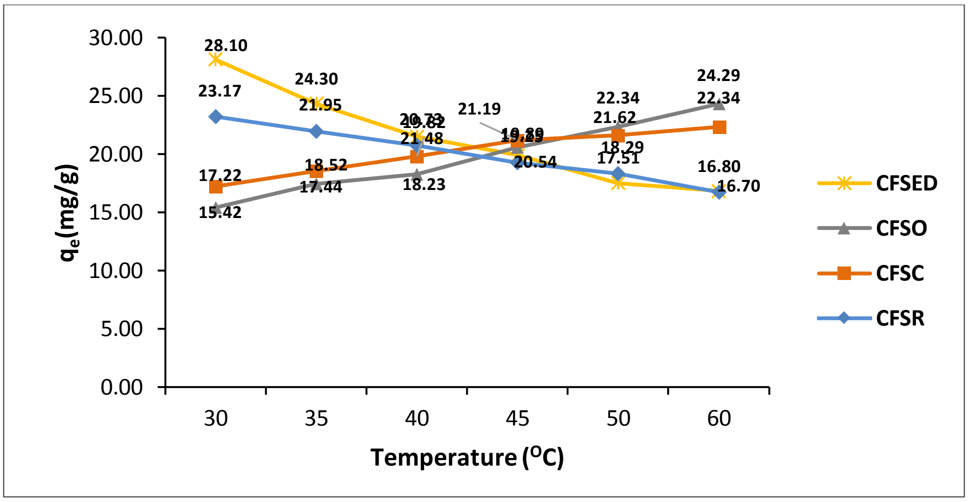

Fig 5: Effect of temperature on the adsorption of Congo red dye by *Cassia fistula* shells

Adsorption isotherm studies of Congo red dye by *Cassia fistula* shells

The equilibrium adsorption capacity of *Cassia fistula* was found to increase with increase in initial concentration. This indicates that there are many adsorption sites in adsorbent available for the adsorption.

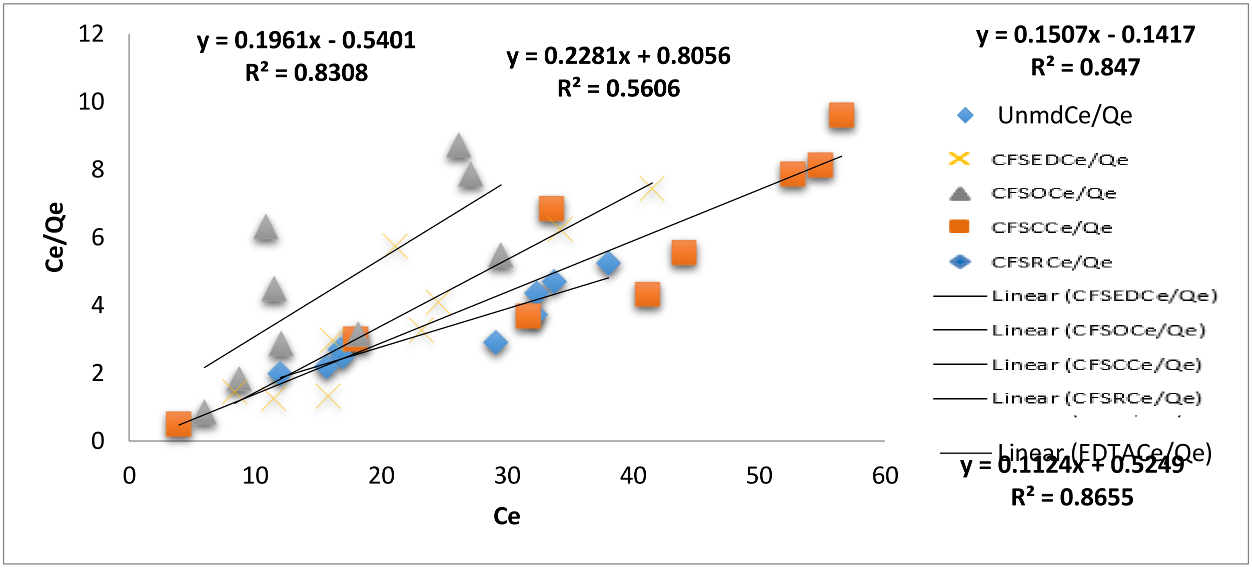

Fig. 6: Langmuir adsorption isotherm plot of Congo red by *Cassia fistula* shells

