Removal of Safranin Dye from Aqueous Solution using Surfactant-Modified Carbonized Olive Stones

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ABSTRACT

The adsorption study of safranin dye by surfactant modified carbon MCOS produced from olive stone under batch adsorption process was undertaken to check the influence of varying different experimental conditions; initial safranin concentration, pH, adsorbent dosage, temperature, counter ions and time on safranin removal by our adsorbent. Physiochemical characterizations including moisture content, ash content, bulk density etc. was also undertaken. Two well known adsorption isotherms (Langmuir and Freundlich) and three kinetic models (pseudo first and second order, intra particle diffusion) were used to better understand the mechanism involved in the adsorption process.

Our collected results showed that there was an increase in adsorption capacity of MCOS as initial dye concentration, dose and number of counter ions in solution increased; pH_{pzc} was at pH 6.6 while maximum adsorption capacity was 7.30mg/g obtained at pH 7. Langmuir isotherm which implies monolayer coverage by MCOS well represented our equilibrium data with a higher correlation coefficient value of while kinetic study showed that adsorption process followed pseudo second order kinetic model. R_L and n values obtained from both adsorption isotherms used indicates a favorable adsorption process. The spontaneity and exothermic nature was confirmed by negative $\Delta G°$ and $\Delta H°$ values, though spontaneity reduced as temperature increased. Hence, MCOS can serve as an ecofriendly and cheap alternative for removing safranin from industrial waste effluents.

Keywords: Safranin, activated carbon, adsorption, olive stones

ÖZ

Safran boyasının yüzey aktif madde modifiye edilmiş karbonize zeytin çekirdeği MCOS tarafından emilimi üzerine yapılan çalışmada, başlangıçtaki safran konsantrasyonu, pH değeri, emici dozajı, sıcaklık, karşı iyonlar ve safranın kullandığımız emici tarafından adsorbe edilmesi için gereken süre gibi deneysel koşulların adsorpsiyon üzerindeki etkisi kontrol edilmiştir. Nem içeriği, kül içeriği, yığın yoğunluğu gibi fizyokimyasal nitelemeler de üstlenmiştir. Adsorpsiyon işleminin mekanizmasını daha iyi anlayabilmek içi, iki iyi bilinen adsorpsiyon izotermi (Langmuir ve Freundlich) ve üç kinetik modeli (yalancı birinci ve ikinci dereceden, partikül içi difüzyonu) kullanılmıştır.

Elde edilen sonuçlar; başlangıçtaki boya konsantrasyonu, çözeltideki doz ve karşıt iyon sayısı arttıkça, MCOS'un adsorpsiyon kapasitesinde bir artış olduğunu göstermiştir; pH değeri 7 iken, maksimum adsorpsiyon kapasitesi 7.30mg / g olarak elde edilmiş, ve pH_{pzc} değerinin pH 6.6 olduğu gözlemlenmiştir.

Bu çalışmada, adsorpsiyon prosesinin yalancı ikinci dereceden kinetik modeli izlediğini göstermekle birlikte, MCOS tarafından tek katmanlı kapsama alanını ifade eden Langmuir izotermi, denge verilerimizin daha yüksek bir korelasyon katsayısı değeri ile temsil edildimiştir. Kullanılan her iki adsorpsiyon izoterminden elde edilen R_L ve n değerleri, elverişli bir adsorpsiyon olayını gösterir. Sıcaklık arttıkça spontaneliğin azalmasına rağmen, spontanelik ve ekzotermiklik, negatif $\Delta G°$ ve $\Delta H°$ değerleri ile teyit edilmiştir. Bu nedenle, MCOS, endüstriyel atık çıkışlarından safran giderimi için çevre dostu ve ucuz bir alternatif olarak hizmet verebilir.

Anahtar Kelimeler: Safran, aktif karbon, adsorpsiyon, zeytin çekirdeği

DEDICATION

This thesis is dedicated to my parents; Justice Umar Muhammad Dutse and Hajiya Khadija Umar for their spiritual, moral and financial support towards my entire educational career. May Almighty sustain them from all evil, increase their health, bless their life and grant them with paradise Ameen.

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INTRODUCTION

1.1 Environmental issues

Numerous industries make use of dyes for their industrial processes thereby producing high quantities of colored waste water which is sometimes released into the environment untreated and becomes a major source of environmental pollution (Pereira et. al., 2006; Huo et al., 2013). Even at very low concentrations, the presence of these dyes in water is very displeasing because of their color which is visible to humans (Al-Degs et al., 2000). Many of these dyes also contain recalcitrant organic molecules that are toxic, stable to light, carcinogenic and inhibit light penetration into water which may have adverse effects on biological processes occurring in water (Mohammadi et al., 2011).

Safranin also known as Basic Red 2 ($C_{20}H_{19}N_4Cl$) belongs to the quinone-imine group and is one of the oldest known synthetic cationic dyes. It is used as a food additive; to flavor and color candies and cookies. It also finds a wide range of applications in the textile industries to dye various materials like wool, tannin, blast fibers etc. (Shah, 1998). Several health defects have been associated with safranin (Rejniak and Piotrowska, 1966; Gupta et al., 2006). As clean water is important to our existence, it is imperative to eradicate safranin from industrial wastewater bodies before release into the environment.

In recent times, numerous techniques have been proposed for waste water treatment and recycling. These methods; adsorption (Coro and Laha, 2001), electrocoagulation and electrocoagulation/flotation (Emamjomeh and Sivakumar, 2009), oxidation (Perez et al., 2002), advanced oxidation process (Sanchez et al., 1998), ion exchange (Dabrwoski et al., 2004) etc. are available to treat industrial wastewater. Adsorption exhibits several advantages when compared to all other methods because it has been found to be a reasonably cheap and energy conserving process, effective for the removal of a wide range of pollutants, easy to operate and recover etc. (Mahvi et al., 2009; Iram et al., 2010; Ali and Gupta, 2007; Amin, 2009).

One of the most widely used adsorbent in waste water remediation due to its ability to remove various pollutants is activated carbon (AC). AC has a large surface area and pore volume with a broad pore size distribution that makes it efficient and effective in the adsorption process (Gupta et al., 2011). However, there are some shortcomings encountered in the use of these commercially produced activated carbons. These include; difficulty to regenerate and reuse the AC, high cost of producing conventional ACs and the management of exhausted adsorbent after use (Gupta et al., 2012). Researchers are now investigating the adsorptive potential of applying low cost, ecofriendly, renewable and cheap materials to serve as precursors for production of commercial ACs (Baccar et al., 2010).

In line with this trend, our work focuses on the use of olive stone which is an agricultural waste in olive oil processing as a cheaper and renewable precursor to producing commercial AC.

1.2 Aim and objectives of research

1.2.1 Research aim

The main aim of carrying out this study is to prepare carbonized olive stone using a cheap and renewable waste (olive stone), modify it with an anionic surfactant sodium lauryl sulfate (SLS) and use it under laboratory simulated conditions to adsorb safranin from aqueous solution.

1.2.2 Objectives of this study are;

i. To optimize performance of carbonized Olive Stones by modifying it with SLS.

ii. To access the adsorptive potential of the as-prepared adsorbent.

iii. To determine the effect of different experimental parameters like solution pH, counter ions, dosage, time etc. on adsorption efficiency of the prepared adsorbent.

iv. Finally, to investigate and use the most appropriate isotherm(s) and kinetic model(s) to explain the adsorption mechanism.

