Bio-based Adsorbent for Removal of Safranin Dye from Aqueous Solutions

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ABSTRACT

The potential of dried (CC) and anionic surfactant modified (MCC) prickly pear cactus cladodes as an ecofriendly and low cost material for safranin removal from simulated wastewater was evaluated. Effect of several operational parameters including; pH of safranin solution, counter ions, dosage etc. on the adsorption capacity and removal efficiency of safranin was investigated. Physiochemical characterization of the adsorbents was also undertaken. The experimental data obtained was then tested using different mathematical adsorption isotherms and kinetics.

Results obtained in this study found that the modified cactus samples MCC performed better than the unmodified one CC in all experiments conducted. The adsorption capacity of both samples towards safranin decreased with increasing concentration of competing ions, ionic strength and dosage. Kinetic studies followed the pseudo second order kinetic model; intraparticle diffusion was involved but wasn’t the rate determining step while equilibrium process was well represented by the Freundlich model for MCC. Positive $\Delta H°$ (30.4 and 9.2 KJ/mol) and $\Delta S°$ (109.7 and 47.6 J/mol K) values coupled with negative $\Delta G°$ for both CC and MCC determined from the thermodynamic study confirmed the process to be a spontaneous, endothermic and random disorderly process. Generally, adsorption of safranin by CC and MCC proved to be effective and suggests that they can be used as an alternative adsorbent for wastewater rich in safranin.

Keywords: cactus cladodes, adsorption, safranin, waste water treatment

ÖZ

Anyonik yüzeyaktif madde modifiye ve kurutulmuş çevre dostu ve düşük maliyetli materyal olan babutsa yaprağı, yapay atık sulardan safranın gideriminde incelenmiştir. safranın pH değeri, anti-iyon, dozaj gibi parametrelerin, safranın adsorpsiyon kapasitesi ve giderim etkinliği üzerindeki etkisi araştırılmıştır. Aynı zamanda, sorbentlerin fizikokimyasal nitelendirilmesi de tetkik edilmiştir. Deneysel veriler, farklı matematiksel adsorpsiyon izotermi ve kinetiği kullanılarak test edilmiştir. Bu araştırmada elde edilen sonuçlar, modifiye edilmiş babutsa örneklerinin, modifiye edilmemişlere kıyasla daha iyi performans göstermektedir. Her iki örneğin de safran adsorpsiyon kapasiteleri, iyonların konsantrasyon artışı, dozajı ve iyon gücü ile ters orantı göstererek azalmıştır.

MCC için Freundlich modeli, Kinetik; partikül içi diffüzyonu gerçekleşmiş, ancak hız belirleme basamağı

Partikül içi difüzyonun gerçekleşmesine karşın hız belirleme basamağını içermeyen ve MCC için Freundlich modeli tarafından iyi tanımlanan bu sistemde çalışmalar yalancı ikinci dereceden kinetik modele uymaktadır. eşleşmiştir

Pozitif ΔH° (30.4 ve 9.2 KJ/mol) ve ΔS° (109.7 ve 47.6 J/mol K) değerleri termodinamik çalışmalar sonuçu belirlenmiş negatif ΔG° ile hem CC hem de MCC için eşleşmiş olup; sürecin sürekli, endotermik ve gelişigüzel düzensiz olduğu teyit edilmiştir.

Safranın CC ve MCC tarafından emilmesinin genellikle etkili olduğu kanıtlanmış olup, safranca zengin atık suların absorplanmasında alternatif olarak kullanılabileceği önerilmiştir.

Anahtar Kelimeler: kaktüs yaprağı, adsorpsiyon, safran, atık su iyileştirilmesi

DEDICATION

My thesis work is dedicated, first of all, to my parents for their endless support and opportunity to get a master's degree in one of the well-known universities in the world. I will always be grateful to them for their love, care and funding, and thus, will bring all my knowledge and experience obtained to be professional in my field so they can be proud of me. Secondly, I want to dedicate this thesis to my soul mate, my inspiration, my future wife InShaAllah. Throughout the study she helped me to overcome the obstacles I faced in the education route. She also gave her moral support during the period of writing the thesis.

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INTRODUCTION

1.1 Background of study

Fast industrialization and population growth has triggered an increasing demand for synthetic dyes in several industries (Konicki et al., 2013). Thus, the application of dyes is widespread. This in turn has led to the generation of a large amount of colored industrial effluents which when discharged untreated into water bodies cause severe environmental pollution worldwide (Gupta et al., 2000). It is crucial to the surroundings to remove dyes out of aqueous effluents (Konicki et al., 2013).

Safranin is a well-known cationic dye used in the food industry to add flavor and color to candies and cookies. It is also applied in textile, paper and leather industries and also as a biological stain in researches related to histology and cytology (Moawed & Abulkibash, 2012). Safranin when present in water can pose several heath issues such as; skin, mouth, throat and tongue irritation, stomach pains leading to nausea etc. (Rani et al., 2015, Gupta et al., 2006). That said, it is of dire environmental importance to remove all traces of this toxic dye from industrial effluents before discharge into water bodies.

Numerous technologies have so far been proposed in wastewater treatment for removal of dyes. These methods include; ion exchange, oxidation process, reverse osmosis, photo-degradation techniques, nanoflitration, biodegradation, coagulation/flocculation and adsorption (Lorenc-Grabowska & Gryglewicz, 2007; Annadurai et al., 2008; Gómez et al., 2007; Barka et al., 2013). Most of these methods listed above have numerous limitations including; high cost, inability to completely remove pollutants at very low concentrations, the generation of toxic byproducts, complexity of process etc. (Fu and Wang, 2011;Mittal et al., 2009).

Adsorption has been widely used for the removal of many pollutants from industrial waste water because it exhibits several advantages over other methods such as; cost effectiveness, high efficiency and little or no release of toxic materials. Commercial activated carbon on the one hand has shown excellent results when used in adsorption processes. However, because of the high cost of preparation and regeneration, non-selectivity and ineffectiveness against disperse and vat dyes, recent research is now focused on finding inexpensive and cost effective materials that can replace activated carbon (Crini, 2006; Yagub & Sen, 2014). Some reported examples of the use of unconventional adsorbents for removal of various dyes from solutions has shown promising results (Wu et al., 2013; Anandkumar & Mandal, 2011; Preethi et al., 2006; Barka at al., 2013). For example, Wu and his colleagues prepared hydrogels and aerogels from water melon which served as the source of carbon. The watermelon biomass showed excellent results in electrochemical transportation of ions and electrolytes, and potentially can be used as adsorbent due to its 3D porous structure (Wu et al., 2013). In line with this trend, our study will focus on the potential of dried prickly pear cactus as an unconventional absorbent to treat waste water containing safranin dye.

1.2 Research questions posed in this study

a) Is it possible to convert dried prickly pear cactus into an effective absorbent?

b) What will be the effect of modifying dried prickly pear cactus with an anionic surfactant Sodium lauryl sulfate (SLS) on adsorption?

c) Can the dried and/or modified prickly pear cactus be more efficient than other reported absorbents for removal of safranin?

d) What are the operational factors we need to optimize so as to determine the maximum efficiency of our adsorbents for removal of safranin from wastewater?

1.3 Objectives of research undertaken

The main research objectives we hope to achieve in our study are to:

i. Determine the adsorptive potential of both dried and modified prickly pear cactus for removal of safranin.

ii. Identify the impacts of several adsorption conditions such as; CC and MCC dosage, dye solution pH, salinity, counter ions, temperature etc. on safranin removal from aqueous solution under laboratory conditions.

iii. Determine the amount of safranin absorbed during experimental runs.

iv. Carry out an investigation using suitable isotherms and kinetic models to better understand our adsorption mechanism.

v. Verify if the dried and/or modified prickly pear cactus can be used as alternative to existing commercial adsorbents to eradicate safranin from industrial effluents.

1.4 Limitation(s) encountered in this study

Our current study focused only on applying both the dried CC and modified MCC prickly pear cactus for the removal of safranin dye under laboratory conditions. Efficiency of the prepared adsorbents were not investigated under industrial conditions or using real waste water rich in safranin obtained from an industry. These reasons mentioned above might act as limitations to this research work.

1.5 Outline of research work

Chapter 1 will offer a simple introduction of the topic, the research aims and objectives and any limitations we might face carrying out this research work. A brief literature review will be undertaken in the second chapter which will include current knowledge and findings previously reported. Chapter 3 will focus on the experimental procedures we used while the results obtained from these adsorption experiments will be discussed in the fourth chapter. Finally, the last chapter will give conclusion and recommendation(s) based on our research study.

Chapter 2

LITERATURE REVIEW

Several industries make use of dyes in their production processes and this has led to the generation of colored wastewater which when released into the environment untreated pose serious environmental problems (Gupta et al., 2000). Recently, adsorption has received immense attention from researchers worldwide as a control technology to treat various water pollutants hence, the need to develop eco-friendly and cheap adsorbents for waste water treatment (Barka et al., 2013). Recent research has focused on using cheap, non-conventional materials from different sources such as; industrial and agricultural by-products/waste, natural materials like zeolites,clay etc. and biomass as alternatives to commercial activated carbon due to its numerous shortcomings (Crini, 2006).