The results of the adsorption isotherm investigations are shown in Figures 6–9. The influence of adsorption isotherms was investigated, and it was discovered that all forms (both unmodified and chemically modified) of *Cassia fistula* shells conform to both Langmuir and Freundlich adsorption isotherms (Table 1). The Langmuir R^2 values as well as quantity of Congo red dye adsorbed per gram of the *Cassia fistula* shells (q_e) for all forms of *Cassia fistula* shells are in the order of CFSED > CFSO > CFSC > CFSR (Table 1). When compared to the unmodified form of *Cassia fistula* shells (CFSR), all chemically treated forms of *Cassia fistula* shells provided improved R^2 and q_e values. CFSED has the highest Langmuir R^2 value, which is very near to 1, indicating that it conforms to this isotherm. CFSED has the highest q_e value.

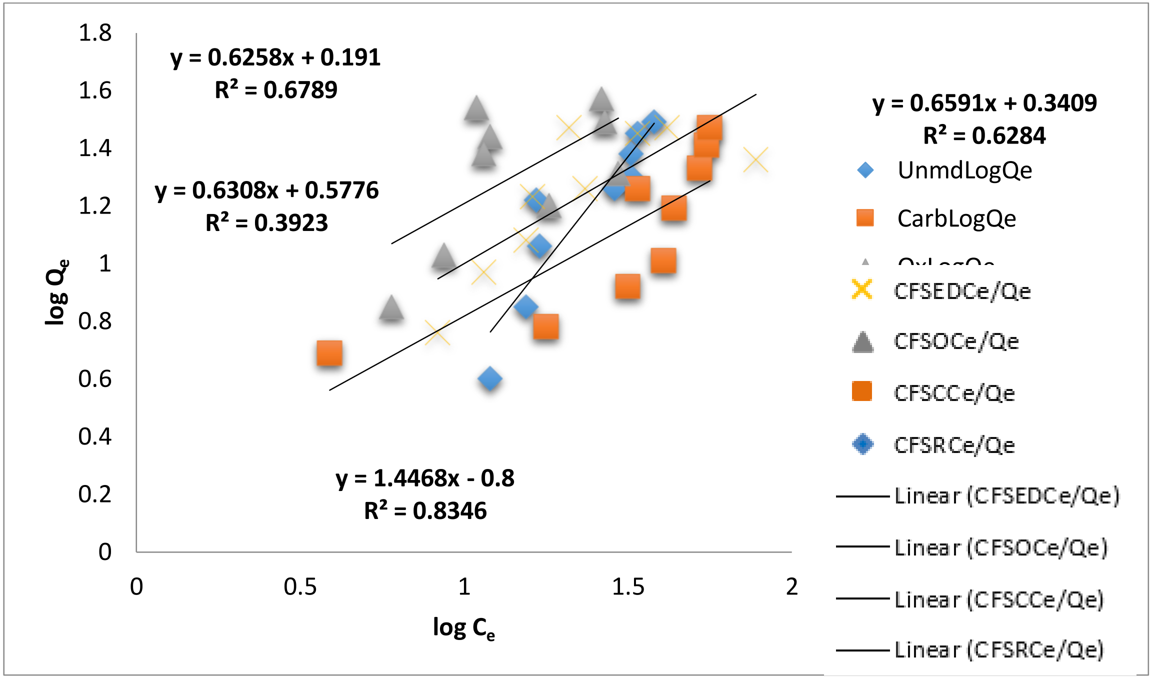

Fig. 7: Freundlich adsorption isotherm plot of Congo red by *Cassia fistula* shells

For all kinds of *Cassia fistula* shells, the Freundlich R^2 values and quantity of Congo red dye adsorbed per gram of *Cassia fistula* shells (q_e) are in the sequence CFSED > CFSO > CFSC > CFSR (Table 1 and Figure 8). Furthermore, in accordance with the Langmuir isotherms of all chemically treated *Cassia fistula* shells, Freundlich results clearly reveal that all chemically treated forms of *Cassia fistula* shells behaved better, with higher R^2 and q_e values, as compared to the unmodified form of *Cassia fistula* shells (CFSR) (Table 1). The best Freundlich R^2 value is likewise seen with CFSED, indicating that the EDTA offered the *Cassia fistula* shells the most ideal treatment, exposing the surface for adsorption.