Chapter 2

LITERATURE REVIEW

2.1 Olive tree

The olive tree is one the oldest known cultivated tree in the world and according to reports; about 97% of current olive oil cultivation in the world is done in the Mediterranean countries with 90% of olives harvested used mainly to produce oil (Uylaser and Yildiz, 2014). The origin of the tree itself is not known and has been subject to a lot of debate with some believing it was discovered in Africa while others say the origin can be traced back to 5,000 years ago in ancient Persia and Mesopotamia (kapellakis et al., 2008). Different industrial methods depending on the region are used to process olives. Both the fruit and oil contain several phenolic compounds that give them antioxidant properties which make it nutritional and medicinal when consumed (Uylaser and Yildiz, 2014). Olive stone is a by-product obtained in large amounts from olive oil production and has no real economic value; hence there is ongoing research to find other uses for this by-product (Calero et al., 2016).

2.2 Composition of olive stone

Olive stone OS is a lignocellulosic material. Chemical composition of OS and its husk show that cellulose (31.9% and 36.4%), Hemicellulose (21.9% and 26.8%) and lignin (26.5% and 26.0%) are the main components though there are small amounts of fats (5.53% and 1.01%) and protein (3.20% and 1.29%) also (Heredia et. al., 1987). Characteristics of OS and activated carbon produced using olive stone as precursor (OSAC) were determined in a previous study and are shown in Table 1 (Tamer et al., 2013).

Table 1: Properties of OS and OSAC

Physical properties	OS	OSAC
Particle size (mm)	2-4.75	2-4.75
Particle density (t/m^3)	1.24	0.8
Bulk density (t/m^3)	0.596	0.22
Specific gravity	1.24	0.8

2.3 Application of olive stone

This section briefly describes studies previously undertaken to identify different uses of OS. Studies by several researchers have identified the use of OS as an adsorbent to remove several heavy metals such as Ni^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} from water (Calero et al., 2006; De Catro et al., 2004; Fiol et al., 2006; Bla’zquez et al., 2006). It has also been used as filler in the plastic industries both to counter the impact of the environment on plastics and to promote clean technologies and recycled products. Incorporating OS with polymers to form composite materials would aid the biodegradability and form new thermoplastic polymers with unique properties (Siracusa et al., 2001). The cosmetics industry also makes use of OS as an additive to aid removal of old dead skin cells in their products i.e. exfoliation (Cosmoliva and Korres 2007). Numerous research has also been undertaken using OS as a cheap precursor to make AC to treat industrial effluents though none has seen by the author used the same idea of our thesis work (Perez et al., 2006; Sheik et al., 2004; Stravopoulos and Zabaniotou, 2005; Baccar et al., 2015; Hazzaa and

Hussein, 2015). Figure 1 below shows natural olive stones and AC prepared from OS at different temperatures. Other reported uses of OS include as abrasive, solid fuel and source of phenol formaldehyde resin (Dawson 2006; Ricardez et al., 2003; Rodriguez et al., 2008).

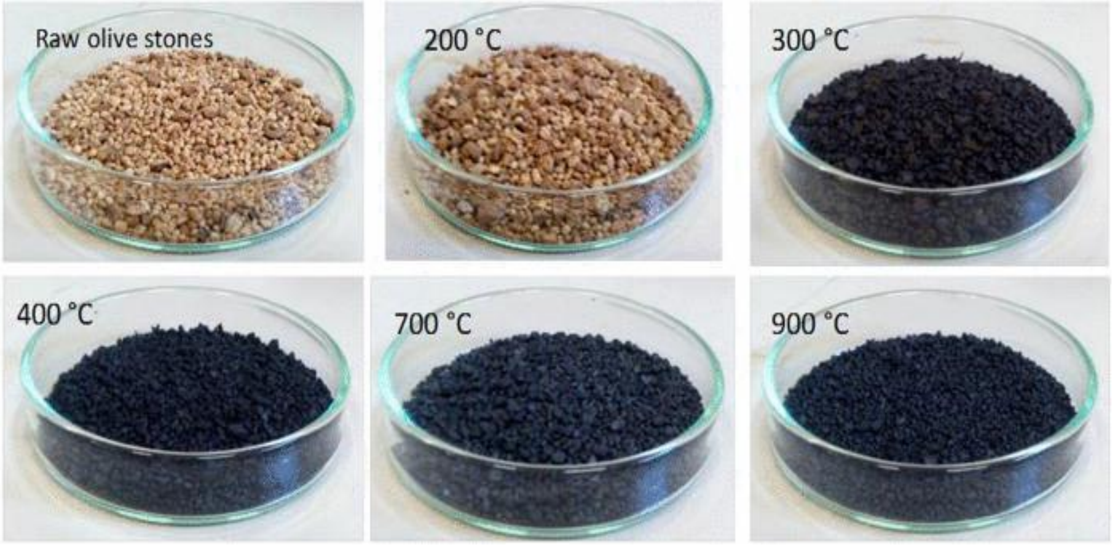

Figure 1: olive stones and activated carbon (COS) at different temperatures such as 200, 300, 400, 700 and 900^{o}C
Source: (www.wikipedia.olivestone.com)

2.4 Activated carbon

AC are thermally stable, porous and large surface area adsorbents prepared from various carbonaceous materials. In fact, virtually any carbonaceous material can serve as a precursor for making AC (Crini, 2006). They can either be produced via chemical (impregnating chemicals e.g. $ZnCl_2$, NaOH, HNO_3 etc. and carbonizing) or physical activation using steam or Carbon dioxide. AC can now be tailor made for different functions since the porosity characteristics such as shape of pore, pore size distribution etc. and surface chemistry can be altered by the type of precursor used, activation method and conditions used (Kilic et al., 2012). To overcome some of the challenges faced with using commercial activated carbon, recent research is now geared towards finding cheaper materials to serve as source of carbon to make AC. Also, surface modification using surfactants can significantly enhance the adsorption capacities of AC (Hou et. al., 2013). AC is now used in many industries; food, chemical, water treatment, pharmaceutical industries, in recovering metals, catalysis etc.

Numerous precursors: rice husk, coconut shells and wood (Polido-Novicio et al., 2001), peach stones (Galiatsatou, et al., 2016), almond shells (Iniesta et al., 2001), plum stones (Gierak, 1996), palm oil shells (Hashim, 1994), viscose fibre based materials (Rodriguez Reinoso et al., 1994), coal (Li and lin 1999), cane bagasse (Bernardo et al., 1997), aromatic polyimide films (Doyama et al., 2001), esparto grass (Doyama et al., 2001) used tires (Helleur et al., 2001) and olive stones (Overend and Chornet, 1999) etc. have been used to prepare AC.

2.5 Safranin dye

Safranin is a water-soluble dye that finds a wide range of applications in many industries today. In fact, it falls into the category of the frequently used cationic dyes in several industries (Rani et al., 2015). Figure 2 depicts the structural formula of safranin:

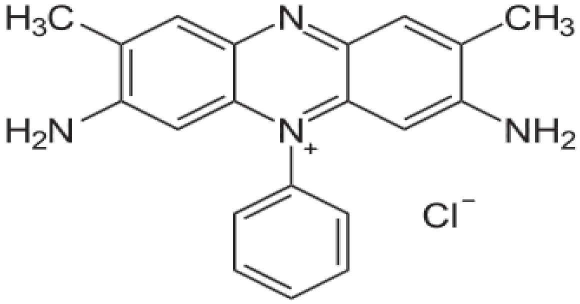

Figure 2: chemical structure of safranin dye
• Molecular weight: 350.84g/mol

2.5.1 Application of safranin dye

Safranin can be used as a biological stain in histology and cytology researches (Moawed and Abulkibash, 2012). It also finds a wide range of applications in the food, paper and textile industries.