2.1 Dyes

The number of synthetic dyes produced yearly for industrial use has been increasing rapidly (Lim et al., 2014). There are more than 100,000 synthetic dyes now sold worldwide today (Gupta 2006; Ramírez-Montoya et. al., 2014). Two main classification of synthetic dyes is based on either their chemical structure (e.g. azoic, antraquinone, triphenylmethyl, phthalocyanine dyes etc.) or mode of application to substrate (acidic, basic, reactive, mordant, vat dyes etc. (Iglesias et al., 2013; Forgacs et al., 2004).

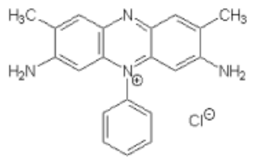
Most of these dyes possess complex chemical structures. They are also non-biodegradable and are not easily removed from waste water using conventional methods (Stawinski et al., 2016). They are known to contain complex recalcitrant organic molecules that are toxic and harmful to animals living inside water, are mutagenic and carcinogenic (Hameed, Din & Ahmad, 2007; Preethi et al., 2006). Also, these dyes impede light penetration which affects aquatic biota (Gomez et al., 2012). Hence, there is a need to eradicate these dyes from water bodies.

2.1.1 Safranin

Safranin (3,7-diamino-2, 8-dimethyl-5-phenyl chloride; $C_{20}H_{19}N_4Cl$) is among the oldest known and widely used synthetic cationic dye**.** It is a water-soluble dye that is mainly used in the food industry to flavor and color candies and cookies (Gupta et al., 2006). It is also used in the textile industry to dye different stuffs like cloth, paper, leather etc. (Shah, 1998). Chemical properties of safranin dye can be found in Table 1.

Figure 1: Solid safranin (left) and safranin in aqueous solution (right)

Table 1: The chemical properties of safranin

Dye	Structure	Chemical formula	MW, g/mol	Solubility in water
Safranin		$C_{20}H_{19}ClN_4$	350.85 g/mol	Soluble

2.1.2 Effects of safranin on environment

The presence of safranin in industrial waste water which upon discharge untreated into water bodies can make water undesirable because of the color even at low dye concentration (Al-Degs et al., 2000). The dye could also affect the photosynthetic process of aquatic plants in water since sunlight would not be able to penetrate into lower layers (Reife and Fermann, 1996). It can also lead to an increase in the COD (chemical oxygen demand) of polluted water bodies.

2.1.3 Effects of safranin on human health

Along with the environmental damage caused by safranin, safranin also affects humans when they come in contact with it (Gupta et al., 2006). According to a survey carried out, more than 90 percent of the 4000 dyes studied have LD50 values higher than 2g/kg, which means that this amount of dye is sufficient to cause the death of 50 % of test animals (Robinson et al., 2001, Shore, 1996). It was shown that safranin causes skin irritation and can lead to serious eye damage (Clarke and Anliker, 1980; Anliker 1986).

2.2. Dye removal methods from wastewater

In recent times, several techniques have already been used to eradicate dyes from industrial effluents. Some of these methods include; nanofiltration, electrolysis, adsorption, precipitation, irradiation, oxidation etc. (Fu and Wang, 2011; Srinivasan and Viraraghavan, 2010; Lorenc-Grabowska and Gryglewicz, 2007; Annadurai, Ling & Lee, 2008; Gómez, Larrechi and Callao, 2007; Barka et al., 2013). Several drawbacks of some of these proposed methods which include; high energy use, membrane fouling and clogging, high cost of operation and generation of toxic byproducts etc. have limited their use in waste water remediation (Ramsay and Nguyen, 2002; Barka et al., 2013; Nharingo and Moyo, 2016).

2.3 Adsorption

Adsorption which is the displacement of a substance (known as adsorbate) present in a given phase by accumulation on another surface (adsorbent) has been discovered to be an effective waste water remediation technology. Several advantages such as cost, design simplicity, no harmful by-products generated etc. have made adsorption more attractive to use in waste water remediation (Ali and Gupta, 2007; Amin 2009).

Commercially produced activated carbon has proven to be an effective adsorbent to remove pollutants from water due to several characteristics (Gupta et al., 2011). However, difficulties encountered during regeneration and reuse and its high cost of production has severely hampered its use in waste water treatment (Rani, Sumanjit, & Mahajan, 2015). Many researchers are now investigating the potential of several precursors such as industrial and agricultural waste products, biomass etc. to be used as sources of activated carbon to reduce the cost involved in the production process (Preethi et al., 2006).

Currently as earlier noted, recent research has focused on the removal of different dyes using these non-conventional low cost materials. For example, Gupta, Kushwaha and Chattopadhyaya applied waste obtained from a potato plant industry to remove two cationic dyes (malachite green and methylene blue) from water (Gupta, Kushwaha & Chattopadhyaya, 2011). Robinson and his colleagues also used apple pomace and wheat straw to remove five reactive dyes from simulated waste water (Robinson, Chandran & Nigam, 2002). The findings in Akar et al.'s studies demonstrate that modifying *Pyracantha coccinea* enhanced its removal efficiency for Acid red 44 (Aker et al., 2010). Their results showed that adsorption process using these non-conventional low cost materials was effective in dealing with several pollutants.

According to IUPAC nomenclature, hydrogels possess 3D solid networks that allow the retention of water inside them (Wu et al., 2013). These 3D networks that the hydrogels possess have nanoporous structures which aid the effective diffusion of liquid and gas phase substrates (Liang et al., 2012; White et al., 2009). Unique properties such as their; osmotic pressure, high water retention, elasticity and presence of many micropores make them applicable as adsorbents (Wu et al., 2013). There are numerous studies in which carbon-based aerogels were prepared showing clear advantages in adsorption, separation, and electrochemical applications (White et al., 2014).

However, these traditional approaches for preparing the gels involve expensive chemicals and supercritical drying. Another disadvantage is that these synthetized hydrogels display poor mechanical stability which might affect their use in waste water treatment (Wang et al., 2012; Fellinger et al., 2012).

2.3.1 Factor affecting adsorption

The rate and efficiency of the removal of dyes from wastewaters by adsorbents depends on many factors including; particle size, solution pH, contact time, temperature and adsorbent dose, pore size, adsorbent affinity for adsorbate etc. Therefore, we will briefly review some of these factors and their effects.

2.3.1.1 Effect of contact time

The rate of adsorption is usually rapid at the initial stage due to the empty/vacant sites present on the surface of the adsorbent. As time proceeds and the vacant sites become filled with the adsorbate, the rate of adsorption reduces until equilibrium is achieved whereby there is no further uptake of adsorbate from the solution (Rani, Sumanjit & Mahajan, 2015).

2.3.1.2 Particle size

The size of adsorbent particles has been discovered to be an important factor that affects the efficiency of an adsorbent. Rani et al., showed that decreasing the particle size of their adsorbent increased dye adsorption at equilibrium (Rani et al., 2015). According to Aksu et al., rapid rate of adsorption and increase in the adsorption capacity of adsorbents as particle size reduces is due to the larger surface area readily accessible for adsorbates, which also provides more contact between both the adsorbent and pollutant (Aksu et al., 2015). Moreover, it was shown that reducing the particle size reduced the time required for equilibrium to be achieved (Shawabkeh et al., 2003; Vasanth et al., 2005).

2.3.1.3 Solution pH

Dye removal from aqueous solution is greatly affected by the adsorbents point zero charge pH_{pzc} and the variation in solution pH due to the presence of H^+ ions(Gupta et al., 2006; Gupta and Rastogi, 2008). The pH_{pzc} is very important because at this pH value, the surface of adsorbent becomes electrically neutral i.e. no charge. At pH lower than the pH_{pzc}, the adsorbent becomes positively charged while at higher pH values, it becomes negatively charged. Therefore, based on the surface chemistry of the adsorbent, removal of cationic pollutants from aqueous solutions is expected to be enhanced when the pH of solution is higher than the pH_{pzc} and vice versa in the case of anionic pollutants (Mall et al., 2006).

2.3.1.4 Effect of temperature

Changes in solution temperature have been found to have an impact on the adsorption process. An increase in temperature could either increase or reduce the adsorption capacity of an adsorbent. In the first case, increasing temperature can reduce solution viscosity which aids the movement of dye molecules from solution to adsorbent surface (Dogan et al., 2007). Preethi et al. in their study of safranin removal using activated carbon prepared from corncob found that adsorption was favored at higher temperatures while the exact opposite was found in a study by Barka and colleagues for removal of three different dyes using cactus cladodes (Preethi et al., 2006; Barka et al., 2013).

2.3.1.5 Co-existing or interfering ions

The presence of co-existing ions has a significant influence on adsorption capacity of any adsorbent. However, the exact mechanism is not clear and highly depends on the nature of interfering group. For example, Lim and his colleagues investigated the impact of increasing ionic strength on the removal efficiency of methylene blue. Their study showed that on adding a known amount of KNO_3 into dye solution, the removal efficiency of their adsorbent decreased while Chieng and co., in their own study discovered their removal % of Rhodamine B dye increased on adding KNO_3 (Lim et al., 2014; Chieng et al., 2015).