CFSED has the best Freundlich parameters k_f n, and q_e, which are 3.776, 1.60, and 70.24, respectively. These numbers represent the calculated sorption capacity, sorption intensity, and maximal adsorption capacity. The numerical value n <1 indicates that bound sorbate molecules interact in such a way that as more sorbate binds, the binding strength increases. Alternatively, n > 1 can indicates that sorption capacity is only minimally decreased at lower equilibrium concentrations, implying many binding sites, with the strongest sites binding the sorbate first.

The Freundlich sorption isotherm presents an equation that includes surface heterogeneity, the exponential distribution of active sites, and surface multilayer sorption. According to the Freundlich isotherm, the highest capacity of 1 gram of *Cassia fistula* shells was 70.24 mg of Congo red. Temkin graph and parameters do not conform to adsorption of Congo red by *Cassia fistula* shells (Fig. 8).

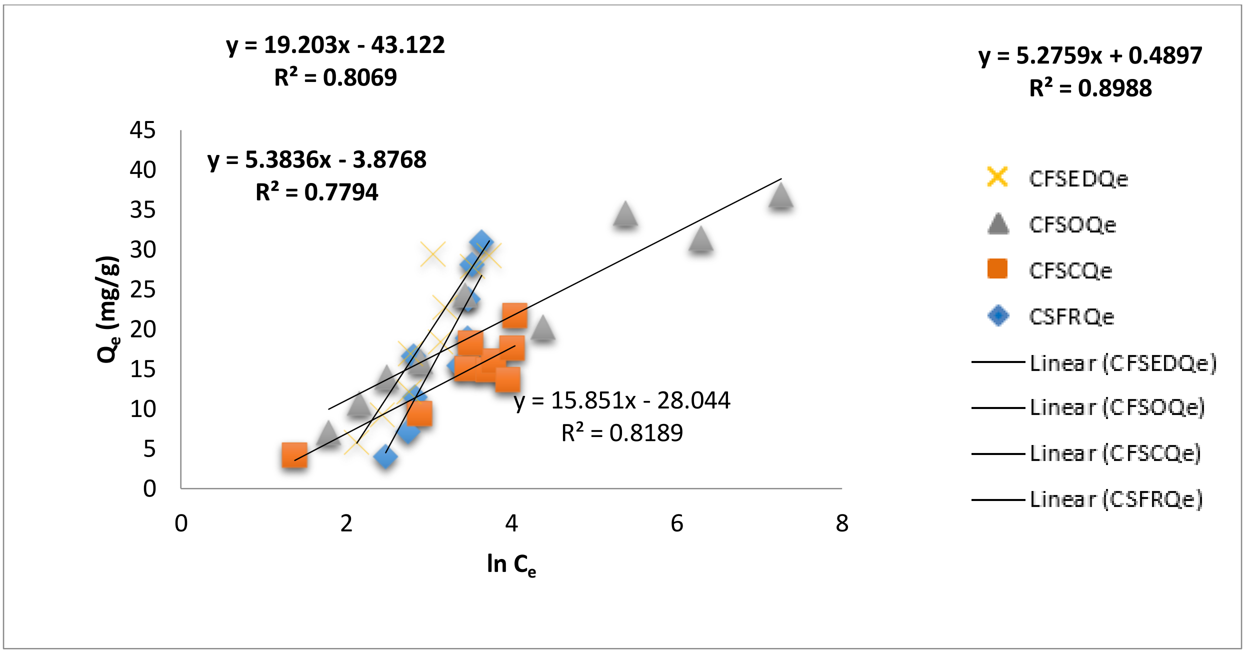

Fig. 8: Temkin adsorption isotherm plot of Congo red by *Cassia fistula* shells

Table 1: Isotherm parameters for the adsorption of Congo red over *Cassia fistula* shells