2.5.2 Effects of safranin dye

Long term human exposure to this dye usually causes respiratory tract and skin irritation (Gupta et al., 2006). Other adverse effects of safranin to humans include causing diarrhea, vomiting and nausea (Rejniak and Piotrowska, 1996). As earlier said, the dye when present in water leads to pollution and makes water habitat unfit for aquatic life (Preethi et al., 2006). In worse case scenarios, the harmful impacts of this dye can be felt by future generations since it could result in gene mutation and birth defects (Mahmoud et al., 2016).

2.6 Treatment technique: adsorption

Adsorption is the increase in the amount/concentration of one component known as adsorbate on the surface (of adsorbent) or the interface between two phases (Gupta et al., 2012). It occurs at the interphase between the solid and liquid thereby reducing the concentration of the pollutant (adsorbate) in solution.

Four-stage adsorption mechanism proposed to explain dye adsorption is shown below (Sivakumar and Palanisamy, 2010);

Stage I: Bulk Diffusion i.e. dye molecules diffuses from the solution towards the adsorbent.

Stage II: Pore diffusion involving the adsorbate movement through adsorbent boundary layer at the adsorption interface.

Stage III: Monolayer sorption of dye molecules involving adsorption on single layer of adsorbent.

Stage IV: Multilayer adsorption of dye molecules involving adsorption in more than single layer of adsorbent.

2.6.1 Classes of adsorption

There are two classes of adsorption depending on the type of forces involved, enthalpy and activation energy of the adsorption process (Nhatasha, 2006).

Table 2: Physical and chemical adsorption

	Physical	Chemical
Force	Van der Waal	Covalent
Enthalpy (KJ/mol)	Low (0-40)	High (80-400)
Activation Energy (KJ/mol)	Low (5-40)	High (40-800)

2.6.2 Factors affecting adsorption

Adsorption efficiency is affected by many factors. They include pore size, degree of ionization of adsorbate, adsorbent affinity for adsorbate, contact time, adsorbate solubility, solution pH, ionic strength, agitation speed, adsorbent dosage and size etc. These factors either increase or reduce the rate of adsorption process and efficiency. For example, decreasing particle size of adsorbent was found to increase the amount of dye absorbed and adsorption efficiency by several researchers at equilibrium (Ali et al,. 2017; Preethi et al., 2006; Barka et al., 2013) while another research found that it had no effect (Taha et. al., 2011). Another good example is the impact of increasing ionic strength of dye solution by adding salts. Chieng and colleagues found that on adding KNO_3 to Rhodamine solution, the % removal increased while Lim in their own studies found the exact opposite (Lim et al., 2014).

2.7 Adsorption isotherms

Adsorption isotherms are applied by measuring the amount (at a fixed temperature) of adsorbate present in the solution before and after adsorption is carried out (Crini and Badot, 2008). It is very essential for design purposes, to determine a suitable model from different isotherm models by analyzing the equilibrium sorption data (Bharathi and Ramesh, 2013). These isotherms are divided into monolayer and multilayer isotherms before further subdivisions into 2, 3, 4 and 5 parameter equilibrium isotherm models (Saadi et al., 2015).

$$q_e = f(C_e) \qquad (1)$$

Where:

f is the function of C_e

C_e is equilibrium dye concentration in solution (mg/L)

q_e is equilibrium sorption uptake rate of adsorbent (mg/g).

Various mathematical isotherms have been formulated based on 3 fundamental approaches; kinetics, thermodynamics and potential theory (Foo and Hameed, 2010). Examples include: Langmuir, Freundlich, Sips, Toth, Flory-Huggins, Redlich-Peterson etc. These mathematical models are important because they help to identify interactions between adsorbate and surface of adsorbent e.g. adsorbent affinity, surface properties, adsorbent capacity etc. The commonly used isotherms (Langmuir and Freundlich) were applied in our study.

2.7.1. Langmuir isotherm

Langmuir isotherm is a 2-parameter isotherm model that is one of the most useful and simplest isotherms for both types of adsorption process (Saadi et al., 2015). Assumptions based on this model are shown below.

Characteristics of this model are;

1. Monolayer and homogeneous type of adsorption
2. Adsorption is at specific sites i.e. localized surface adsorption.
3. Finite capacity of adsorbent for adsorbate
4. Identical sites of adsorbent surface having same energy and affinity for adsorbent.
5. No interaction between adsorbents occupied on neighboring sites.

Mathematical expression and linearized form of this model is shown below (equations 2 and 3);

$$q_e = \frac{Q_o K_L C_e}{1+K_L C_e} \qquad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (3)$$

Langmuir plot of C_e/q_e versus Ce is used to determine the values of q_m (monolayer adsorption capacity) and K_L(Langmuir constant). Important information obtained from this isotherm is the separation factor (R_L).

$$R_L = \frac{1}{k_L C_i + 1} \qquad (4)$$

C_i is initial concentration (mgL-^{1})

Several probabilities obtained from R_L values are;

R_L greater than1: unfavorable

$R_L = 1$: linear

$0 < R_L < 1$: favorable

R_L equal 0: irreversible

2.7.2 Freundlich isotherm

This isotherm is applicable to identify multilayer adsorption.

1. Multilayer adsorption.
2. Adsorption occurs on heterogeneous surfaces.
3. Stronger binding sites based on their energy are first occupied by adsorbate.
4. Exponential decrease in adsorption energy on completion of the adsorption process.

Equation 5 and 6 shows the Freundlich equation and its linearized form;

$$q_e = K_F C_e^{1/n} \qquad (5)$$

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (6)$$

q_e and C_e used in the equation are same as that of Langmuir above, n is the adsorption intensity and K_F is the Freundlich constant known as adsorption coefficient. Both values are determined by plotting log q_e against log C_e. Value of n greater than unity indicates favorable adsorption process while 1/n greater than unity shows cooperative adsorption (Fytianos et al., 2000).

2.8 Adsorption kinetics

Kinetic models are very useful in examining the mechanism (such as chemical reaction, diffusion mechanism and adsorption surface) controlling the adsorption process. Three kinetic models were applied to determine the rate and mechanism of adsorption.

2.8.1 Pseudo first and second order kinetic models

The first order model proposed by Lagergren in 1898 assumes that difference in adsorbent concentration at equilibrium or saturation is directly proportional to uptake of adsorbate while second order kinetic proposed by Ho and McKay says the rate limiting step in adsorption is chemisorption (Ali et al., 2017). The equations for both models are depicted below.

$$\log\,(q_e - q_t) = \log q_e - k_1 t \qquad (7)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{qe^2 k_2} \qquad (8)$$

Where;

q_e = amount of dye adsorbed at equilibrium

q_t = amount of dye absorbed at specific time intervals

k_1 and k_2 = pseudo first and second order rate constant

Graph of log (q_e-q_t) and t/q_e versus t is used to determine the calculated values of q_e and rate constants k_1 and k_2.

