

## Sorption Studies on the Removal of Industrial Dye Aniline Yellow From Aqueous Solution Using Surfactant Modified Iron Filings

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**Abstract** The potential of iron filings for efficient removal of aniline yellow (a cationic dye) from aqueous solutions was investigated. The iron filings were characterized by XRD, SEM and FTIR techniques. To remove aniline yellow, the surface of the iron filings was modified with sodium dodecyl sulfate (SDS) as an anionic surfactant. Also, the various parameters affecting dye removal were investigated and optimized. Dye adsorption equilibrium data fitted well into Temkin isotherm and Redlich Peterson isotherm. The adsorption process was pH-dependent and the results indicate that the optimum pH for maximum adsorption occurred at pH 8.0 for the modified and pH 6.0 for the unmodified adsorbents having maximum removal efficiencies of 95.5 and 82 % respectively. Kinetic studies for aniline yellow adsorption showed rapid sorption dynamics according to the second-order kinetic model, suggesting that chemisorption must have played a major role in the adsorption process. Studies on the effect of temperature showed that adsorption capacity increased with increase in temperature for both adsorbents. The results indicate that, SDS-coated iron filings can be used as a cheap and efficient adsorbent for removal of cationic dyes from aqueous solutions.

**Key Words:** Contamination, water, aniline yellow dye, remediation, adsorption, iron filing

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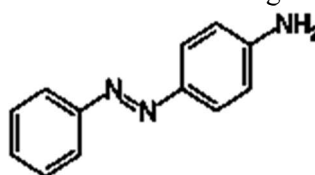
### 1.0 Introduction

Water is a major component of the environment required for the sustenance of life and the entire ecosystem. Therefore, its availability in volume and quality is a significant factor that defines quality life (Eddy and Ekop, 2007). Any substance that alters the quality of water significantly is not desirable for defining portable water and is therefore defined as water contaminant (Charles and Ogoko, 2012). When the concentration of the contaminant is increased in such an amount that it could lead to injurious or toxic effect on man and the environment, it constitutes water pollutants (Eddy, 2009; Eddy and Odoemelam, 2009; Odoemelam and Eddy, 2009). A natural mechanism which has the function of purifying the water system in the world has been significantly stressed by actions and inactions of man, especially linked to urbanization, population explosion and industrialization (Ogoko, 2017). Large volumes of untreated wastes are often discharged by industries into the water system. These wastes may contain

heavy metals, organo-leptic contaminants, microorganism, antibiotics, etc (Awuh *et al.*, 2009; Sun *et al.*, 2004). Most of the industrial wastes have been deeply studied and some successful ameliorative measures have been implemented but studies on the pollution of aquatic system by dye are still receiving significant research interest. Some industries including ternary, leather, paint, pigment, construction, textile and other industries uses dyes and are often constraints on the treatment process that will significantly reduce the impact of the dye-rich water on the environment (Dos Santos *et al.*, 2007). Most often, dye contaminated waste water is discharged directly to the water bodies (Adedirin *et al.*, 2011). Apart from the fact that some dyes are toxic, the presence of dye in a water body can alter the light penetration to the water and thus interfere with photosynthesis process needed to maintain aquatic life (Tahir *et al.*, 2016). Dyes can also form complexes with heavy metals and create toxic chemicals within the aquatic system (Lellis *et al.*, 2019). Synthetic organic dyes are persistent and can not be degraded by natural biodegradable agents implying that they can bioaccumulate in algae, fish and other aquatic organism over time and consequently be transferred to man through the food chain, thereby impacting its toxic effect (Beradi *et al.*, 2019). Their existent in aquatic environment can also cause significant alteration in the ecological conditions of the aquatic fauna and flora and impact negatively on the equilibrium of the aquatic system through oxygen depletion, eutrophication, colour alteration, turbidity and odour (Beradi *et al.*, 2019). Long term effect of dyes on aquatic system may attract persistence, bioaccumulation of carcinogenic aromatic products and formation of by-products of chlorination, mutagenicity and carcinogenicity (Odoemelam *et al.*, 2018).

Therefore, the discharge of dye rich effluents without proper treatment can contaminate surface and ground water which may eventually find its way into drinking water (Acemioglu, 2004). Most dyes and their degradation products such as benzidine, naphthalene and other aromatic compounds are toxic, allergenic, carcinogenic or mutagenic to living beings. Azo dyes containing one or more azo bonds (-N=N-) are known to be persistent in the environment, because of their low reactivity thus making them resistant to degradation (Zohra *et al.*, 2008). Research efforts

aimed at developing technologies for the treatment of dye contaminated waste water have led to the conclusion that the implementation of the adsorption process is one of the best options (Odoemelam and Eddy, 2009). Adsorption involves selective removal of undesirable components (i.e dye) from a solution through physical or chemical or both mechanisms (Eddy and Ekop, 2005; Pearce *et al.*, 2003). Aniline yellow (Fig. 1) is a yellow azo dye and an aromatic amine, it is a derivative of azo benzene which has the appearance of an orange colour powder with a molecular formula of  $C_{10}H_{11}N_3$ . It has a melting point of 125 °C, a boiling point of 360 °C and a molar mass of 197.24 g/mol.



**Fig. 1: Chemical structure of aniline yellow**

Adsorption is an economical and effective technique for the removal of dyes and coloured pollutants from wastewater (Hashemian, 2009; Eddy, 2009; Eddy and Odoemelam, 2009). It is a process in which molecules in a solution are drawn and accumulated to the internal surfaces of an adsorbent material. Many adsorbents have been used for the removal of dyes in wastewater. Such adsorbents include egg shell powder (Tsai *et al.*, 2008) pearl millet husk (Inbaraj *et al.*, 2002) castor seed shell (Oladoja *et al.*, 2008) Peanut hull (Ozer *et al.*, 2007) activated carbon (Ghaedi *et al.*, 2014) natural adsorbent perlite (Malakootian *et al.*, 2011), alumina (Bhargavi *et al.*, 2015) neem (*Azadirachta indica*) leaf powder (Bhattacharyya and Sharma, 2005; Odoemelam *et al.*, 2018), graphite oxide and nanographene oxide (Odiongenyi, 2009), aluminum oxide and nano aluminum oxide, (Odiongenyi and Afangide, 2019), wood saw dust (Akpanudo and Chibuzo, 2020), fly ash (Janos *et al.*, 2003) etc.