Freundlich Isotherm Parameters					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	**K_F**	0.158	1.552	2.188	3.776
	n	0.692	1.517	1.587	1.6
	q_e(cal)	8.695	54.873	59.89	70.24
	R^2	0.392	0.678	0.8308	0.8628
Langmuir Isotherm Parameters					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Paramet	**q_o**	8.929	6.667	4.286	5.102

ers	**b**	0.214	-1.064	0.283	-0.363
	q_e(cal)	3.89	5.47	6.78	7.95
	R^2	0.560	0.847	0.830	0.865
Temkin Isotherm Parameters					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	b_T	10.825	38.612	39.403	13.114
	A_T	0.019	0.904	0.012	0.118
	$q_{e(cal)}$	-2897.874	21.179	-5.301	25.186
	R^2	0.806	0.779	0.818	0.898

Adsorption Kinetic studies of Congo red over *Cassia fistula* shells

The kinetic data acquired from the kinetic investigation of Congo red adsorption were analysed using the following models: pseudo-first order, pseudo-second order, Elovich model, and intra-particle model. The results of the adsorption kinetics studies are shown in Figures 9–12.

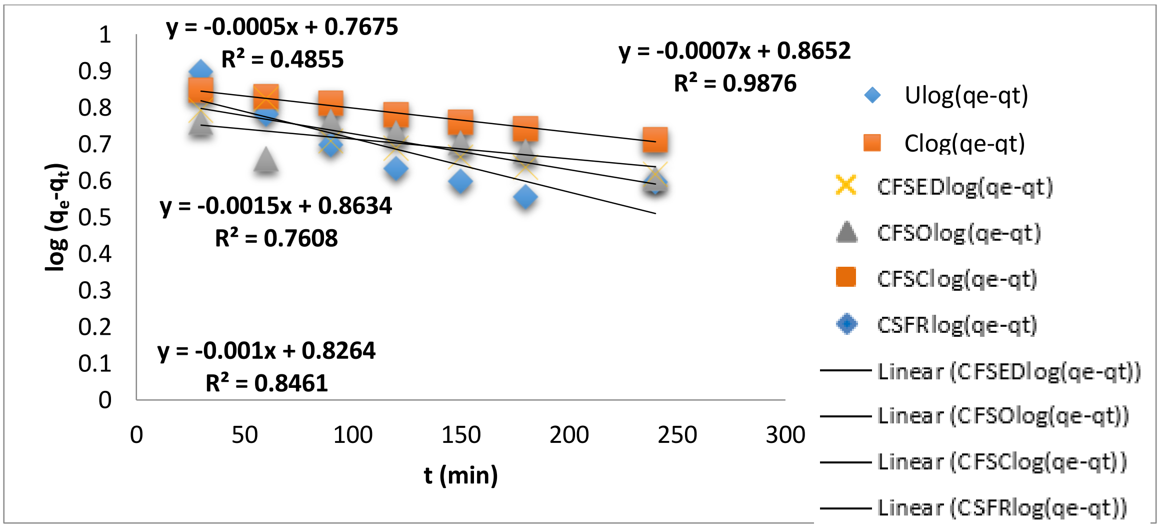

Fig 9: Pseudo first order kinetics plot of Congo red over *Cassia fistula* shells

The quick adsorption of Congo red dye over *Cassia fistula* shells is confirmed by the fact that all varieties of *Cassia fistula* shells adhere to pseudo second order kinetics with R^2 values greater than the R^2 values of pseudo first order kinetics law. This also suggests that both physi-sorption and chemisorption are involved in adsorption. Researchers on dye adsorption obtained similar results [1, 12, 10]. CFSED demonstrated a good adsorption capacity with a correlation coefficient of 0.994 (Table 2), and when the half-life of the kinetic process ($t_{1/2}$), which is the time required for half of the adsorbate concentration to be removed, a very fast adsorption kinetic reaction that reaches half its equilibrium in less than 30 minutes was observed for the Congo red dye.