2.8.2 Intraparticle diffusion model

This model is represented by equation 9 below and is used to describe the nature of rate limiting steps in batch system to determine the properties of the solute and adsorbent (Weber and Morris, 1962).

$$q_t = C + k_p t^{1/2} \qquad (9)$$

Where;

K_p = constant related to intra particle diffusion model ($mgg^{-1}min^{-1/2}$)

$t^{1/2}$ = diffusion time ($1/min^{1/2}$)

q_t = adsorption capacity of adsorbent at pre-determined time (mgg^{-1})

Plotting q_t against $t^{1/2}$ will give values of K_p and constant, C. This plot can be used to determine multi-linearity i.e. if two or more stages occurred during adsorption process and whether intraparticle is the rate determining step (Feng et al., 2001).

Chapter 3

EXPERIMENTAL

3.1 Materials and equipment

Olive Stones used as precursor for carbonized olive stones (COS) was collected from an olive oil producing industry. Safranin dye was purchased from Fluka while anionic surfactant used to modify AC sodium lauryl sulphate; SLS and hydrochloric acid were both purchased from BDH, England. Absolute ethanol, sodium hydroxide, sodium chloride and potassium nitrate was obtained from Aldrich.

Equipments used in this study include; Water proof pH meter (HANNA HI 98127), electronic balance, mechanical stirrer (Heidoph MR Hei standard), mechanical agitator (SL350), centrifuge (NF 815), UV-spectrophotometer (T80+ Version 5.0), muffle furnace (Nabertherm GmbH model) and drying oven (Binder GMPH).

3.2 Preparation of carbonized olive stones using olive stones (COS)

Olive stones OS previously collected from the olive oil producing industry was cleaned several times with ordinary tap water and then distilled water to remove all traces of dirt and unwanted particles before drying it at 70°C for 48 hours using a conventional oven. Carbonization of OS was achieved by putting 100g of OS into a muffle furnace and heating it at a heating rate of 5°C per minute till we attained required carbonization temperature (500°C). On attaining this required temperature, the sample COS was left for another 30 minutes for complete carbonization. Afterwards, the product obtained COS was crushed using a mechanical blender and sieved with the aid of a 500μm sieve to get uniform sizes. COS was then washed several times using ethanol and hot distilled water. Finally, mass of COS was measured to determine our yield.

3.3 Modification of COS using SLS

Carbonized olive stones obtained from olive stones COS was modified using sodium lauryl sulfate by a similar method found in literature (Hou et. al., 2013). 20g of OSAC was added to 100mL of 0.05M SLS (2g of OSAC per 10mL SLS solution) and stirred at 250 rpm overnight at ambient temperature. Product obtained MCOS was filtered, washed several times using hot distilled water till the pH of our filtrate became neutral. The product was then transferred into the oven and dried at 70°C until a constant weight was obtained. MCOS was kept in a petri dish until further use.

3.4 Batch adsorption studies

The adsorption studies were performed using the batch system to better understand the effect of varying some experimental conditions such as; initial safranin concentration (20 - 100mg/L), adsorbent dosage (0.1g, 0.25g, and 0.5g), pH (2-10), temperature (25, 35 and 50^0 C) and time. Dye solutions of known concentrations containing a known amount of adsorbent were put in 250mL Erlenmeyer flasks under constant agitation speed of 150rpm. The flasks were agitated to allow for adequate contact between the MCOS and the safranin solution. Solution pH was fixed to the desired pH value by adding either one of HCL or NaOH (0.1M). Concentration of safranin remaining at pre-determined time intervals was analyzed by taking the absorbance of the samples after centrifugation at 2000rpm for 10 minutes using a UV-visible spectrophotometer (517nm). Finally, amount of safranin dye absorbed at equilibrium q_e and removal efficiency MCOS was calculated from Equations 10 and 11.

$$q_e = (c_i - c_e)\frac{v}{w} \qquad (10)$$

$$\% \text{ Removal} = \left(\frac{(c_i - c_e}{c_i}\right) \times 100 \qquad (11)$$

C_i: initial safranin concentration (mgL^{-1})

C_f: final safranin concentration (mgL^{-1})

V: volume safranin dye (L)

w: mass of MCOS (g)

3.5 Adsorbate preparation

Safranin stock solution (500mg/L) was prepared by dissolving 500mg of safranin in 1L deionized water. Serial dilutions of our stock solution was used to prepare working solutions of different concentrations. The Calibration curve of safranin dye was done by preparing six different dye concentrations (2, 4, 6, 8, 10 and 30mg/L) and the absorbance of each solution was measured. Calibration curve shown in Figure 3 was plotted to obtain the absorbance-concentration profile and used to determine unknown dye concentration.

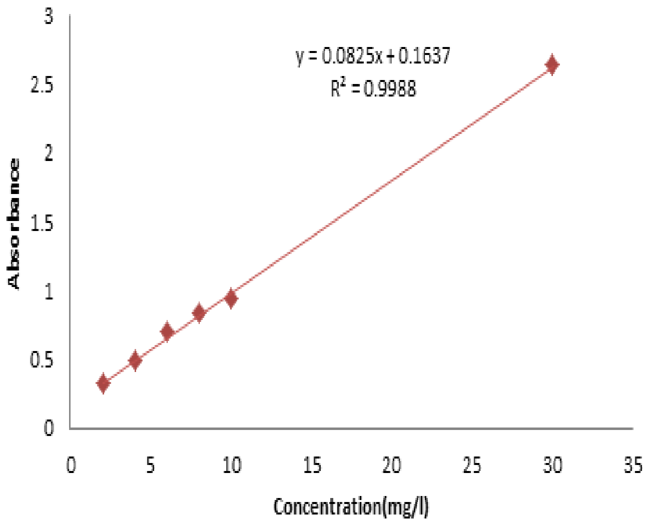

Figure 3: Calibration curve of safranin

3.6 Physiochemical characterization of MCOS

The zero point charge (pH_{pzc}) of OSAC was investigated using pH adjustment. Briefly, 50mL of 0.1M NaCl solutions was put in several conical flasks. The pH of each solution in the conical flasks was adjusted from 2-10 by adding either a 0.1M solution of HCl or NaOH. To each separate flask, 100mg of MCOS was added and agitated for 24hrs before final solution pH was taken. A plot of initial versus final pH was used to determine the pH_{pzc} (where pH initial is equal to pH final) of MCOS. Physiochemical characterizations such as yield percentage, weight loss, moisture and ash content, bulk density etc. was also undertaken.

Chapter 4

RESULT AND DISCUSSION

4.1 Characterization

Physiochemical characteristics of the adsorbent was studied and parameters such as bulk density, yield%, weight loss%, moisture and content%, pH_{pzc} and pH values are given in Table 4 below.

Table 3: Physiochemical characterization of MOSAC

Adsorbent	**Parameters**	**Values**
MCOS	Yield (%)	29.90
	Weight loss (%)	70.10
	Bulk density(g/cm^3)	0.494
	Moisture content (%)	1.00
	Ash content (%)	2.00
	pH_{pzc}	6.60
	pH	7.00

The plot of initial and final solution pH of MCOS is shown in Figure 4. The pH_{pzc} of MCOS was found to be 6.6. When the pH is greater than 6.6, the surface of MCOS will be negatively charged which is expected to enhance the adsorption of positively charged dye ions via electrostatic force of attraction (Asabuwa, 2014).