2.3.1.6 Adsorbent dose

Adsorbent dose is an important operational parameter because it helps to determine the capacity of an adsorbent for an initial dye concentration. According to Chowdhury et al., the adsorption capacity of *Ananas comosus* (pineapple leaf powder) towards Basic Green 4 increased as adsorbent dose increased. This was attributed to the increase in surface area and available binding sites of the pineapple leaf powder as dosage increased (Chowdhury, Chakraborty & Saha, 2011). Sen et al. also found that increasing the dosage of *Pinus radiate* (100-500mg) led to an increase in the % removal of methylene blue due from aqueous solution while a further dosage increase did not have any significant impact on the removal efficiency of the adsorbent as equilibrium had already being achieved between dye molecules in solution and on adsorbent surface (Sen et al., 2011; Barka et al., 2013).

2.4 Adsorption isotherms

Over the years, numerous adsorption equilibrium isotherms have been formulated and used to explore how pollutants interact and bind with adsorbents. These isotherms are also important in the practical designing and operation of a single stage batch adsorber (Sen et al., 2011). Some of the widely applied isotherms include; Freundlich, Langmuir, Temkin, Flory-Huggins, Toth, Sip, Dubinin-Radushkevich etc. Our study will focus on the first three models listed above.

Langmuir isotherm is a two parameter isotherm that assumes monolayer coverage of adsorbate by the adsorbent, and that all sites on the adsorbent surface are finite, equivalent and identical. It also assumes homogeneous adsorption whereby all sites have the same affinity for the adsorbate (Foo and Hameed, 2010). The linearized form of the Langmuir isotherm used in our study is shown in equation 1 below.

$$\frac{C_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \quad (1)$$

Where;

C_e is equilibrium dye concentration (mgL^{-1})

q_e is adsorption capacity at equilibrium (mgg^{-1})

K_L is the Langmuir constant (Lmg^{-1})

q_m is monolayer adsorption capacity (mgg^{-1})

Freundlich isotherm assumes surface heterogeneity whereby the available sites for adsorption are not equal and possess different energy in which case binding sites with higher energy are occupied first (Mahmoud et al., 2016). Equation 2 shows the linearized mathematical representation of this model.

$$log q_e = \log K_F + \frac{1}{n} log C_e \quad (2)$$

K_F and 1/n are the Freundlich constants related to adsorption capacity and intensity respectively. n values greater than unity or 1/n less than 1 indicate a favorable adsorption process (Bulut and Aydin, 2006).

The Temkin model (equation 3) suggests that there is a linear decrease in the heat of adsorption as coverage of adsorbent by adsorbate increases due to indirect interactions between them.

$$q_e = BIn\, A_t + BIn\, C_e \ (3)$$

B is related to the heat of adsorption (Jmol^{-1})

A_t is the equilibrium binding constant (L/mg)

2.5 Adsorption kinetics

Three kinetic models (as seen in Table 2) were applied in this study to determine the mechanism of the adsorption process. Selecting the model that shows the best fit in relation to experimental data was based on their correlation coefficient values i.e. R^2 values.

Table 2: Kinetic models

Models	**Equations**
Pseudo first order PFO	$\frac{dq}{dt} = k_1(q_e - q)$
Pseudo second order PSO	$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$
Intra-particle Diffusion	$q_t = k_{id}\, t^{½} + C$

From the equations in Table 2 above; q_e (mgg^{-1}) is the amount of dye adsorbed at equilibrium, q_t (mgg^{-1}) is the amount adsorbed at different pre-determined time intervals. k_1, k_2 and k_{id} are kinetic rate constants for PFO, PSO and intra-particle diffusion respectively.

2.6 Cactus cladodes (*opuntia ficus indica*)

The origin of the cactus cladodes can be traced to the United States of America, Mexico and South America. The plant also thrives well in several other areas, like Africa, Australia and the Mediterranean part (Barka et al., 2013). Figure 2 shows the picture of prickly pear cactus used in our study.

Figure 2: Prickly pear cactus

It yields an edible fruit called the prickly pear. In Morocco, the prickly pear cactus is used as hedges or demarcation to fight against erosion, for improvement of pastoral perimeters or for its fruits (Khatabi et al., 2016). It is a hetero-polysaccharide; with a molecular weight of about $2.3\text{-}3*10^4$ g/mole (Cardenas, Higuera-Ciapara & Goycoolea, 1997).

Cactus prickly pear is a fruit rich in vitamins, some amino acids, sugars and minerals (Stintzing et al., 2003). It is also used in food industries, for medical applications, cosmetics and for the production of cochineal (Khatabi et al., 2016). Other studies have shown that the juice obtained from the fruit is rich in polyphenols (Galati et al., 2003). Polyphenols, as antioxidants, can resist oxidative stress preventing various cardiovascular diseases and cancer (Scalbert & Williamson, 2000; Basdevant et al., 2001). The pharmaceutical potential of *Opuntia ficus indica* has also been widely investigated (Nharingo & Moyo, 2016).

Chapter 3

EXPERIMENTAL

3.1 Materials and equipment

Cactus Cladodes were collected within the territory of Eastern Mediterranean University (Faculty of Art & Sciences) Famagusta, North Cyprus. Analytical grade reagents used for this thesis work include; Sodium hydroxide, Copper (II) chloride as well as Safranin which were all obtained from Sigma-Aldrich. Hydrochloric acid, Sodium Chloride and Sodium lauryl sulfate SLS were purchased from BDH while Magnesium Chloride is a product of Alfa Aeser. Solution pH was measured using a hand held pH meter; HANNA, HI 98127. Conventional oven (BINDER GmbH, Model BD 115) was used to dry the Cactus Cladodes and adsorbent samples. Ash and moisture content was determined using a muffle furnace (Nabertherm GmbH model, Germany). Continuous stirring of adsorbents with adsorbate was achieved with the aid of a laboratory shaker (Nüve SL 350) while the concentration of safranin remaining in solution was determined by a T80+ UV-VIS Spectrometer (PG Instruments Ltd, version).

3.2 Adsorbent preparation

3.2.1 Initial pre-treatment of cactus cladodes

Cactus cladodes obtained from EMU was rinsed with tap water to remove dirt before it was washed again with distilled water. The cladodes were then cut into smaller sizes and dried directly under sunlight for three weeks before it was transferred to a conventional oven for final drying at 70^{o}C for 48 hours to ensure that all moisture present inside was removed. The dried cladodes were crushed with the aid of an electrical blender into powdered form and sieved to get the desired uniform particle size before it was stored in a Petri dish until further use. Sample was labeled as CC.

3.2.2 Modification of cactus cladodes

CC obtained in section 3.2.1 above was modified using an anionic surfactant SLS according to a method obtained in literature with little modification (Rani et al., 2015). A known mass of CC was transferred into 50mL solution of 0.01M Sodium Lauryl Sulfate (1g CC per 20mL surfactant solution) and stirred continuously at 150rpm for 24 hours at ambient temperature. The precipitate was then filtered, washed using ethanol and distilled water before it was put in an oven to dry at 70°C. The modified form of CC labeled as MCC was put into a separate Petri Dish until further use.

3.3 Preparation of adsorbate

Safranin stock solution was prepared by dissolving 100 mg of Safranin dye in 100 mL of distilled water (1000mg/L). Multiple dilutions were performed to prepare different working dye solutions. Calibration curve used in this study is presented in Figure 3.

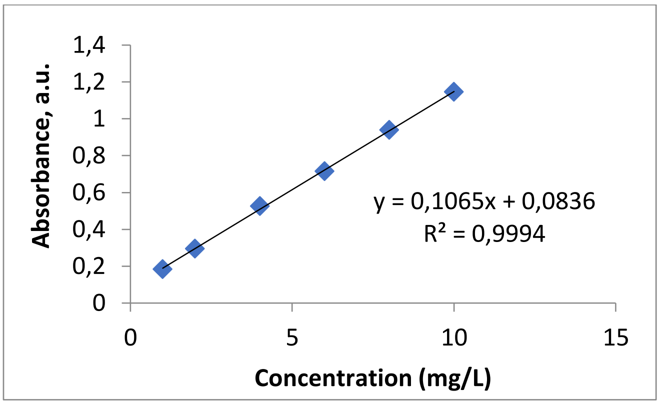


Figure 3: Calibration curve

3.4 Batch experiments

Batch adsorption experiment was carried out to evaluate both adsorbent's capacity to adsorb the selected dye at different dye solution pH, dose of CC and MCC, adsorbate concentration, temperature, and contact time. The effect of salinity and counter ions on adsorption was also examined.