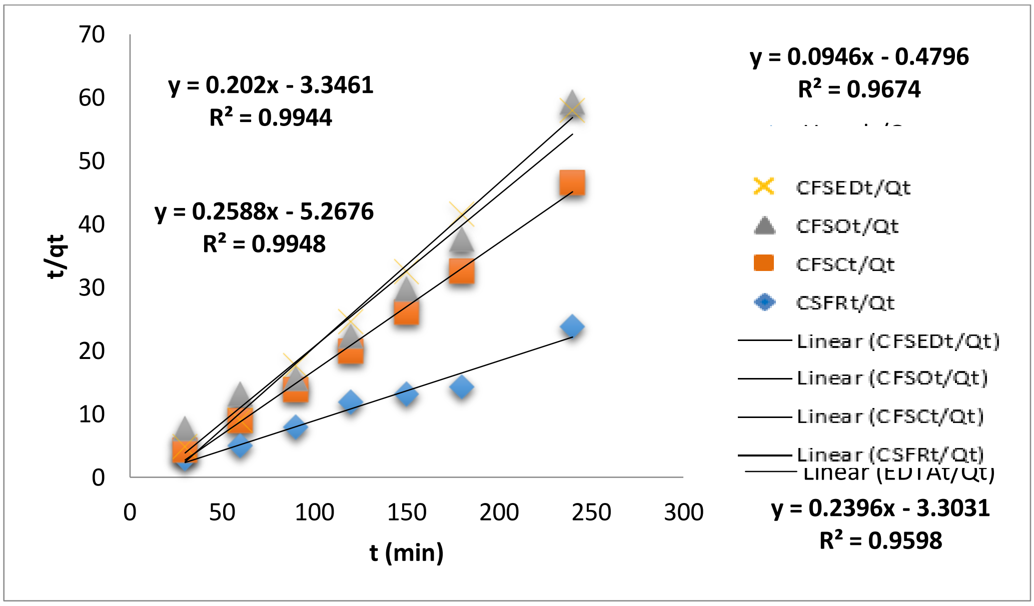

Fig. 10: Pseudo second order kinetics plot of Congo red over *Cassia fistula* shells

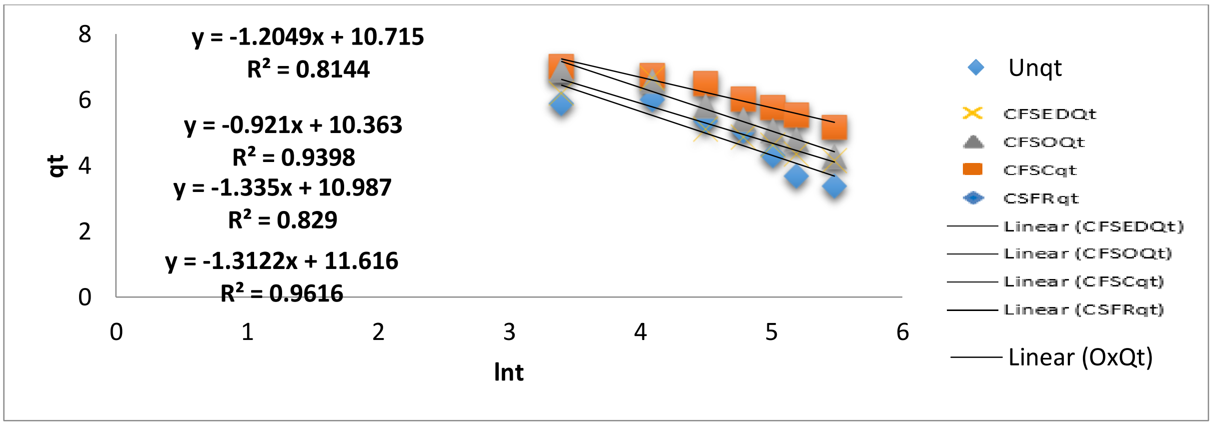

Fig. 11: Elovich kinetic model plot of Congo red over *Cassia fistula* shells

In adsorption kinetics, the Elovich equation was used to describe the chemical adsorption of Congo red dye over *Cassia fistula* shells. The R^2 values of all *Cassia fistula* shells are close to one, indicating that chemisorption is the mechanism responsible for the adsorption reaction, which is consistent with the pseudo second order kinetics plot. Furthermore, the Elovich model plot clearly showed that CFSED has the highest value of R^2 values (Table 2), suggesting that the quick and maximum uptake of Congo red is due to chemisorption.