Research in the development of alternatively cheaper, environmentally friendly and efficient adsorbents are constantly being studied, and iron waste in the form of iron filings is one of such materials, considering that iron is one of the abundant metals found in the earth crust. Iron filings are suitable for removal of dye since they have a higher specific surface area and reactivity,



high magnetic properties, which enhances high adsorption efficiency and high removal rate of contaminants. A major drawback in the use of bare iron filings is the ease of agglomeration, due to its high chemical activity and fast oxidizing nature. Often times, surfactants, or other surface modifiers are used to enhance its dispersibility (Kassaei 2011, Mangal *et al.*, 2013).

The current work investigates the efficiency of surface modification of iron filings with sodium dodecyl sulfate (SDS) for the removal of aniline yellow as a cationic dye from aqueous solution.

## 2.0 Materials and Methods

### 2.1 Materials

All reagents used were of analytical grade. Iron filings, sodium dodecyl sulphate (SDS) and the azo dye (aniline yellow with molecular formula  $C_{10}H_{11}N_3$  and a molar mass of 197.24 g/mol), were supplied by Loba Chemie Pvt. Ltd. Colado, Mumbai, India. All absorbance measurements were obtained using a B-braun (UV-2602, England) UV-Vis spectrophotometer. For absorbance measurements, 400 nm was obtained as the maximum absorbance wavelength ( $\lambda_{max}$ ) of aniline yellow. A temperature controlled shaker was applied for shaking of the dye solutions in isotherm and kinetic studies at constant temperature.

### 2.2 Preparation of dye solution

A stock solution (500 mg/L) of the dye was prepared by dissolving 0.125 g of aniline yellow in 250 ml volumetric flask and was made up to the mark with distilled water. From this stock solution, various aliquots were pipetted into 50 ml flasks and made up to the mark with distilled water to give a range of concentrations between 100 mg/L and 10 mg/L. The maximum absorption wavelength of the dye was determined by scanning samples with different concentrations using UV-Vis Spectrophotometer (UV-1800PC) at a wavelength of 800–380 nm, and the maximum absorption wavelength for aniline yellow was observed at 400 nm.

### 2.3 Modification of adsorbent

The iron filings and SDS were mixed in a ratio of 1:2.5 in a 100 ml beaker, 1 g of the SDS + iron filings mixture was used for adsorption purpose. For the unmodified adsorbent, 1 g of the iron filings was used directly for the adsorption experiment.

### 2.4 Instrumentation

The iron filings were characterized using Fourier transform infra-red (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction (XRD) patterns were determined using a high-resolution Bruker D8 Advance diffractometer of Cu  $K\alpha$  ( $\lambda = 1.54050 \text{ \AA}$ ) radiation. The samples (1 g) were scanned from  $15^\circ$  to  $90^\circ$   $2\theta$  range with a step size of  $0.02^\circ$  and a step rate of  $0.454^\circ \text{ s}^{-1}$ . Infrared spectra were obtained by using a Fourier transform infrared spectrometer (FTIR) (Perkin-Elmer Spectrum RX1). The analysis was performed to confirm the presence of surface functional groups. The powder samples (99 mg) were mixed well with 1 mg of potassium bromide (KBr) and pressed into pellets under vacuum, until they appeared clear and not translucent. The pellets were then carefully removed from the disc, placed in the FTIR sample holder and analyzed by the transmission mode with a resolution of  $4 \text{ cm}^{-1}$ . The spectra of the different samples were recorded in the wavenumber range of  $4000$  to  $400 \text{ cm}^{-1}$ . The morphology of the iron filings was characterized with a Scanning Electron Microscope (SEM) (JSM5910, UK).

### 2.5. Adsorption experiments

A batch adsorption experiment was carried out to determine the effects of parameters such as pH, contact time, dosage, initial dye concentration, and temperature on the adsorption of the dye. The following procedure was used for the optimization studies: (i) 50 mL aqueous solution of the dye ( $50 \text{ mg L}^{-1}$ ) was poured in a 250 mL beaker, (ii) 1.0 g each of the adsorbents were added to the dye solution, (iii) pH of the solutions were adjusted to the desired value by using either hydrochloric acid ( $0.01 \text{ mol L}^{-1}$ ) or sodium hydroxide solutions ( $0.01 \text{ mol L}^{-1}$ ), (iv) the mixture was thoroughly shaken in a thermostated water bath shaker at 120 rpm for 60 min, (v) at the expiration of 60 min; the iron filings were quickly separated from the sample solutions using a Watmann filter paper (vi) the filtrate solutions were analyzed for the residual dye concentration with a UV-Vis Spectrophotometer (UV-1800PC) using a calibration curve. Subsequently, The adsorbent dose, initial dye concentration, temperature and contact time were altered and variations in the amounts of dye up-take by the adsorbents were analyzed. The dye removal efficiencies were calculated using:



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

where  $C_o$  and  $C_e$  are the initial and final dye concentrations respectively.

### 3.0 Results and Discussion

#### 3.1 Characterizations of adsorbent

The adsorbent's crystalline phase was identified by X-ray diffraction (XRD) and the spectrum obtained is shown in Fig. 2. The XRD pattern showed three characteristic peaks (110), (200), and (211) at  $2\theta$  angle values of  $44.662^\circ$ ,  $65.006^\circ$ , and  $82.311^\circ$

which are in line with the main phases and planes of the pure iron diffraction peaks when compared with the JCP2 06-0696 iron (Fe) file. From these results, it can be seen that the preferred crystal orientation of the iron filings is in (110) direction, this is because of the strong diffraction peak observed at this plane. Also, the SDS coating on the iron filings did not influence the crystalline phases, as observed in the XRD pattern (Fig 2).