Solution pH effect on safranin removal was determined by shaking 200mg of CC and MCC in a known volume of the safranin dye solution (10 mg/L) at several pH (2 – 10) values. CC and MCC dosage (0.1 – 0.5g), safranin concentration (10-100mg/L), temperature (298, 308 and 323K), contact time (30-1440 minutes) was investigated to find the optimum batch adsorption conditions. Also, effect of salinity (0.2 – 1g NaCl) and counter ions (0.2 – 1g of $MnCl_2$ and $CuCl_2$) were also examined. At predetermined time intervals, a known amount of sample were withdrawn from the bulk solution, centrifuged at 2000 r.p.m for 10 mins and analyzed with the aid of a UV/VIS Spectrometer at λ_{max} 517nm.

The safranin uptake capacity and removal efficiency was calculated using Equations 4 and 5 below;

$$q_e = \frac{C_1 - C_2}{mass} \times V \qquad (4)$$

Where;

C_1- Initial safranin concentration (mg/L)

C_2- Final safranin concentration (mg/L)

Mass of adsorbent in g

V is the volume in L of safranin solution

$$\% \, removal = \frac{C1 - C2}{C1} * 100 \quad (5)$$

3.5 Physiochemical characterization of CC and MCC

The zero point charge pH_{pzc} of CC and MCC was obtained by mixing in separate conical flasks, 0.1g of adsorbent and 50mL of 0.1M NaCl solutions that the initial pH had been adjusted to pH values ranging from 2 – 10 using either 0.1mol/L solution of HCl or NaOH. These solutions were then agitated for 24 hours before the final solution pH was taken. pH_{pzc} was obtained as point of intersection after plotting initial solution pH against the final solution pH. Other physicochemical parameters of the adsorbent such as; bulk density, ash content, moisture content, self pH values were also determined.

Chapter 4

RESULTS AND DISCUSSION

4. 1 Characterization

Chemical and physical characteristics of both CC and MCC are reported in Table 3. Results showed that there was not much difference in the values obtained for both samples after modification. For example, modification with SLS did not have any considerable impact on the pH_{pzc}, ash content and self pH though it was observed that the MCC contained less moisture than CC.

Table 3: Physiochemical characteristics of CC and MCC

Parameters	Value	
	CC	**MCC**
Bulk density (g/cm³)	0.4255	0.3645
Ash content, %	27	28
Moisture content %	21	17
pH_{pzc}	6.1	6.1
pH value	6.2	6.4

The pH_{pzc} of CC and MCC were evaluated and plotted in Figure 4. The pH_{pzc} of both CC and MCC was found to be same at 6.1. Hence, modification of CC with SLS did not affect the surface chemistry. Similar result was reported by (Rani et al. 2015).

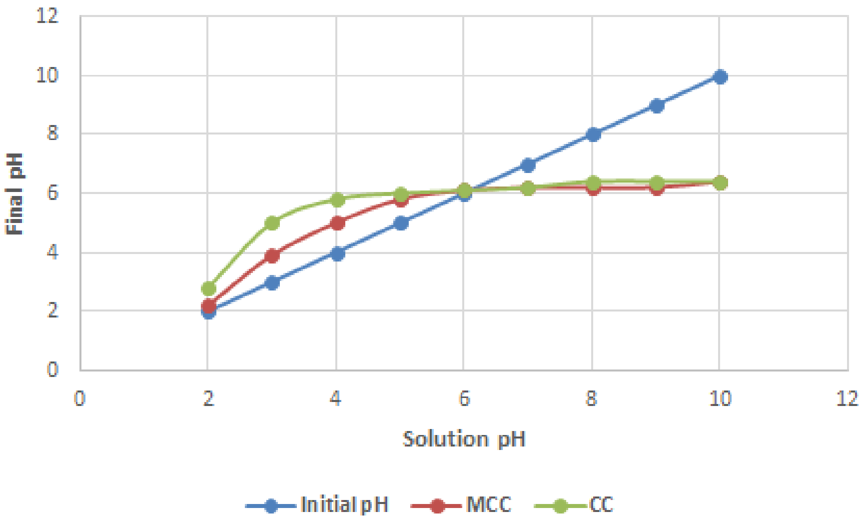


Figure 4: Determination of point zero charge of samples

4.2 The influence of operational parameters on removal of safranin

4.2.1 Safranin solution pH

The pH of a solution is known to affect any adsorption process. Therefore, the impact of adjusting solution pH (2-10) on safranin removal by CC and MCC was established. As shown in Figure 5, MCC samples have better adsorption efficiency in comparison with CC.

In the case of CC, as pH increases from 2-6, the % removal increases with maximum removal obtained at pH 8 while in the case of MCC, there was not much difference in the % removal after pH 2 but we still obtained highest removal at pH 8 also. This can be attributed to the zero point charge for CC and MCC samples which was 6.1. When pH of safranin solution is less than our determined pH_{pzc}, the surface of both

CC and MCC is positively charged due to the H^+ ions and since our dye is also positively charged, there is an electrostatic repulsion between safranin molecules both adsorbents. On the other hand, when pH of safranin solution is higher than our pH_{pzc}, the surface of both CC and MCC become negatively charged which resulted in an increase in safranin uptake via electrostatic attraction. Dye adsorption in our study was favored at $pH > pH_{pzc}$ which is similar to studies reported elsewhere (Mall et al., 2006; Rani et al., 2015). The optimum pH was found to be 8 for both adsorbents.

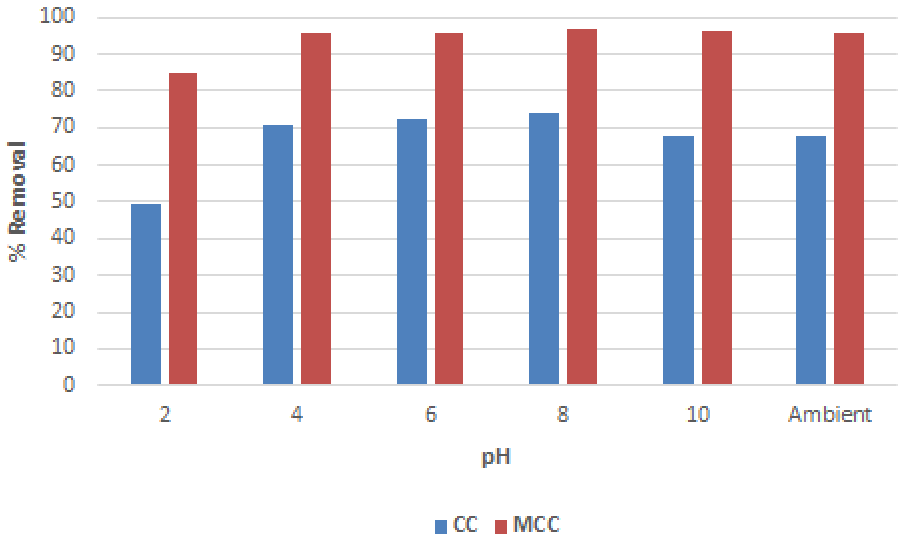


Figure 5: The effect of safranin solution pH on % removal by CC and MCC (Co= 10mg/L, mass= 0.1g, v=25mL, t=1440 minutes and T=20°C)

The final pH of all solutions after adsorption was taken and is shown in Figure 6. It can be observed from the graph that beyond pH 6, the final safranin solution pH is lower than its initial solution pH. This is due to the exchange of H^+ ions present on the surface of both adsorbents with the safranin ions in solution during adsorption. Therefore, we concluded ion-exchange might have played a part in the removal of safranin dye by both CC and MCC (Kannan & Thambidurai, 2008).

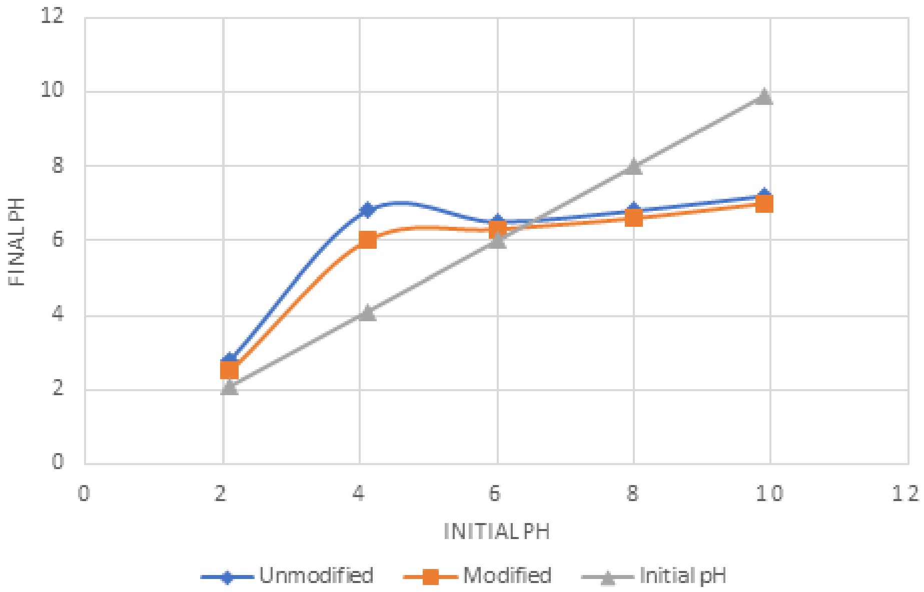


Figure 6: The relationship between final and initial pH of solutions with samples

4.2.2 Effect of adsorbent dosage

After determining the optimum pH for the adsorption process, the effect of varying the CC and MCC dosage on adsorption capacity and % removal of safranin was investigated to determine optimum dosage to be used for other experimental conditions. Figure 7a and b, shows that the adsorption capacity of both CC and MCC reduces with increasing adsorbent dosage while increasing dosage had a small impact on the % removal of both samples. The reduction in adsorption capacity from 3.37 to 0.70mgg^{-1} for CC and 4.32 to 0.96mgg^{-1} for MCC with increase in dosage (0.1 to 0.5g) could be attributed to the concentration gradient between the concentration of solute in solution and that on adsorbent surface (Sen et al., 2011).