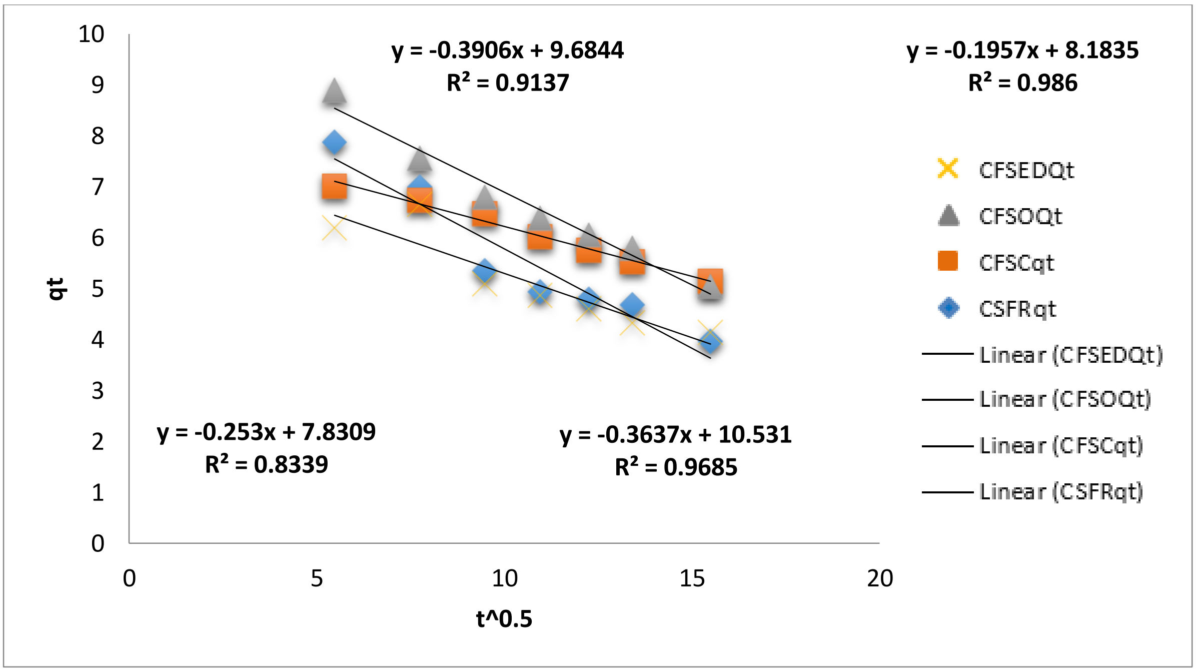

Fig. 12: Intraparticle kinetic model adsorption plot of Congo red over *Cassia fistula* shells

The *Cassia fistula* shells are assumed to have uniform pores size, upon which the Congo red dye molecules form a monolayer in this model. It is used to determine whether the adsorption process is diffusion-controlled, which means that the adsorption process is much faster than diffusion. The outcome was depicted in Figure 12 and Table 2. When compared to the unmodified *Cassia fistula* shells (CFSR), all chemically treated *Cassia fistula* shells showed higher R^2, indicating that the chemical treatment improves intraparticle diffusion adsorption between the Congo red dye molecules and the chemically treated *Cassia fistula* shells. CFSED, as predicted, fit best into this kinetic model, indicating quick intraparticle diffusion-controlled between Congo red dye molecules and *Cassia fistula* shell pores.

Table 2: Kinetics and model parameters for the adsorption of Congo red over *Cassia fistula* shells

Pseudo first order kinetics					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	K_1	0.001	0.000	0.000	0.001
	q_e(cal)	7.295	7.328	5.848	6.699
	R^2	0.485	0.760	0.846	0.987
Pseudo second order kinetics					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	K_2	-0.018	-0.012	-0.017	-0.013
	q_e(cal)	10.638	4.950	4.184	3.876
	R^2	0.959	0.967	0.994	0.994
Elovinch Model					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	α	$-5.75X10^{-7}$	$-1.19x10^{-5}$	$1.88x10^{-4}$	$-1.65x10^{-4}$
	β	-0.749	-1.086	-0.762	-0.831
	R^2	0.814	0.829	0.939	0.961
Intraparticle Model					
	Cassia fistula	**CFSR**	**CFSC**	**CFSO**	**CFSED**
Parameters	K_i	-0.390	-0.195	-0.363	-0.253
	C	9.684	8.183	10.53	7.830
	R^2	0.833	0.913	0.968	0.986