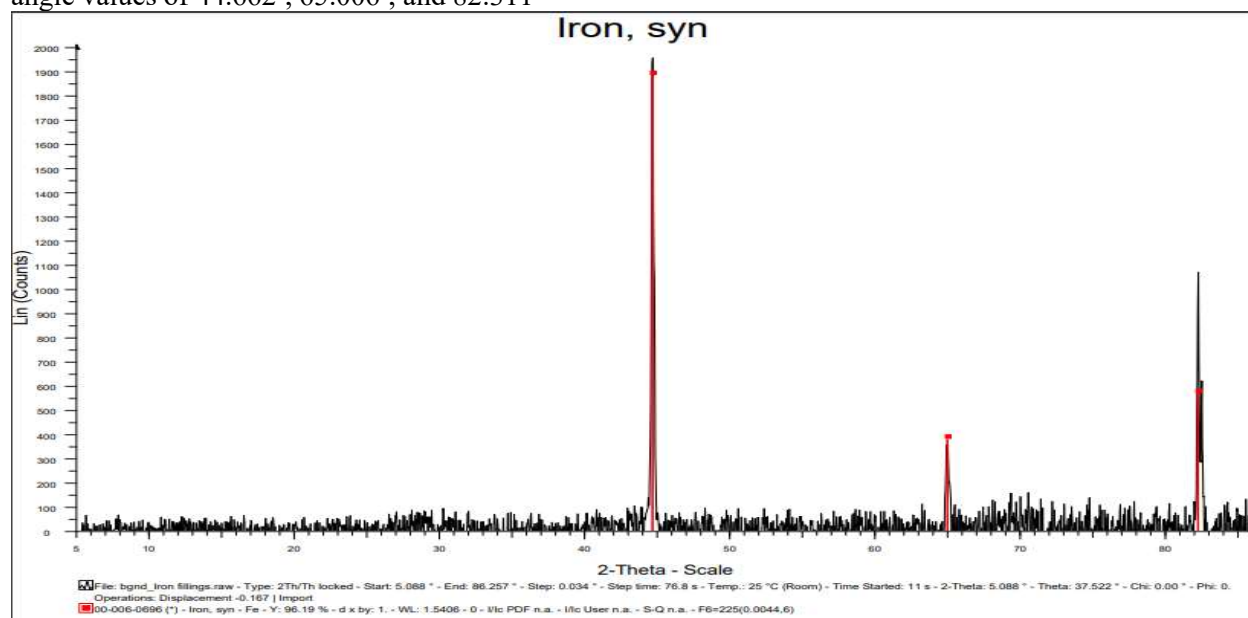


Fig. 2 XRD pattern of SDS-coated iron filings

SEM images of the modified and unmodified iron filings (Fig 3) when compared with each other show that the SDS changed the morphology of the iron filings by reducing the average particle size, thereby creating a large surface area for adsorption. Also, the SDS modified iron filings appear more dispersed than the unmodified iron filings.

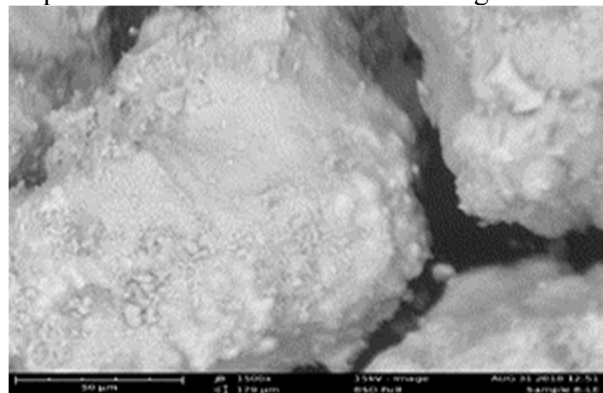


Fig. 3a: Scanning electron micrograph of iron filings

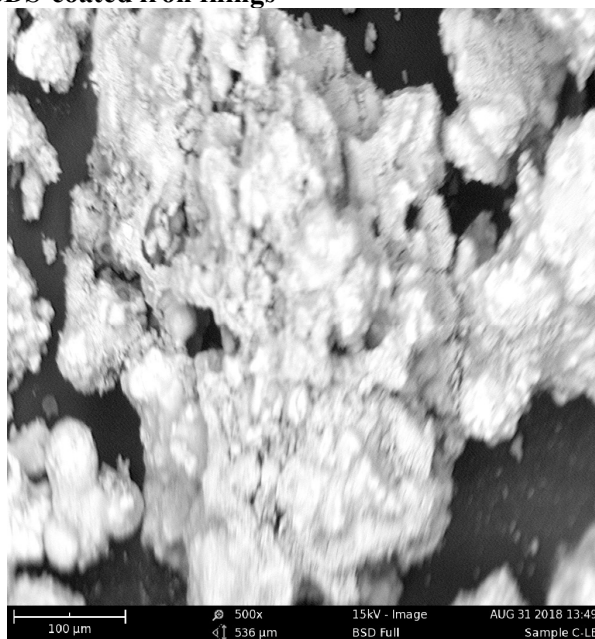
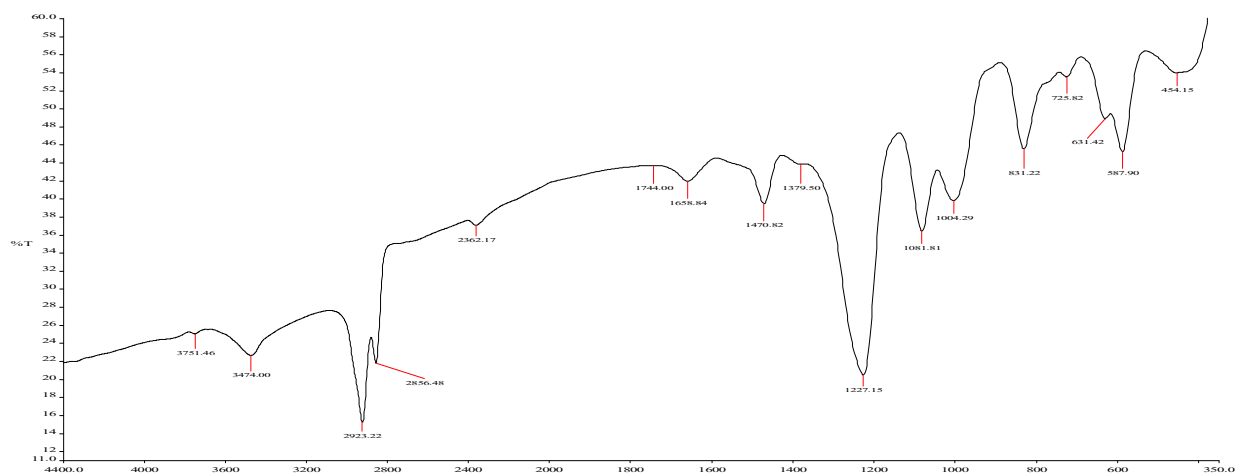