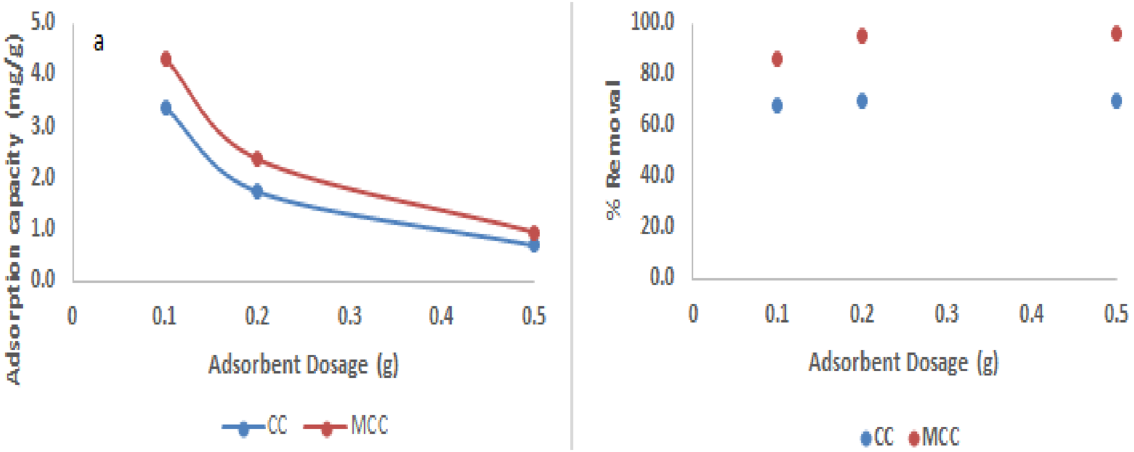


Figure 7: The effect of CC and MCC dosage on safranin removal % and adsorption capacity (Co= 10mg/L, mass= 0.1 - 0.5g, v=50mL, t=1440 minutes, pH 8 and T=25°C)

On the other hand, as CC and MCC dosage increased, there was a slight increase in % removal for both CC (68-70%) and MCC (86-96%) as seen in Figure 8b. More importantly, MCC showed higher removal efficiency of about 18-26% when compared to CC. This is due to the anionic surfactant used in modifying it that incorporated more negative active sites on MCC to bind the positive safranin ions. According to Chowdhury, the observed increase in % removal as adsorbent dosage increased for both adsorbents is due to an increase in the surface area and number of binding sites of both adsorbents (Chowdhury, Chakraborty & Saha, 2011). This proved that incorporating the anionic surfactant in the cactus Cladodes enhanced its uptake capacity and removal efficiency. Optimum dosage for adsorption for both CC and MCC was 0.1g.

4.2.3 Effect of contact time

The effect of q_e (equilibrium adsorption capacity) with respect to contact time for CC is depicted in Figure 8. Both adsorbents showed similar trends. There was an initial rapid rate of adsorption due to vacant sites present on the surface of both adsorbents. As time proceeds, the rate of adsorption reduced before equilibrium was attained at about 3 hours. This could be because the exterior surface of adsorbent is saturated and there were no more vacant sites present for adsorption. Beyond 60 minutes, there was no significant uptake observed hence, the contact time used for the remaining effects was taken as 60 minutes.

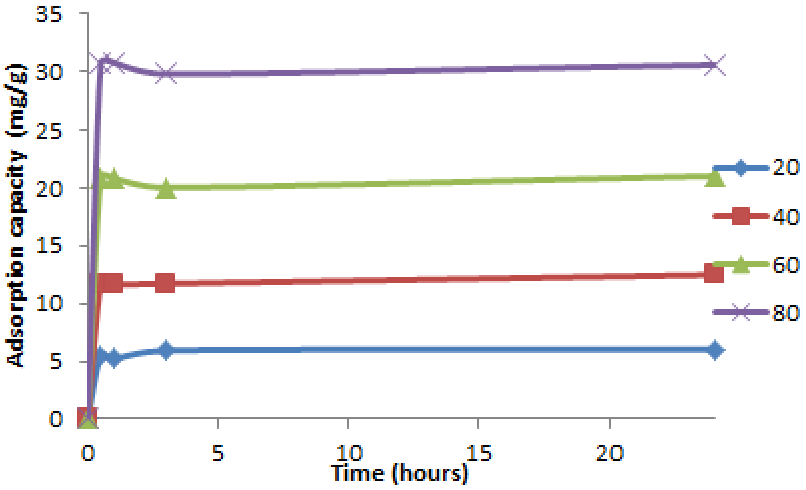


Figure 8: The effect of contact time on adsorption capacity of CC (Co= 20 - 80 mg/L, mass= 0.1g, v=50mL, t=1440 minutes, pH 8 and T=20°C)

4.2.4 Effect of initial dye concentration

The ability of CC and MCC to adsorb safranin was investigated at several initial dye concentrations (10 - 100 mg/L). As depicted in Figure 9, the results indicate that the ability of both adsorbents to remove safranin increase as dye concentration increase. This increase is possibly due to the increase in the driving force required to remove the mass transfer resistances between safranin solution and adsorbent surface as initial concentration of dye increased (Hazzaa & Hussein, 2015). Also, at high concentrations, the amount of initial dye molecules available for adsorption relative to the surface area of CC and MCC is high which resulted in higher adsorption capacity displayed by both adsorbents (El Haddad et al., 2013).

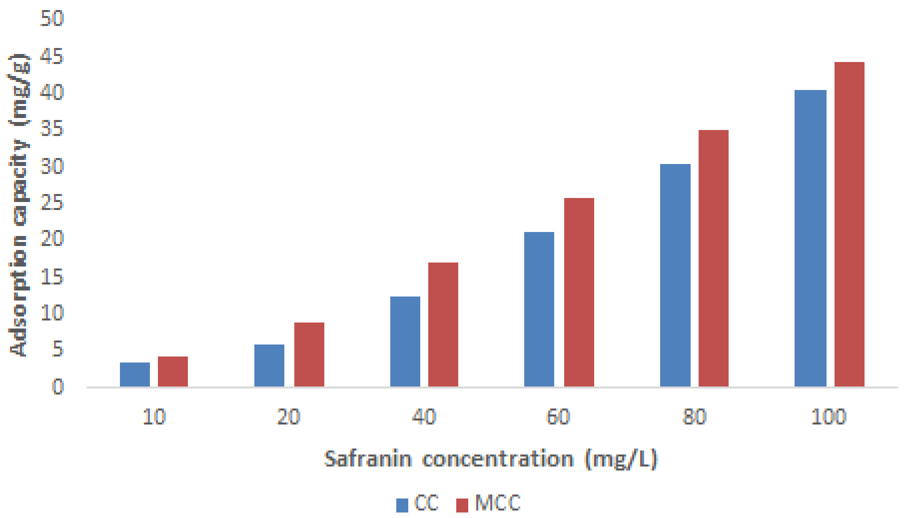


Figure 9: The effect of safranin concentration on adsorption of CC and MCC (Co= 10 - 100 mg/L, mass= 0.1g, v=50mL, t=60 minutes, pH 8 and T=20°C)

Figure 10 shows the effect of increasing the amount of safranin in solution on the removal efficiency of both CC and MCC. Increasing safranin concentration from 10-100mg/L did not have much impact on the removal efficiency of MCC (85-89%) as compared to CC. Removal percentage of CC increased as concentration increased with 81% removal obtained at 100mg/L as compared to 60% in 20mg/L.