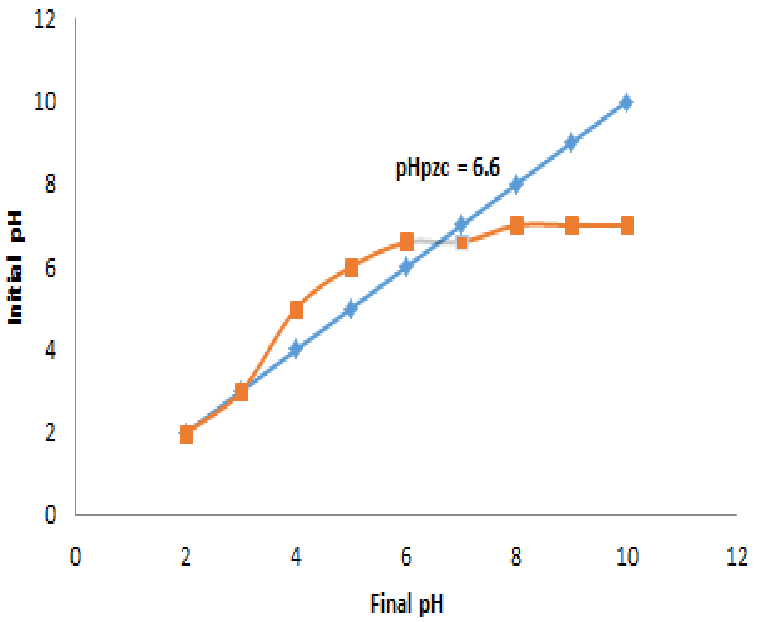

Figure 4: pH_{pzc} of MCOS

4.2 Effects of different experimental conditions on safranin removal

4.2.1 Dye solution pH

Figure 5 shows the relationship between the removal efficiency of safranin dye using MCOS and changes in solution pH. The result shows that adsorption of safranin dye on MCOS is pH dependent. Removal efficiency of safranin by MCOS increases (28.9% to 42.6%) from pH 2–6 and attains maximum removal (66.2%) at pH 7. Further increase in pH value reduced the removal efficiency of MCOS hence; pH 7 was taken as the optimum pH for adsorption. This can be explained based on the surface chemistry of MCOS. At pH lower than our pH_{pzc}, MCOS is positively charged due to presence of H^+ ions on its surface. There is an observed electrostatic repulsion between MCOS and safranin molecules which causes a decrease in removal of the dye as seen in the graph (Garg et al., 2004). When the pH> pH_{pzc}, the surface of MCOS carries a negative charge and can easily adsorb/attract the basic safranin dye molecules via electrostatic forces of attraction (Auta and Hameed, 2011). This is similar to what has been reported in a previous study (Amin, 2009).

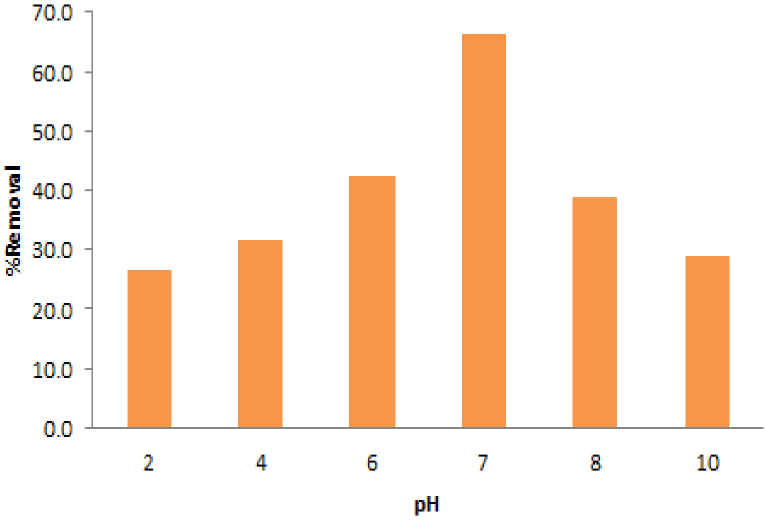

Figure 5: Effect of pH on removal efficiency of MCOS

4.2.2 MCOS dosage

Different masses of MCOS (0.1g, 0.25g, and 0.5g) were added to 50mL of 30mg/L dye concentration at pH 7 and agitation speed of 150rpm to check the effect of varying our dosage on the capacity of MCOS to adsorb/remove the dye from solution. As seen from Figure 6 below, increasing the dosage did not lead to much increase in the adsorption capacity of MCOS (2.7mgg^{-1} at 0.1g to 2.9mgg^{-1} at 0.5g) but when taking into consideration the removal efficiency as shown in Figure 7, 0.5g adsorbent had the highest removal efficiency.

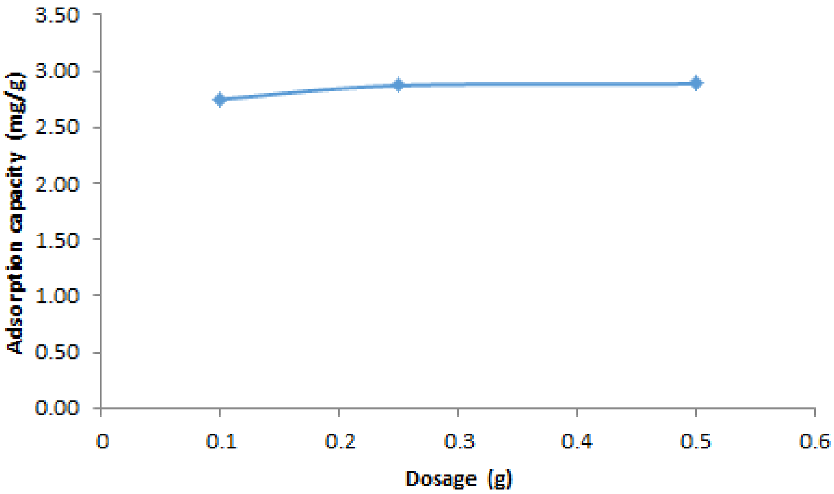

Figure 6: Effect of dosage on adsorption capacity of MCOS

The increase observed from 18% in 0.1g to about 97% in 0.5g MCOS can be attributed to the availability of more binding sites of MCOS for same volume of dye as dosage increases (Mahmoud et al., 2016). Therefore, 0.5g of MCOS was taken as our optimum dosage.