Fig. 3b: Scanning electron micrograph of SDS-coated iron filings





**Fig. 4:** FTIR spectra of the SDS-modified iron filings before adsorption of dyes

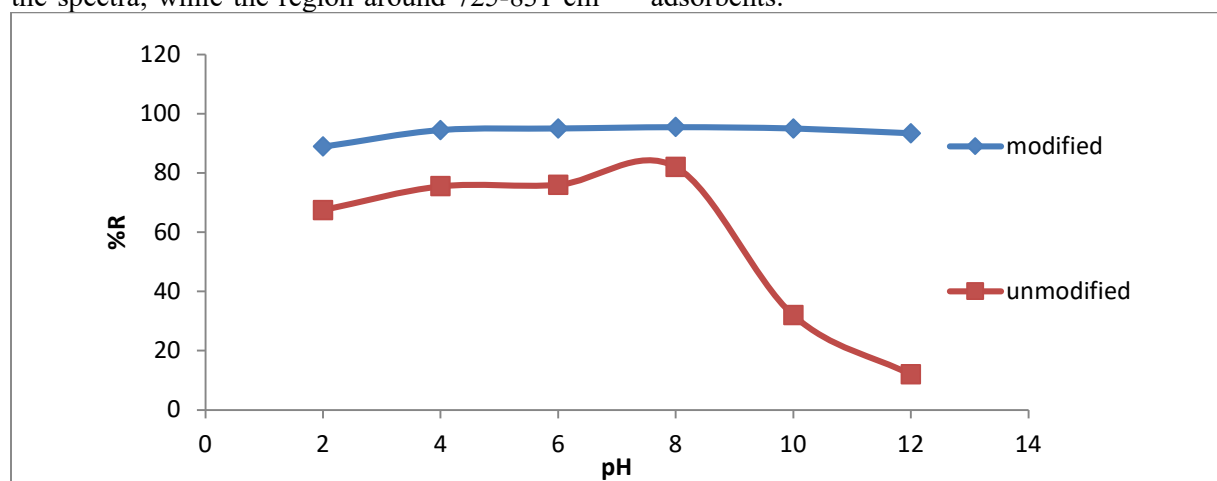
The various vibrational frequencies for the SDS-modified iron filings are shown in Fig. 4. The peaks at 2923 and 2856  $\text{cm}^{-1}$  represent the asymmetric and symmetric  $\text{CH}_2$  stretching vibrational frequencies respectively, these stretching features of  $\text{CH}_2$  can be used to describe the packing and conformation of SDS molecules. According to Sperline (1997), frequency values of  $\text{CH}_2$  higher than 2852  $\text{cm}^{-1}$ , indicates the presence of micelles and liquid crystals. Peaks located at 1379–1470  $\text{cm}^{-1}$  are characteristic of the  $\text{CH}_2$  wagging modes. The most prominent and intense peak at 1227  $\text{cm}^{-1}$  represents the asymmetric vibrational frequency of  $\text{SO}_2$ . It is a grouping of various overlapping peaks, and it is commonly seen as double band (Prosser and Franses, 2002), located at 1081 and 1004  $\text{cm}^{-1}$  in the spectra, while the region around 725–831  $\text{cm}^{-1}$

shows the characteristic absorption peaks for Fe as observed in Fig 2. The FTIR result therefore indicates that the SDS molecules completely coated the iron filings surface thus stabilizing the particles in aqueous suspension.

### 3.2. Adsorption properties of the adsorbents

#### 3.2.1 Effect of initial pH on the adsorption

pH of the bulk solution is a significant factor that can influence adsorption through protonation and adsorption. The degree of uptake of dye ions onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH (Ramakrishna and Viraraghavan, 1997). From Fig 5, the removal efficiencies of dye ions by the adsorbents increased as the pH of the solution increased from pH 2.0 to pH 8.0 but decreased above pH 8.0 for both adsorbents.



**Fig. 5:** Variation of percentage of aniline dye adsorbed by modified and unmodified iron filings with pH.

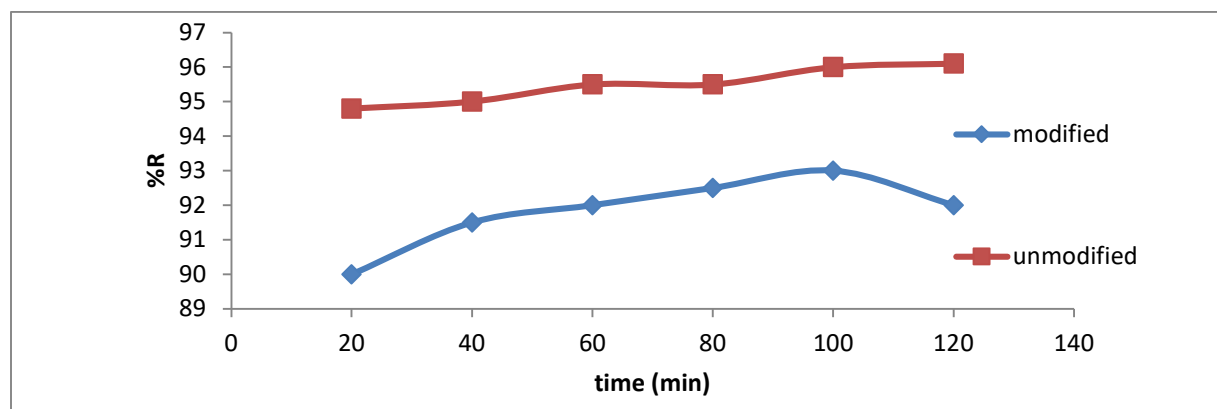


At low pH, the protons compete with the dye ions for the binding sites on the adsorbent surface leading to a reduced adsorption of the dye ions by the adsorbents as a result of electrostatic repulsion effect. At higher pH, the proton concentration decreases thereby creating more binding sites on the adsorbent leading to enhanced dye uptake. It is clear that modified adsorbent has higher removal efficiency than the unmodified at the pH values considered.