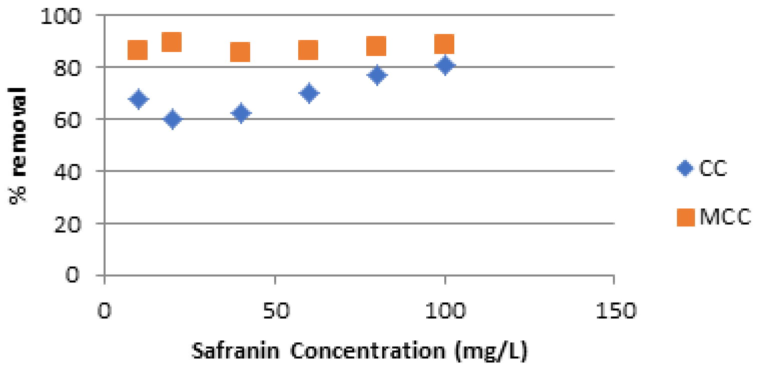


Figure 10: Initial safranin concentration on removal efficiency of CC and MCC (Co= 10 - 100 mg/L, mass= 0.1g, v=50mL, t=60 minutes, pH 8 and T=20°C)

4.2.5 Effect of temperature

Figure 11 shows that the amount of dye removed by both samples increases as temperature increased. This implies that the adsorption process is possibly an endothermic one though CC and MCC showed different trends. For CC, an initial increase in temperature from 298 to 308K increased adsorption but a further increase to 323K reduced the adsorption capacity. This may be because an increase in temperature to 323K resulted in the structure of CC becoming weak which in turn affected the active sites on its surface hence, reduced its capacity to remove safranin from the solution. Similar observation was reported elsewhere (Ben-Ali et al., 2017). MCC showed an initial increase in adsorption capacity as temperature increased to 308K. A further increase in temperature to 323K did not have any significant impact on adsorption. The initial increase in adsorption capacity of both adsorbents as temperature increased is probably as a result of the increased mobility of dye molecules because of reduced solution viscosity as temperature increases (Briand et al., 2000).

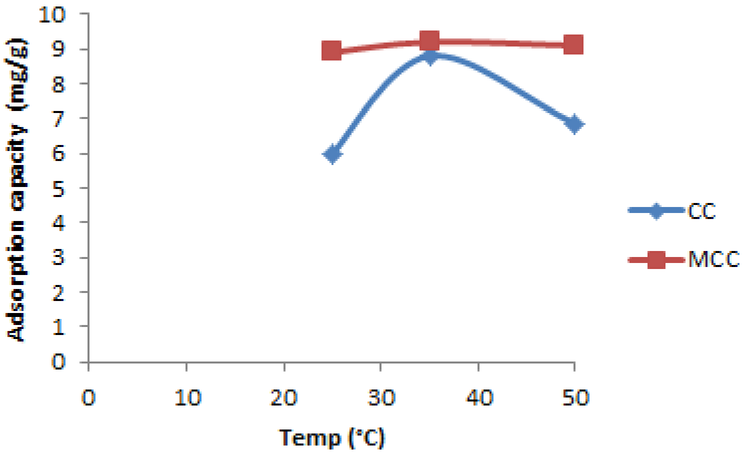


Figure 11: Effect of temperature on removal of safranin with CC and MCC

4.2.6 Effect of salinity

Presence of salts in industrial waste water could lead to increase in ionic strength which could in turn affect the ability of adsorbents to eradicate dyes from solution (Chieng et al., 2015). Figure 12 shows that increasing the amount of NaCl in the dye solution results in decreasing adsorption capacity of both adsorbents. This slight reduction in the capacity of CC and MCC to absorb safranin could be because of the suppressive effect of electrostatic interaction between safranin molecules and Na^+ ions. Na^+ ions present in dye solution and on adsorbent surface led to repulsion between safranin and the Na^+ ions which resulted in a reduction in adsorption capacity of CC and MCC. Similar type of results was reported elsewhere in literature (Sen et al., 2011; Yagub et al., 2014).

In the absence of any salt, removal efficiency for both CC and MCC at pH 7 and dye concentration of 20mg/L was 60% and 90% respectively. Increasing the concentration of NaCl in dye solution from 4g/L-20 g/L decreased removal efficiency of CC by about 15% as compared to 11% in the case of MCC. This shows that modifying the CC with SLS slightly enhanced its adsorption and removal efficiency as ionic strength increased.

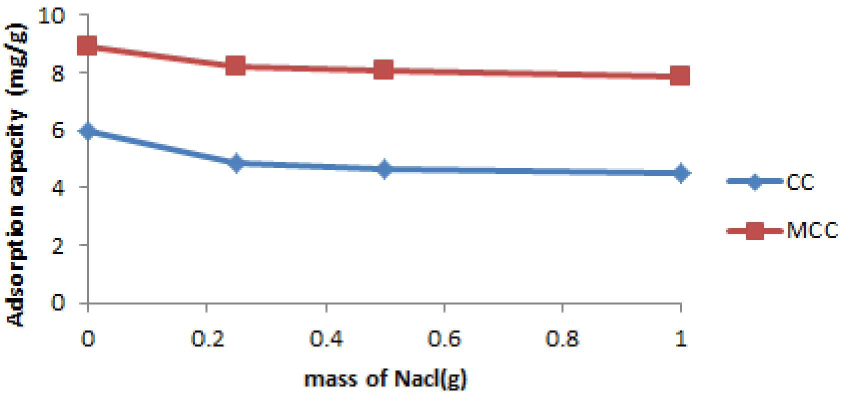


Figure 12: Effect of salinity on adsorption capacity of CC and MCC

4.2.7 Effect of competing ions

Since waste water usually contain co-existing pollutants which could either increase or retard adsorption process, the effect of two competing ions (Mn^{2+} and Cu^{2+}) on removal efficiency of safranin by CC and MCC was also investigated and depicted in Figures 13 and 14. In the presence of 4g/L of Mn^{2+} and Cu^{2+}, the percentage removal of safranin decreased by about 22% and 23% for CC and 5.7% and 11.2% for MCC. This is as a result of competition for the active sites of CC and MCC by safranin and the positively charged competing ions. This shows that the counter ions had more effect on the binding efficiency of CC than in MCC.

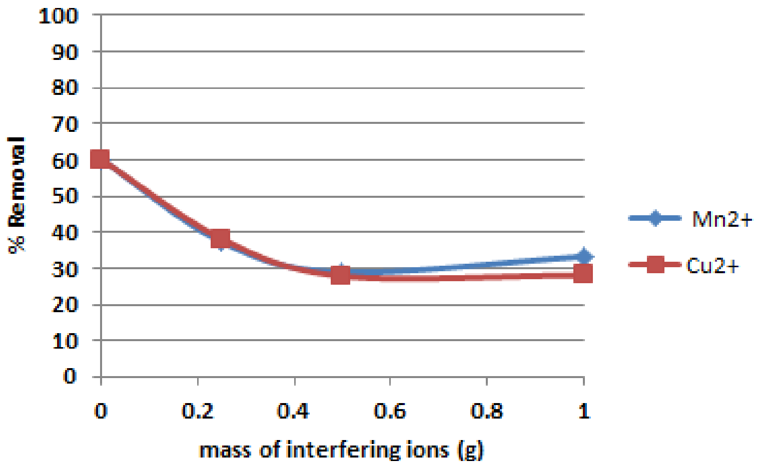


Figure 13: The Effect of competing ions on CC removal efficiency

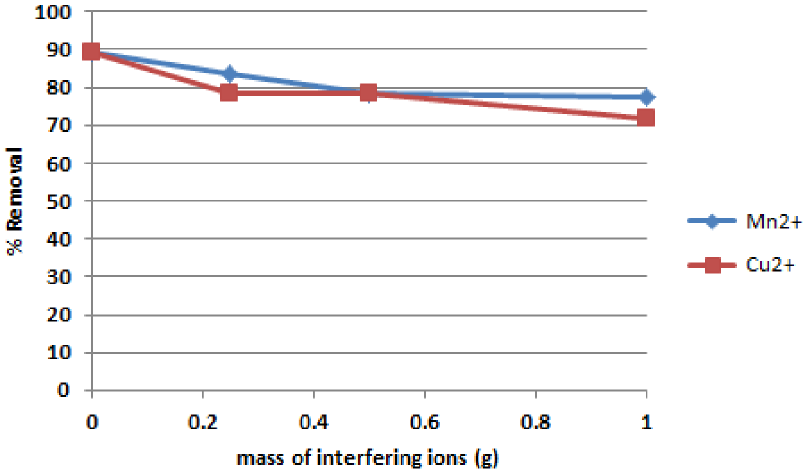


Figure 14: The Effect of competing ions on MCC removal efficiency

4.3 Adsorption isotherms

Three different isotherm models were applied in our study to determine the adsorption capacity of safranin by CC and MCC. The isotherm equation that shows the best fit model is related to the correlation coefficient value that is close to unity.

Langmuir model in its formulation describes monolayer coverage with adsorption occurring at fixed number of sites that are identical and possess same affinity for the adsorbate (Foo and Hameed, 2012). The linearized form of the Langmuir equation was used to plot a graph of $1/q_e$ Vs $1/C_e$. The constants q_m and K_L which are the monolayer adsorption capacity and Langmuir constant were determined from the intercept and slope respectively.

Freundlich isotherm assumes heterogeneous nature of the adsorbent surface and that adsorption will occur at sites that have different energy (Freundlich, 1906). A plot of In qe against In C_e is used to find the Freundlich constant; K_F (capacity of adsorbent) and 1/n (adsorption intensity). Figures 15 and 16 below show the graphs of both isotherm models for CC.