Scanning electron microscopy of *Cassia fistula* shells

Zeiss Neon 40 EsB field emission scanning electron micrograph was used for the scanning of *Cassia fistula* shells before and after adsorption. Figure 13 shows scanning electron micrographs of all types of *Cassia fistula* shells prior to use of the *Cassia fistula* shells in Congo red dye adsorption. Only CFSR and CFSED showed the presence of pores within the structure. Furthermore, scanning electron micrographs of *Cassia fistula* shells after Congo red dye adsorption revealed that the pores vanished, indicating that the *Cassia fistula* shells pores are likely to be filled up with Congo red dye adsorption (Fig. 14). All chemically treated *Cassia fistula* shells changed colour and appearance, which may be attributed to Congo red dye adsorption.

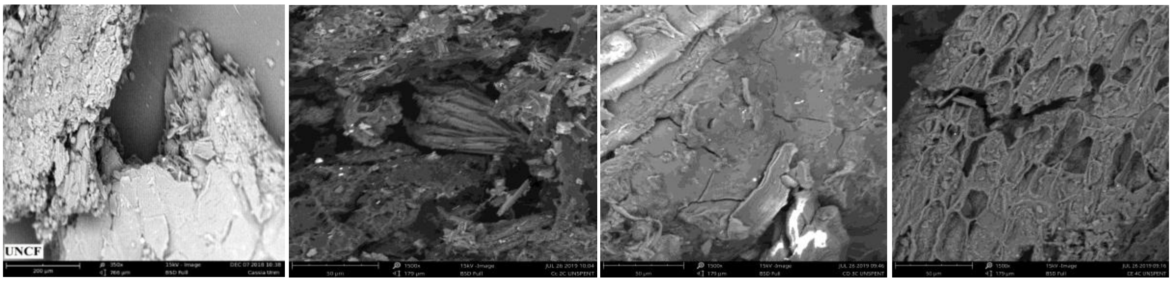

Fig. 13: SEM diagram for CFSR, CFSC, CFSO and CFSED *Cassia fistula* shells before adsorption

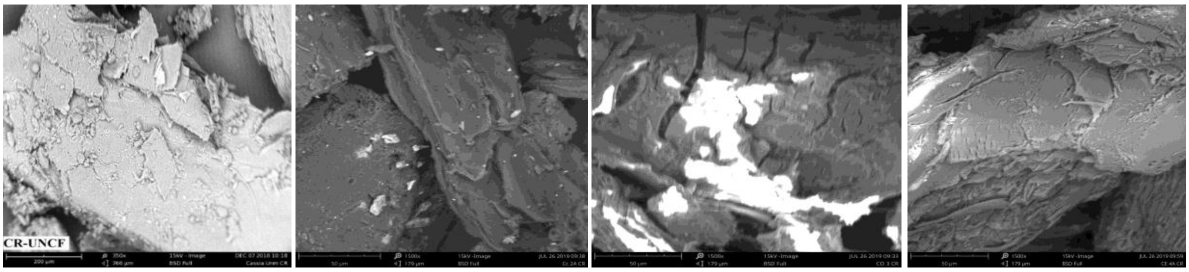

Fig. 14: SEM diagram for CFSR, CFSC, CFSO and CFSED *Cassia fistula* shells after adsorption

CONCLUSIONS

Modified and unmodified *Cassia fistula* shells were used as a low cost adsorbent for the removal of Congo red dye from aqueous solution. The modified *Cassia fistula* shells with good adsorption capacity were favoured by adsorption parameters, isotherms, and kinetics. The experimental data were found to be in good agreement with the pseudo second order kinetic model. With a good adsorption capacity of 70.24 mg/g determined by the Freundlich isotherm, CFSED fit best into pseudo second order kinetic model and Freudlich isotherms with R^2 values of 0.994 and 0.8628 respectively. The greatest CFSED R^2 value indicates that the adsorption process is dominated by a large surface area, a physio-sorption adsorption mechanism, and a multi-layer adsorption system. Pseudo second order kinetics also suggests that CFSED adsorption is caused by both physi-sorption and chemisorption. *Cassia fistula* shell treated with EDTA has the potential to be a new class of adsorbent for Congo red dye mop up.

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