**3.2.2 Effect of contact time**

Fig. 6 is a plot showing the variation of percentage of dye adsorbed by modified and unmodified iron

filings with time. The plots reveals that the uptake of dye witnessed a sharp initial increase (up to 20 minutes) and then gradual for both adsorbents up to 100 minutes which can be regarded as the optimum time for the used adsorbent to be most effective. The observed trend can be explained in terms of increase in diffusion rate and active adsorption site at first but after the critical time, active adsorption sites have been occupied, giving way to distortion of adsorption-desorption equilibrium (Odoemelam *et al.*, 2018). However, after the critical time, the adsorption approached equilibrium and started decreasing gradually.

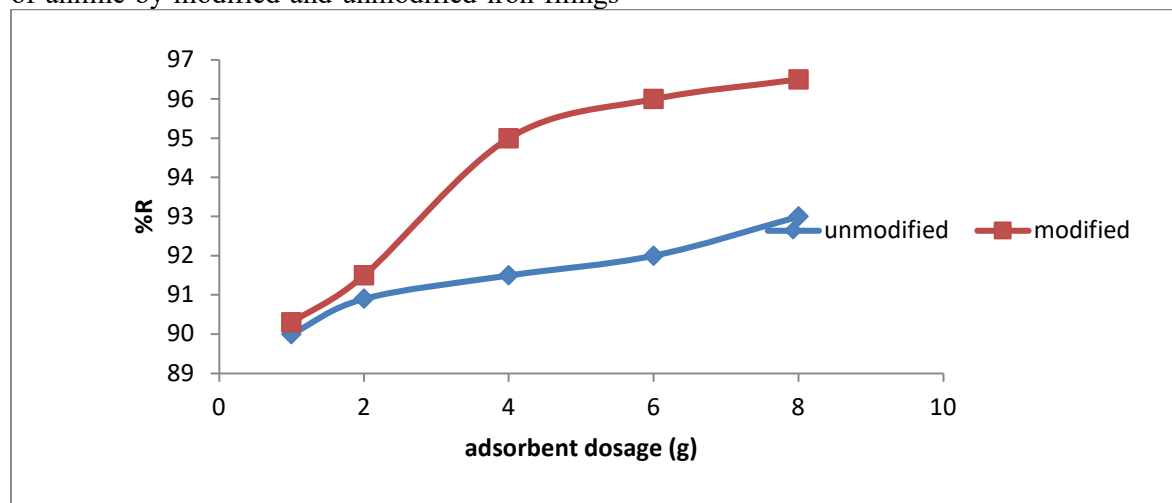


**Fig. 6: Variation of percentage of aniline dye adsorbed modified and unmodified iron filings with time**

**3.2.3 Effect of adsorbent dosage**

The effects of adsorbents dosage on the adsorption of aniline by modified and unmodified iron filings

were evaluated and the results obtained are presented in Fig 7.



**Fig. 7: Variation of percentage aniline adsorbed by modified and unmodified iron filings with adsorbent dosage**



From Fig. 7, it is evident that the % removal of the dye adsorbed by the modified and unmodified NZVI increased with increase in adsorbent dosage. This can be attributed to increase in active adsorption sites due to increase in adsorbent dosage (Ekop and Eddy, 2009; Karthikeyan and Elango, 2009). The observed linear variation of amount of dye adsorbed with adsorbent dosage indicate that within the range of the dosage, adsorption-desorption equilibrium couldn't be attained.

### 3.2.4 Effect of temperature on the adsorption process

Fig 8 suggests that adsorption increased with

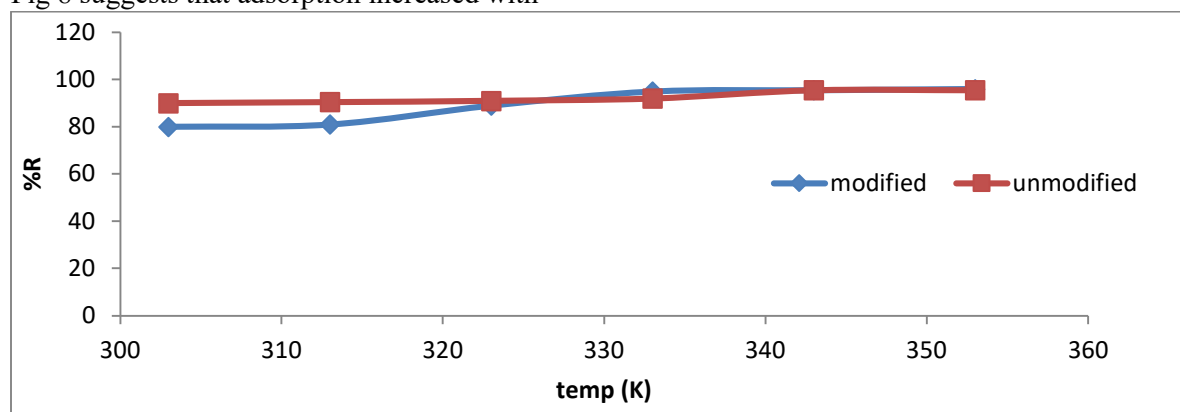


Fig. 8: Variation of percentage of aniline dye adsorbed by modified and unmodified iron filings with temperature.

### 3.2.5 Effect of initial concentration

The dye concentration is a significant factor to be considered for effective sorption process. From Fig. 9, an initial quick uptake of dyes was observed for both adsorbents. Also, the percentage removal of the dye by the adsorbents increased with increase in dye concentration. Maximum removal for the unmodified adsorbent occurred at a

increase in temperature, up to a maximum of 70 °C for both adsorbents after which equilibrium was attained. This suggests that active adsorption site was activated by increasing temperature up to a critical value, which was 70 °C. The observed increase in extent of adsorption with temperature suggest chemical adsorption mechanism (Ogoko *et al.*, 2009). Temperature can also increase the rate of diffusion of the adsorbate to the surface, leading to the attainment of equilibrium within a shorter time. Similar mechanism has been reported by Ho (2003).

concentration of 60 mg/L, after which a decrease in dye uptake was observed at further increase in concentration. Conversely for the modified adsorbent, adsorption kept increasing proportionally with increase in dye concentration. Results further showed that there was greater removal using the modified adsorbent than the unmodified adsorbent from the dye solutions.