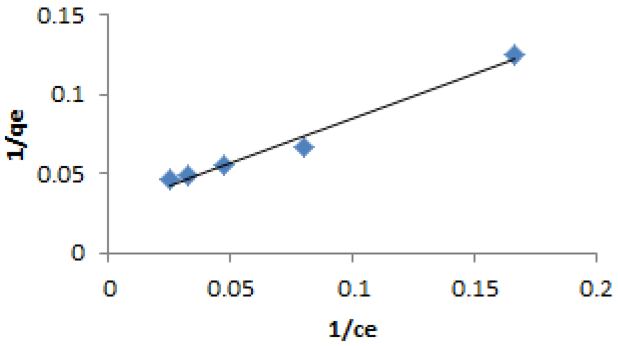


Figure 15: Langmuir model for adsorption of safranin by CC

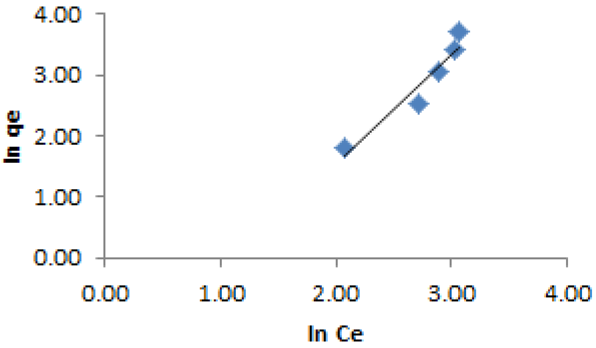


Figure 16: Freundlich plot for adsorption of safranin by CC

Isotherm parameters determined using the plots of the three isotherm models are tabulated below (Table 4). As seen from the table, the Freundlich's isotherm had a higher R^2 value (0.992) for MCC as compared to the Langmuir (0.9652) and temkin (0.8067) model showing that it provides a better fit as compared to CC which obeyed the Langmuir model. Similar observation was reported (Xiao-lan et al., 2013) which attributed this phenomenon to the unevenness of the functional groups on the surface of MCC after modification with SLS. 1/n values calculated which are close to or above 1 indicate cooperative adsorption (Hazzaa & Hussein, 2015; Foo & Hameed, 2010).

Langmuir constants; K_L for both samples were then used to calculate R_L (separation factor).

$$R_L = (1+K_LC_i)^{-1} \qquad (6)$$

Where;

C_i= safranin initial concentration in mg/L. R_L values greater than unity implies that adsorption is not favorable, linear if it is equal to 1, irreversible if it is 0 while favorable if $0 < R_L < 1$. As seen in Table 4 below, R_L values gotten in our study for both adsorbents clearly indicate a favorable adsorption process. The temkin model showed higher binding constant for MCC as compared to CC which confirms the favorable adsorption of safranin dye by MCC.

Table 4: Adsorption isotherm parameters for safranin adsorption by CC and MCC

Isotherm model		**CC**	**MCC**
Langmuir	K_L(L/g)	0.052	0.005
	q_m(mg/g)	34.01	66.7
	R^2	0.9801	0.9652
	R_L	(0.161-0.49)	(0.667-0.909)
Freundlich	K_F(mg/g)(L/mg)$^{1/n}$	0.9245	0.9731
	1/n	1.814	0.992
	R^2	0.9245	0.9731
Temkin	B(L/mg)	29.623	18.553
	A(J/mol)	0.135	0.633
	R^2	0.7421	0.8067

4.4 Adsorption kinetics

Three models as seen in Table 5 below were used to analyze the kinetics of adsorption between safranin and both adsorbents.

Table 5: Kinetic models and plots

Kinetic Models	**Plot**
Pseudo first order PFO	$In(q_e-q_t)$ Vs t
Pseudo second order PSO	t/q_t Vs t
Intra-particle diffusion	q_t vs $t^{1/2}$

For each kinetic model, the different plots for MCC as indicated in Table 6 are shown in Figures 17-19 while the kinetic parameters determined from the graphs at increasing concentration was reported in Table 6 and 7.

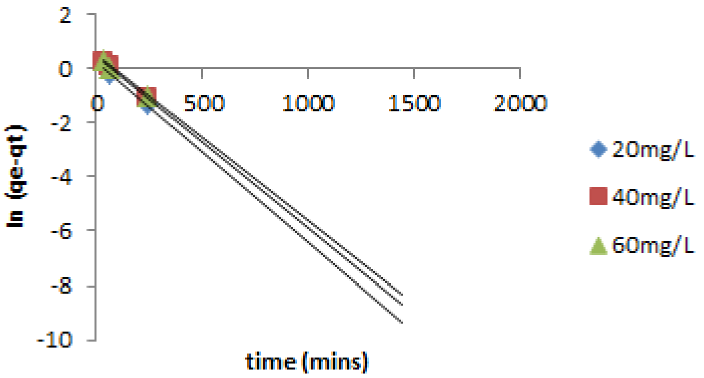


Figure 17: PFO plot for MCC

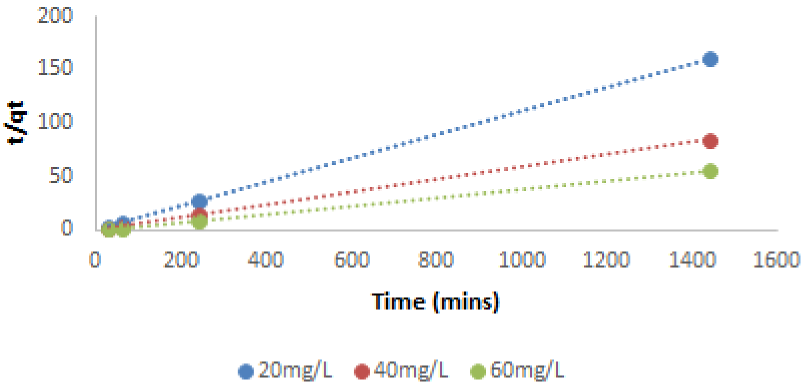


Figure 18: PSO plot for MCC

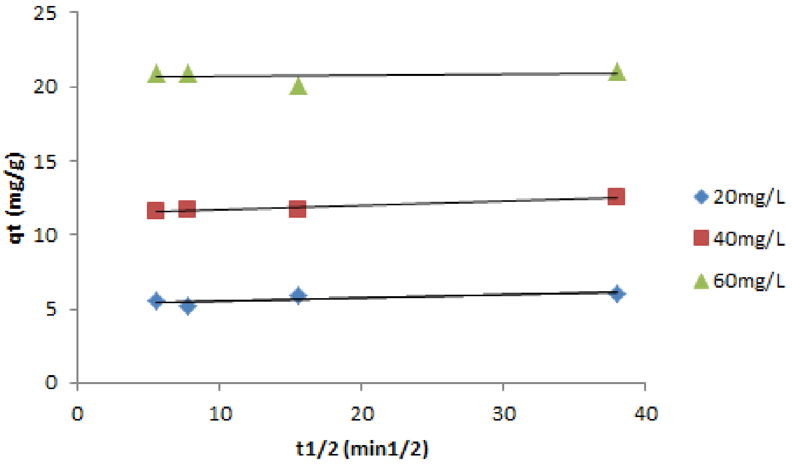


Figure 19: Intra-particle plot for CC

The tables show that of all the kinetics models used in this study, the R^2 values for the PSO are higher when compared to both PFO and intra-particle model. Also, calculated experimental values $q_{e(cal)}$ for PSO are almost the same as those we determined experimentally. As a result of this, the adsorption of safranin onto both adsorbents followed the PSO model.

The PSO model assumes chemisorption to be the rate limiting step where there is sharing and or exchanging of electrons between CC/MCC with safranin dye (Ho & McKay, 1999). It is noticeable that our results in kinetics studies agree with other studies (Barka et al., 2013; Ghaedi et al., 2015).

Both PFO and PSO models cannot be used to explain the mechanism of diffusion. To achieve this, we further analyzed our experimental data using the intra particle diffusion model. For this model to be the rate controlling step, our plot shown in Figure 19 must give a linear plot that passes through the origin. As seen from our graph, the straight line does not pass through the origin which shows that several other mechanisms might be involved in the adsorption process. The value of C from the graph (intercept) is useful in interpreting the thickness of the boundary layer, large values of C obtained shows there is a boundary layer effect and also indicates that our adsorption process is not only controlled by intra-particle diffusion but by other mechanism as well (Hazzaa & Hussein, 2015).