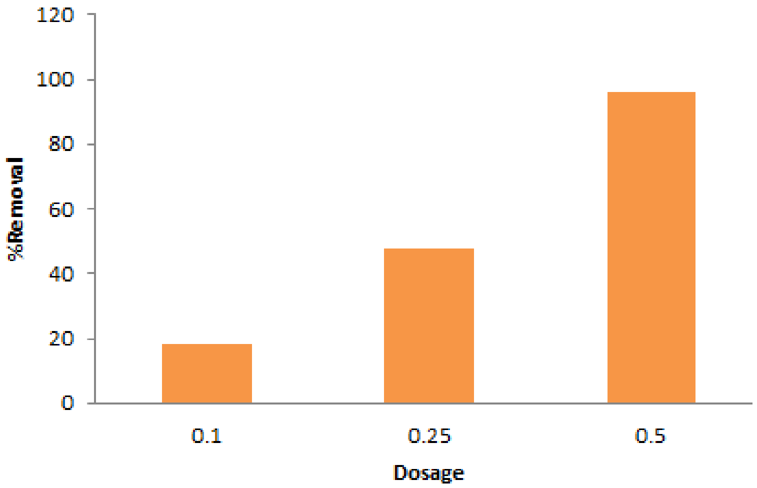

Figure 7: Effect of dosage on the removal efficiency of MCOS

4.2.3 Contact time

Efficiency and optimum removal of safranin by MCOS depends on the time used for the adsorption process. The plot of adsorption capacity (mgg^{-1}) of MCOS with respect to time is depicted in Figure 8. The presence of numerous vacant binding sites on the surface of MCOS at the beginning of the experiment led to an initial rapid uptake of dye after the first 30 minutes before proceeding at a slower rate and finally obtaining maximum adsorption after 24 hours. Similar patterns were observed for all concentrations studied. The dye at the rapid initial stage of adsorption is first of all adsorbed on the external surface of MCOS and when this surface becomes fully saturated, enters the pores of MCOS and become absorbed in the interior surface of our adsorbent (Baccar et al., 2010).. This might have led to the slight increase in adsorption we observed after 24 hours. Extending the time further did not affect the adsorption process (i.e. equilibrium was attained) so we chose a contact time of 24 hours for other experiments

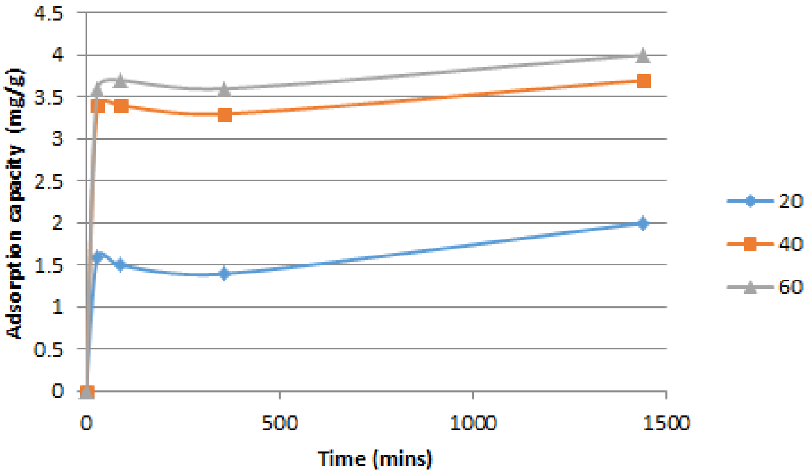

Figure 8: Effect of contact time on adsorption capacity of MCOS

4.2.4 Dye initial concentration

The influence of initial safranin concentration on the adsorption capacity of MCOS can be seen in Figure 9. Initial concentration of dye for this study was varied from 20 to 100mg/L. The Figure reveals that amount of dye adsorbed per unit mass of MCOS increases as the initial dye concentration in solution increased.

This observed increase is as a result of an increase in the driving force between the solution and adsorbent which helped to counter/overcome all mass transfer resistances and therefore enhanced adsorption (Baccar et al., 2010; Bulut and Aydin, 2006).

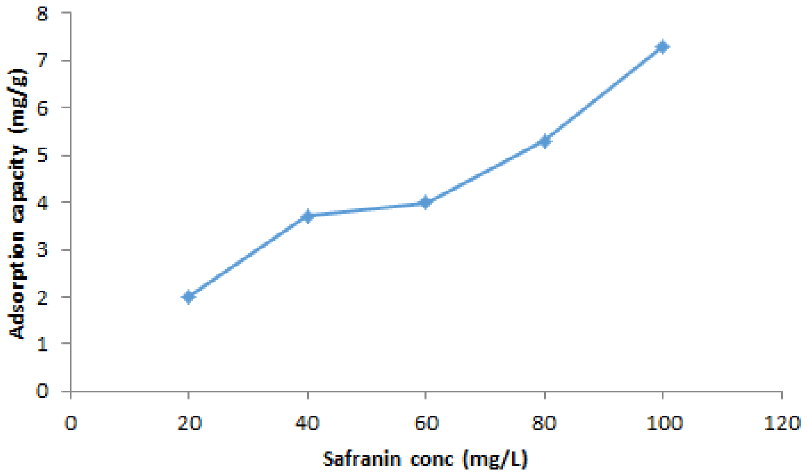

Figure 9: Effect of concentration on adsorption capacity of MCOS

4.2.5 Counter ions

Industrial effluents contain not only dyes but several other dissolved materials such as salts, metals, surfactants etc. that might affect adsorption process. The presence of these inorganic salts such as nitrates, phosphates, chlorides, sulphates etc. might affect the adsorption process via 2 possible mechanisms. It could be either through the preferential adsorption of the salts by the adsorbent or through screening between adsorbent and charged ions (Oladipo et al., 2013). In this study, experimental investigation of this effect was done by adding 0.1 and 0.5M NaCl and KNO_3 to 20mg/L dye solution under optimized experimental conditions previously determined. Figure 10 below shows that increasing the number of counter ions in solution increased the removal efficiency of our adsorbent. Hence, in the presence of counter ions, our adsorbent showed better removal for safranin.

This might be due to the aggregation of safranin molecules as number of counter ions in solution increased. Similar observation was reported by (Chieng et al., 2015). This shows that our adsorbent can be effective in real life waste water treatment.

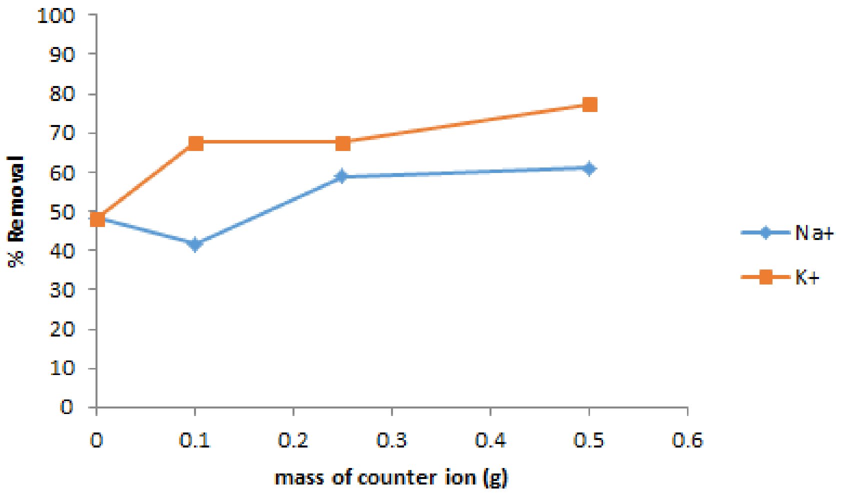

Figure 10: Effect of counter ions on removal efficiency of MCOS

4.2.6 Temperature

Any change in temperature will affect the adsorption capacity and efficiency of an adsorbent (Mahmoud et al., 2016). Increasing dye solution temperature can increase the tendency of deaggregation of dye molecules or reduce solution viscosity which will then aid the diffusion of dye molecules from the liquid phase pass the external boundary of the adsorbent into its internal pores (Karaca et al., 2008). Figure 11 shows this effect i.e. temperature on removal efficiency of MCOS. The trend observed as seen from our graph is that the removal efficiency of safranin by the adsorbent reduced as temperature increased. High removal of safranin 93% was obtained at 25°C as compared to 45.7% at 50°C. Decrease in removal efficiency of MCOS for the dye as temperature increases might be due to the impact that increasing temperature has on solubility of the adsorbate and the chemical properties of adsorbate-adsorbent (Mahmoud et al., 2016). It could also be because the dye molecules escape from the surface of MCOS as temperature increases (Sen et al., 2011). It is evident from this result that the adsorption process is exothermic.