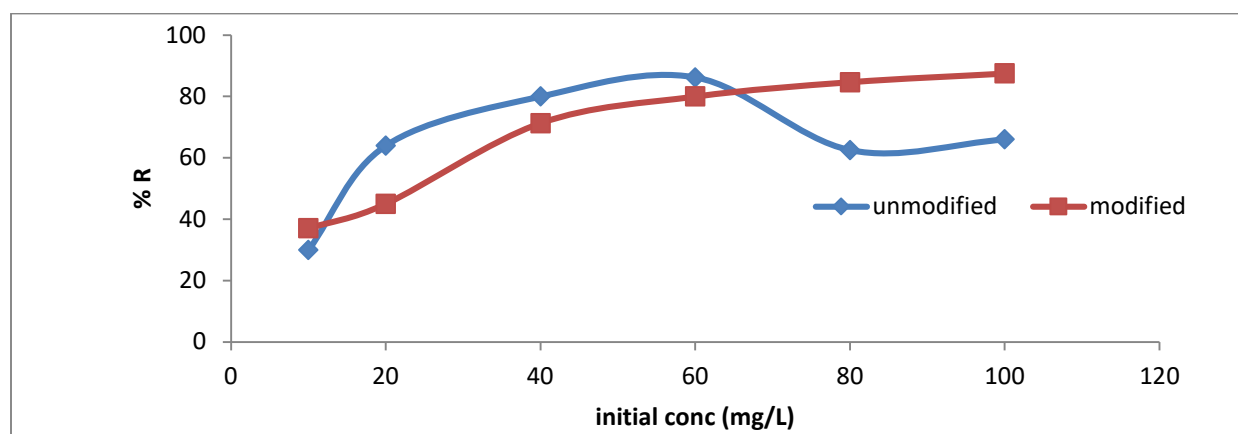


Fig. 9: Variation of percentage of aniline dye adsorbed by modified and unmodified iron filings with initial dye concentration.



### 3.3 Adsorption isotherms

Consideration of the dynamic balance between the concentration of the adsorbate in the bulk solution with the concentration at the interface led to the establishment of best fitted isotherm after tests for fitness to the different adsorption models. The test indicated that the best fitted isotherm is the Temkin adsorption. Temkin adsorption model considers the influence of interaction between the adsorbate and the adsorbing species (Temkin and Pyzhev, 1940). At relatively low concentration, the model assumes that the heat of adsorption (which is a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically

with degree of coverage due to the interaction between adsorbate and adsorbent. The Temkin equation can be written according to equation 2,

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (2)$$

where b is the Temkin constant, which is related to the heat of adsorption (kJ/mol), and K is the empirical Temkin constant related to the equilibrium binding constant and the maximum binding energy (L/mg). Temkin plots for the adsorption of aniline dye on the surface of modified and unmodified iron filing is shown in Fig. 10 while adsorption parameters deduced from the plots are recorded in Table 1.

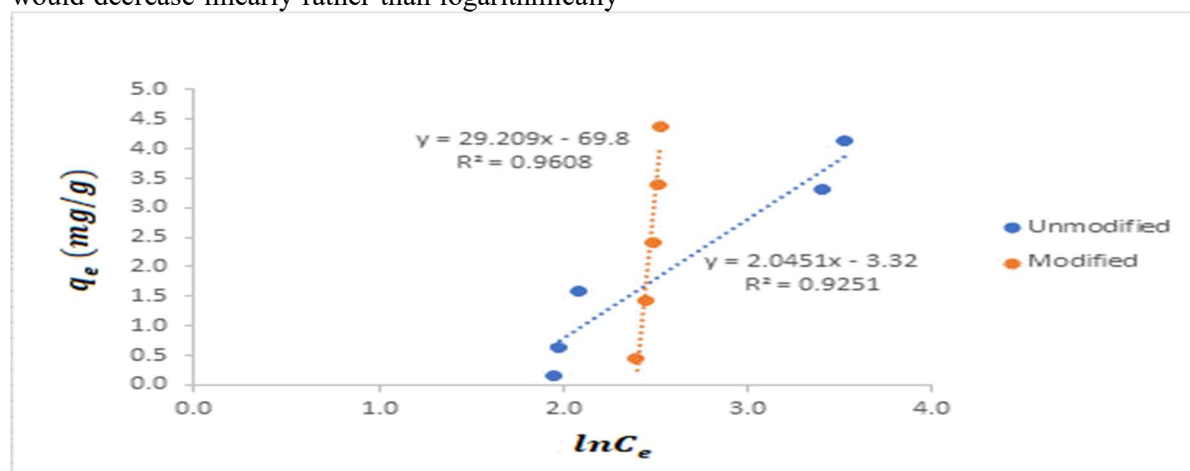


Fig. 10: Temkin plots for the adsorption of aniline dye on the surface of modified and unmodified iron filing

Table 1: Temkin parameters for the adsorption of aniline dye on iron filing surface

	Slope	Intercept	b	lnK <sub>T</sub>	ΔG <sub>ads</sub> <sup>0</sup> (kJ/mol)	R <sup>2</sup>
Unmodified	2.045	-3.32	1231.854	-1.62347	-4.09	0.9251
Modified	29.209	-69.8	86.2454	-2.389674	-6.02	0.9608

The results obtained indicated that binding energy of aniline dye for modified iron filing is greater than the binding energy between the same dye and unmodified iron filling. The plots reveal unparallel relationship which indicates that the modification of the iron filling must have changed the mechanism of the adsorption of the dye. Calculated free energy change was also more negative for the modified adsorbent than for the unmodified adsorbent. However, both points toward physical adsorption indicating that chemisorption, which was earlier inferred through the variation of extent of adsorption with temperature, must have proceeded by physisorption before it occurred.

The adsorption of aniline onto iron filing was also found to fit the Redlich-Peterson isotherm which can be written as

$$q_e = \frac{AC_e}{1+BC_e^\beta} \quad (3)$$

A and B are constants while β is an exponential that lies between 0 and 1. Equation 3 can be rearranged to a linear form as follows,

$$\ln\left(\frac{C_e}{q_e}\right) = \ln\left(\frac{1}{A}\right) + \beta \ln(C_e) \quad (4)$$

Therefore, plots of  $\ln\left(\frac{C_e}{q_e}\right)$  versus  $\ln(C_e)$  were linear as shown in Fig. 11. β values were 13.38 and 16.05 respectively. The Redlich-Peterson constants for aniline dye adsorbed on unmodified and





modified iron filing were  $9.859 \times 10^{12}$  and  $1.088 \times 10^{18}$  respectively. Therefore, the modified iron filing has better adsorption capacity than the unmodified iron filling.

Adsorption kinetics is an effective method of evaluating the rate and mechanism of dye ions adsorption onto the adsorbents. In order to evaluate the kinetic mechanism which controls the process, the Pseudo first order (Lagergren, 1898), and Pseudo second order (Ho and McKay 1998) models were tested and validated by analyzing their linear equations respectively. A relatively high  $R^2$  value shows that the model successfully describes the kinetics of the dye ion adsorption. The different kinetic models are described in the subsections below.

The integrated pseudo first-order equation is generally given as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (5)$$

where  $k_1$ (min) is the pseudo-first-order adsorption kinetics parameter;  $q_t$  is the amount adsorbed at time  $t$ (min); and  $q_e$  denotes the amount adsorbed at equilibrium, both in mg/g. The plot of  $\ln(q_e - q_t)$  as a function of  $t$  yielded straight lines with slope and intercepts equal to  $k_1/2.303$  and  $\log(q_e)$  respectively. Pseudo first order plots yielded low  $R^2$  values and is therefore not applicable for the adsorption of aniline onto modified and unmodified iron filling surface.

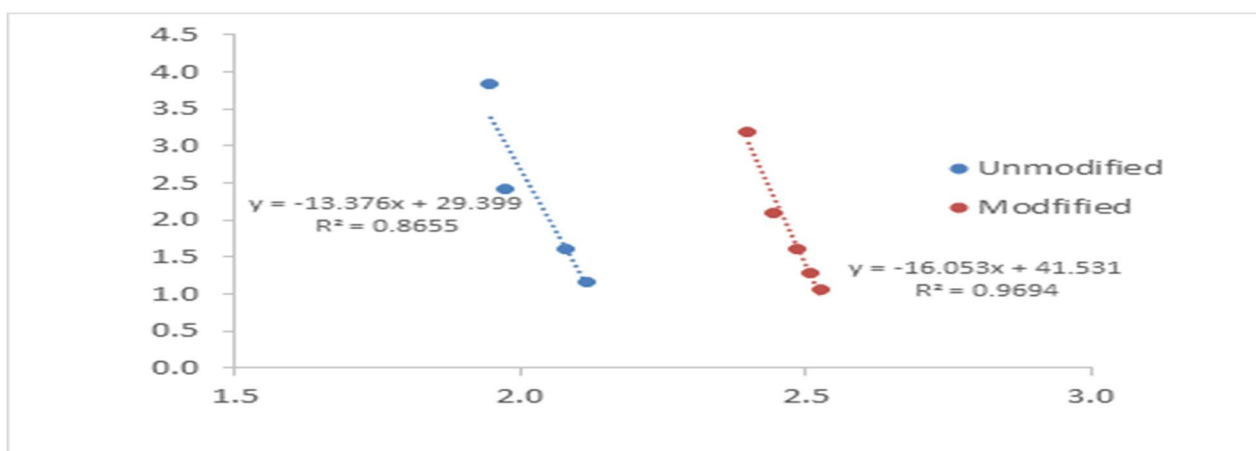


Fig. 11: Redlich Peterson isotherm for the adsorption of aniline dye on iron filing

### 3.4 Adsorption kinetics

The integrated Pseudo second-order model can be written according to equation 6

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where  $h_0 = k_2 q_e^2$  is the initial adsorption rate and measures the adsorption capacity as  $t$  approaches zero. The pseudo second-order model was applied in this analysis and a plot of  $t/q_t$  vs  $t$  (Fig. 12) gave linear plots, which allowed the evaluation of  $q_e$ ,  $k_2$  and  $h_0$  (Table 2)

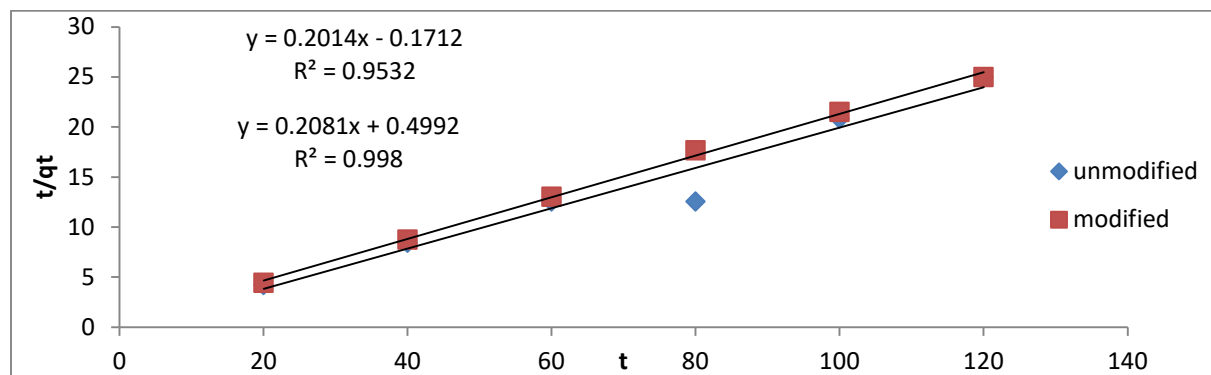


Fig. 12: Pseudo-second order plot of  $\ln(q_e - q_t)$  vs  $t$  for the adsorption of aniline dye onto SDS-modified and unmodified iron filings



. From (Fig. 12 and Table 2) the adsorption data fitted into the pseudo second-order model perfectly, judging by the high correlation coefficients ( $R^2 = 0.998$  and  $0.9532$ ) and this suggests that the rate-limiting step of adsorption by the adsorbents in our study may be controlled by chemisorption (Ho *et al.*; 1995).

The rate constant,  $k_2$ , the equilibrium adsorption capacity,  $q_e$  and the initial sorption rate,  $h_0$ , of the adsorption of the dye ions are presented in Table 2. The equilibrium adsorption capacities,  $q_e$  calculated from the pseudo second-order kinetic model agree closely with the experimental values. The second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other model, it predicts the behavior over the whole range of adsorption.