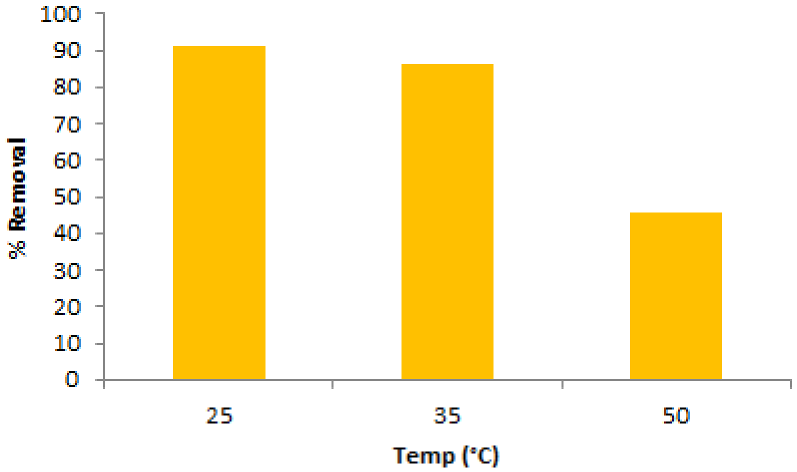

Figure 11: Effect of temperature on adsorption of safranin by MCOS

4.3 Adsorption isotherm models

The adsorption isotherm of safranin on MCOS was studied. Two commonly used adsorption isotherms were used in this study to find the adsorption capacity of safranin dye on MCOS. Applicability of the isotherm equation to adsorption data was based on comparing the R^2 values of the two models used. Both Langmuir and Freundlich plots are shown in Figures 12 and 13 while the adsorption isotherm parameters are tabulated in Table 5.

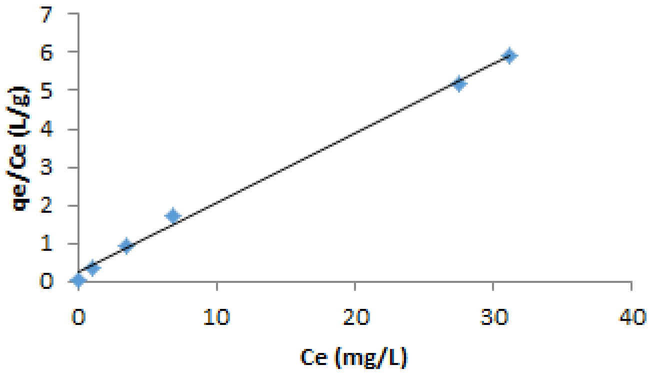

Figure 12: Langmuir plot of safranin on MCOS

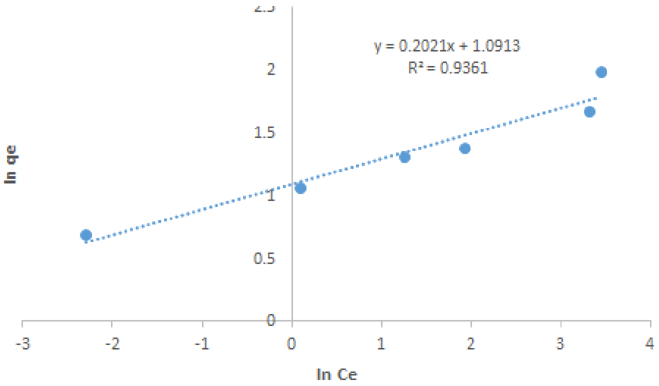

Figure 13: Freundlich plot of safranin on MCOS

As seen from the table, the R^2 value obtained from the Langmuir was higher when compared to that of the Freundlich model hence, our adsorption process obeys Langmuir isotherm model which shows monolayer adsorption. In addition, the values of R_L ranging from 0.017-0.079 and 1/n of 0.202 obtained from both isotherms indicate a favorable adsorption of safranin on MCOS.

Table 4: Isotherm parameters (Freundlich and Langmuir)

Isotherm	**parameter**				
Langmuir	T(K)	q_m (mgg^{-1})	KL (Lmg^{-1})	R_L	R^2
	298	7.46	0.583	0.017- 0.079	0.9968
Freundlich	T(K)	K_f(mg/l)(L/mg$^{1/n}$)		1/n	R^2
	298	2.9		0.202	0.9361

4.4 Adsorption kinetics models

Three kinetic models as earlier said were applied in our study to explain the mechanism of adsorption and interaction between safranin and MCOS. Figures 14-16 below show the plots obtained from each model.