**Table 2: Kinetic rate constants for pseudo first-order and pseudo second order reactions model at 30 °C**

Pseudo-first order	Constants	Modified	Unmodified
	$q_{e \text{ calc}}$ (mg g <sup>-1</sup> )	0.3188	0.1565
	$q_{e \text{ exp}}$ (mg g <sup>-1</sup> )	4.30	2.58
	$k_1$ (min <sup>-1</sup> )	0.0059	0.0288
	$R^2$	0.4669	0.7978
Pseudo-second order			
	$q_{e \text{ calc}}$ (mg/g)	4.8053	4.9652
	$q_{e \text{ exp}}$ (mg/g)	4.30	2.58
	$k_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	$8.6 \cdot 10^{-2}$	1.1764
	$h_0$ (mg.g <sup>-1</sup> .min <sup>-1</sup> )	0.4132	5.8411
	$R^2$	0.998	0.9532

### 3.5 Thermodynamic studies

The activation energy was calculated by using Arrhenius relation: (Odoemelam *et al.*, 2009)

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

where  $k$  is the rate constant,  $E_a$  is the activation energy,  $R$  is the has constant,  $T$  is the temperature and  $A$  is the Arrhenius or pre-exponential constant. The rate constant was obtained from the following relationship (Odoemelam *et al.*, 2018),

$$k = \frac{c_a d}{c_e} \quad (8)$$

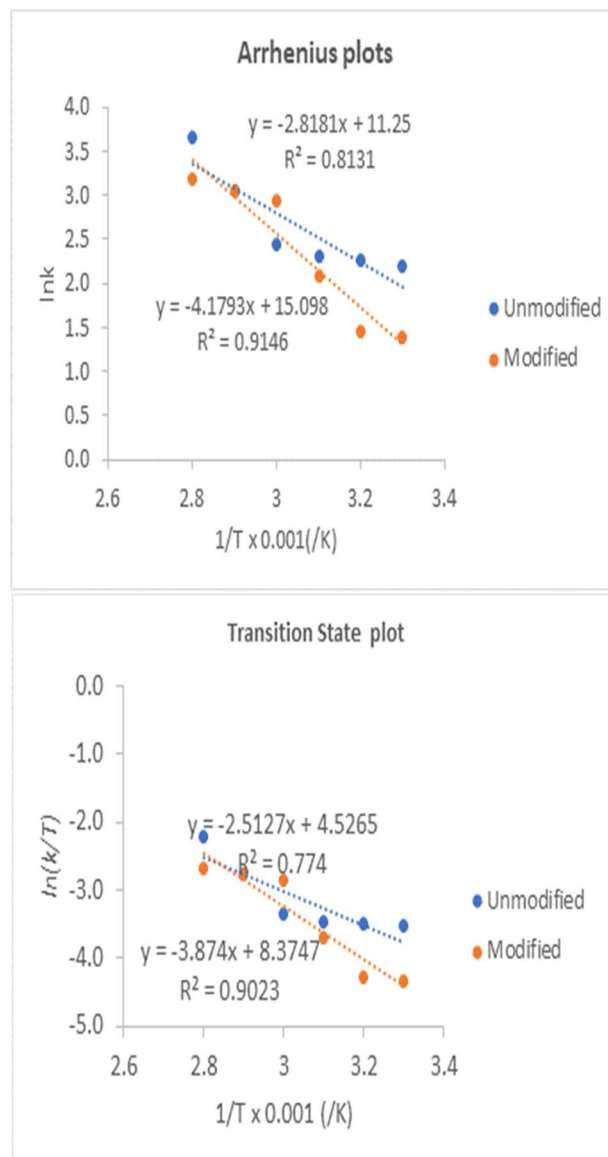
The transition state equation (equation 8) was also applied to obtain thermodynamic parameters (enthalpy and entropy of adsorption) (Hamdy and El-Gendy, 2013).

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{R}{N}\right) + \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

The Gibb Helmolzt equation was used to obtained the free energy change for the adsorption process (equation 11)(ref)

$$\Delta G^0 = RT \ln(K_T) \quad (10)$$

The Arrhenius and transition state plots are shown in Fig. 12. From slopes and intercepts, values of entropy and enthalpy change were estimated according to equation 9 while values of Arrhenius parameters were estimated using equation 7. Estimated values of free energy of adsorption are recorded in Table1.



**Fig. 14: Arrhenius and Transition state plots for the adsorption of aniline yellow dye onto modified and unmodified iron filings**



**Table 3: Arrhenius and Transition state parameters for the adsorption of aniline yellow onto modified and unmodified iron filings**

Adsorbent	slope	Intercept	A	Ea(J/mol)	R <sup>2</sup>
Unmodified	2.8181	11.25	76879.92	23.42968	0.8131
Modified	4.1793	15.098	3605605	34.7467	0.9146
	Slope	Intercept	$\Delta S^0$ (J/mol)	$\Delta H^0$ (J/mol)	R <sup>2</sup>
Unmodified	2.5127	4.5265	475.2573	-20.89059	0.774
Modified	3.874	8.3747	507.2513	-32.20844	0.9023

From the estimated thermodynamic parameters, the adsorption of aniline dye on the surface of modified and unmodified iron filling is exothermic, spontaneous and favours initial mechanism of physisorption, which was succeeded by chemisorption.

#### 4.0 Conclusion

The present study establishes the efficiency and effectiveness of the SDS-coated iron filings as low-cost adsorbent for the removal of dye from wastewater. The adsorption of the dye is significantly influenced by pH, contact time, temperature, concentration and adsorbent dosage were examined. The adsorption fitted the Temkin adsorption models and is exothermic, spontaneous and occurred through initial mechanism of physisorption. Equilibrium experimental data were tested with the Temkin and Redlich Peterson isotherms. The modified adsorbent was observed to have a higher adsorption capacity when compared with the unmodified adsorbent, as a result of the large surface area, enhanced by the SDS surfactant. Studies on batch adsorption using wastewater samples in order to remove dye ions indicate that the adsorbent has a good potential to remove the dye ions from effluents. Further studies on desorption of the dye ions from the adsorbent, could be carried out to ascertain its environmental safety.

#### 5.0 References

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