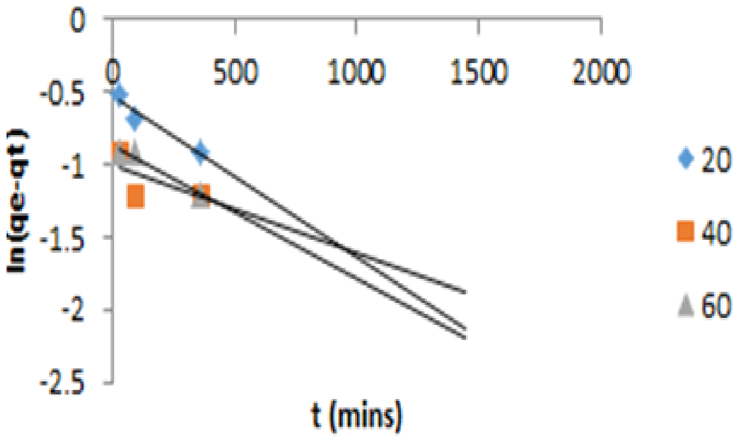

Figure 14: Pseudo first order kinetic plot of MCOS

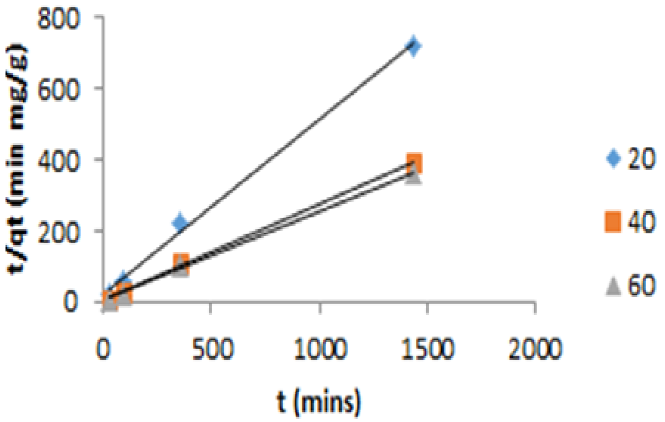

Figure 15: Pseudo second order kinetic plot of MCOS

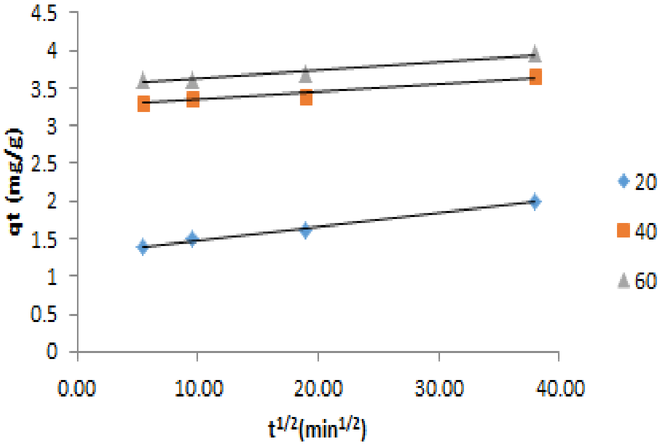

Figure 16: Intra-particle plot of MCOS

Kinetic parameters determined from the kinetic plots above were calculated and the results are tabulated in the Table below. As shown in the table, pseudo second order model has highest correlative coefficient R^2 with values ranging from 0.9967-1.000 when compared to the other two models. Also, the experimental adsorption capacities, q_{eexp} (2.00-7.30mg/g) are very close to the calculated adsorption capacities q_{ecal} (2.05-7.03mg/g). Hence, adsorption system obeys the pseudo second order model.

According to Weber and Morris, for intra particle diffusion to be our rate limiting step, our plot of qt versus $t^{1/2}$ in Figure 16 should be a linear one that passes through the origin (Weber and Morris, 1963). As seen from the Figure, the plot does not start from the origin which is indicative that the process is possibly controlled by other mechanisms. The magnitude of C (where C represents intercept of our plot) tells us how thick the boundary layer between adsorbent and adsorbate is. Large intercept values imply that the boundary layer is high. If intercept C is higher than 0, the adsorption process is said to be complex and comprise of more than one stage but when C is 0, intra-particle diffusion is the rate controlling step (Iriarte-Velasco et al., 2011). The C values increases as initial safranin concentration increases and $C \neq 0$ as shown in the table. This also confirms our earlier assumption that intra-particle diffusion is not the only rate determining step.

Table 5: Adsorption kinetic parameters

	Safranin concentration				
	0.02g/L	0.04g/L	0.06g/L	0.08g/L	0.1g/L
Pseudo First Order					
$q_{e,exp}(mg/g)$	2.00	3.70	4.00	5.30	7.30
$q_{e,cal}$ (mg/g)	0.59	0.36	0.42	0.45	0.39
K_1 (min^{-1})	0.0011	0.0006	0.0009	0.004	0.0019
R^2	0.916	0.4102	0.9709	0.9993	0.9367
Pseudo second order					
$q_{e,cal}$ (mg/g)	2.05	3.67	3.98	5.02	7.03
K_2 $(1/min)$	0.022	0.073	0.072	0.925	0.945
R^2	0.9967	0.9995	0.9994	0.9999	1.0000
Intraparticle diffusion					
Kp $(mgg^{-1}min^{-1/2})$	0.018	0.0105	0.0113	0.0117	0.0102
C	1.3006	3.2408	3.5137	4.8649	6.8921
R^2	0.9862	0.9672	0.9679	0.9809	0.7438

4.5 Thermodynamics analysis

The impact of temperature on the removal of safranin by MCOS was investigated by conducting the experiments at three varying temperatures 25, 35 and 50°C at constant safranin concentration and used to carry out a thermodynamic analysis. Thermodynamic parameters (change in entropy and enthalpy) were determined from the plot using equation 12 known as the Van’t Hoff equation.

$$In\ K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (12)$$

Where;

$K_c = C_a/C_e$

C_s is the concentration in mg/L of dye on adsorbent while C_e is equilibrium dye concentration in solution.

Figure 17 shows the Van't Hoff plot for our study. The plot was used to find from the intercept and slope which represent the change in entropy and enthalpy values respectively. ΔG° was also determined using equation 13.

$$\Delta G^\circ = -RT\ InK_c \qquad (13)$$

Where the universal gas constant represented as R is $8.314 Jmol^{-1}K^{-1}$ and absolute temperature T (Kelvin).

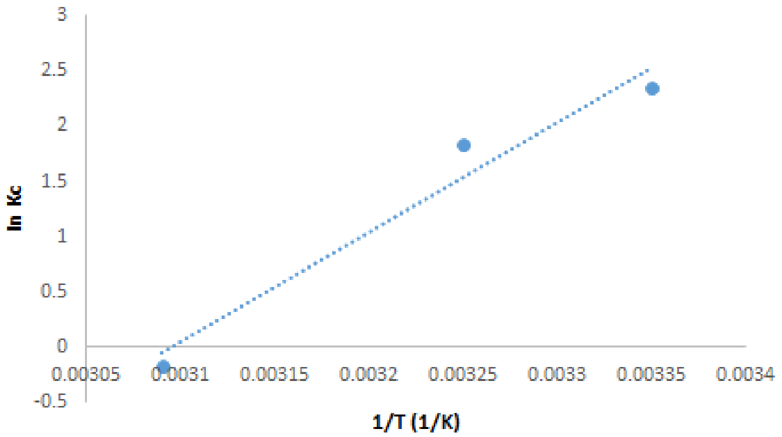

Figure 17: Van't Hoff Plot for safranin adsorption by MCOS

ΔH°, ΔS° and ΔG° values obtained in our study are listed in Table 7. Value of ΔG° determined in our study was negative. This simply shows that the process was feasible and thermodynamically spontaneous though increasing ΔG° as temperature increases shows that spontaneity reduced as temperature increases. The negative ΔS° value implied disorderliness at the interphase was very low while negative ΔH° value suggests the adsorption was exothermic (Seema et al., 2015).

Table 6: MCOS thermodynamic parameters obtained for safranin removal

ln Kc	Ca	Ce	ΔH° (KJ/mol)	ΔS° (J/molK)	ΔG° (KJ/mol)	Temp (kelvin)
2.34	36.5	3.5	-82.46	-255.3	-5.79	298
1.83	34.5	5.5			-4.69	308
-0.17	18.3	21.5			0.46	323

Chapter 5

CONCLUSION

The adsorptive potential of anionic surfactant modified activated carbon using olive stone as precursor (MCOS) for adsorption of safranin dye in aqueous media was evaluated in our research work. The effect of varying several experimental conditions of the adsorption process and adsorbent physiochemical characteristics was also studied. The following results were determined after completion of this research work;

i. Maximum adsorption occurred at pH 7.

ii. The ability of MCOS to remove the dye from solution increased as initial dye concentration and counter ions in solution increased but reduces as temperature increased.

iii. Removal efficiency of MCOS increases as dosage increased. Optimum dosage used for this study was 0.5g.

iv. Adsorption equilibrium was well fitted to experimental data using the Langmuir isotherm due to high value of correlative coefficient R^2 (0.9968) which shows monolayer adsorption on the sorption sites of MCOS.

v. R_L and 1/n values supported favorable adsorption of safranin by MCOS.

vi. Thermodynamic study shows that adsorption of safranin by our MCOS is a spontaneous and exothermic process.

vii. MCOS, as discovered in our study displayed good adsorptive properties for safranin dye and can be a suitable alternative adsorbent to treat waste water rich in safranin.

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