Table 6: PFO, PSO and Intra-particle constants for safranin adsorption using CC

Models	Parameter	Initial Safranin concentration (mg/L)				
		20	**40**	**60**	**80**	**100**
PFO	$q_{e\ exp}$ (mgg^{-1})	6.0	12.5	21.0	30.6	40.7
	$q_{e\ cal}$ (mgg^{-1})	0.9	0.9	0.6	1.3	1.1
	k_1 (1/min)	0.0096	0.0007	0.0067	0.011	0.016
	R^2	0.8798	0.9403	0.5199	0.8038	0.8469
PSO	$q_{e\ cal}$ (mgg^{-1})	6.0	12.5	21.1	30.6	40.5
	k_2 (min^{-1})	0.028	0.011	0.012	0.018	0.012
	R^2	1	0.9999	0.9999	1	1
Intra Particle	C	20.60	11.39	5.33	33.92	43.28
	K_{ip}(mgg^{1}min$^{1/2}$)	0.007	0.028	0.02	0.031	0.032
	R^2	0.0494	0.9721	0.5885	0.911	0.5885

Table 7: PFO, PSO and Intra-particle constants for safranin adsorption using MCC

		Initial Safranin concentration (mg/L)				
Models	Parameter	**20**	**40**	**60**	**80**	**100**
PFO	$q_{e\ exp}$ (mgg^{-1})	8.9	7.1	25.8	35.1	44.3
	$q_{e\ cal}$ (mgg^{-1})	1.3	1.6	1.6	1.2	2.8
	k_1 (1/min)	0.0067	0.0064	0.0061	0.0043	0.021
	R^2	0.9951	0.9993	0.9951	0.9992	0.992

PSO	$q_{e\,cal}$ (mgg^{-1})	8.9	17.2	25.8	35.1	44.4
	k_2 (min^{-1})	0.018	0.014	0.014	0.015	0.030
	R^2	1	1	1	1	1
Intra Particle	C	24.44	15.81	7.89	33.92	43.28
	K_{ip}(mgg^{1}min$^{1/2}$)	0.039	0.037	0.030	0.031	0.032
	R^2	0.8136	0.8202	0.7902	0.911	0.5885

The maximum amount of safranin absorbed in this research was compared with previous reported studies under various operating conditions as depicted in Table 8. It can be concluded that both CC and MCC showed relatively good adsorption capacity for safranin dye and can serve as alternative adsorbents for safranin removal in aqueous solutions.

Table 8: Adsorption capacity of different adsorbents for safranin removal

Adsorbents	pH	C_o (mg/L)	q_m (mg/g)	Reference
Alkali treated rice husks	-	50	9.77	Chowdhury, Misra, Kushwaha & Das 2011
Carbonized Eichornia crassipes	8	40	84.8	Rani et al. 2015
Alkali treated mango seeds	10	100	42	Malekbala et al. 2012
Corncob activated carbon	5-9	3000	1428.57	Preethi, S. et al. 2006
Pineapple peels	6-8	100	21.7	Mohammed, M. et al. 2014
CC	8	100	34.01	Present study
MCC	8	100	66.7	Present study

4.5 Adsorption thermodynamics

The effect of temperature was investigated under 3 different temperatures (298, 308 and 323K) at constant dye concentration of 20mg/L. Change in enthalpy (ΔH°) and entropy (ΔS°) values was calculated using the Van't Hoff equation and plot (Lim et.al. 2014):

$$InK_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7)$$

Where; K_c represents equilibrium constant which can be determined by C_a/C_b. C_a is the amount of the dye absorbed by CC and MCC, and C_b is dye equilibrium concentration remaining in solution.

$$\Delta G^\circ = -RT\ InK_c \qquad (8)$$

ΔG° = Gibbs free energy (kJ/mole), gas constant R is 8.314 J/mole K, absolute temperature T (K).

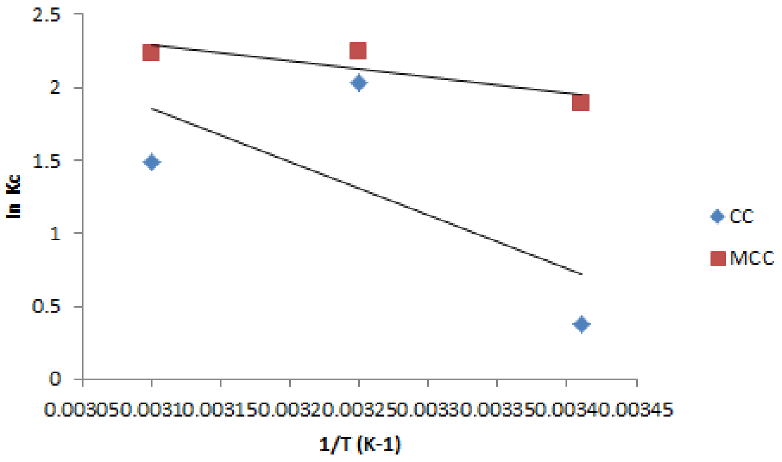


Figure 20: Van't Hoff plot ln Kc vs 1/T

Using the Van't Hoff's plot (Figure 20), change in enthalpy and entropy values of safranin on both adsorbents was determined from the slope and intercept respectively. The values obtained are reported in Table 9.

Table 9: Thermodynamic parameters obtained from CC and MCC at different temperatures for safranin removal

C_o (mg/L)	Temp. (K)	ΔG° (KJ/mol)		ΔS° (J/mol K)		ΔH° (KJ/mol)	
		CC	MCC	CC	MCC	CC	MCC
20	298.15	-0.93	-4.69	109.7	47.6	30.4	9.2
20	308.15	-5.20	-5.73				
20	323.15	-3.99	-5.98				

Δ G° was found to be negative at the three different temperatures studied. This implies that the process is a spontaneous one. Also, positive Δ H° (30.4 and 9.2 KJ/mol) and ΔS° values obtained confirms the endothermic nature of the process and suggests that adsorption of safranin by both adsorbents occurs as a random and disorderly process.

Chapter 5

CONCLUSION

In conclusion, our study investigated the potential of a low cost adsorbent using dried and modified prickly pear cactus for eradication of safranin dye from simulated waste water under laboratory conditions. Physical and chemical characterization of dried and modified samples was carried out.

The following outcomes were revealed after careful analysis of experimental data:

- The removal efficiency of both adsorbents was influenced by several factors including pH, adsorbent dosage, temperature, contact time.
- Modified cactus samples MCC showed better adsorption capacity and efficiency in comparison with unmodified cactus CC for all experiments conducted.
- The adsorption is low in acidic medium and increases with an increase in solution pH. Optimum pH for safranin removal was pH 8.
- Adsorption capacity and removal efficiency of both samples decreased with increasing concentration of competing ions and ionic strength though MCC performed better in both cases.
- Freundlich model provided a better fit for MCC while the Langmuir model showed best fit for CC based on obtained R^2 values. This is due to the uneven distribution of active sites on the surface of MCC after modification with SLS

- Adsorption of safranin by CC and MCC is thermodynamically feasible and an endothermic process.

Finally, both samples i.e. the dried and chemically modified prickly pear cactus showed the potential that they could be applied towards the removal of safranin dye from aqueous solutions but more research can be done to determine the industrial applicability of both adsorbents. Also, the regeneration and reuse of the adsorbents can also be investigated so as to examine the stability and potential of both adsorbents for economical purposes.

REFERENCES

Akar, T., Celik, S., & Tunali, A. S. (2010). Biosorption performance of surface modified biomass obtained from *Pyracantha coccinea* for the decolorization of dye contaminated solutions. *Chemical Engineering Journal*, 160(2), 466-472.

Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, 40, 997–1026.

Al-Degs, Y., Khraisheh, A. M., Allen, S. J., Ahmad, M. N. (2000). Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. *Water Research*, 34 (3), 927-935.

Ali, I. & Gupta, V. K. (2007). Advances in water treatment by adsorption technology. *Nature Protocols*, 1, 2661–2667.

Amin, N. K. (2009). Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials,* 165(1-3), 52–62.

Anandkumar, J., & Mandal, B. (2011). Adsorption of chromium(VI) and rhodamine B by surface modified tannery waste: kinetic, mechanistic and thermodynamic studies. *Journal of Hazardous Materials*, 186(2-3), 1088-1096.

Anliker, R. (1986). Toxic Hazard Assessment of Chemicals. In M. L. Richardson (Ed.). *The Royal Society of Chemistry* (166-187). London, UK.

Annadurai, G., Ling, L. Y., Lee, J. F. (2008). Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials*, 152(1), 337–346.

Basdevant, A., Laville, M., Lerebours, E. (2001). *Traite´ de nutrition clinique de l'adulte*. Paris, France: Flammarion Medecine-Sciences.

Barka, N., Ouzaouit, K., Abdennouri, M., & El Makhfouk, M. (2013). Dried prickly pear cactus (*Opuntia ficus indica*) cladodes as a low-cost and eco-friendly biosorbent for dyes removal from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*, 44(1), 52-60.

Ben-Ali, S., Jaouali, I., Souissi, S. N., Ouederni, A. (2017). Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *Journal of Clean Production*, 142, 3809-3821.

Briand, L. E., Farneth, W. E., Wachs, I. E. (2000). Quantitative determination of the number of active surface sites and the turnover frequencies for methanol oxidation over metal oxide catalysts: I. Fundamentals of the methanol chemisorption technique and application to monolayer supported molybdenum oxide catalysts. *Catalysis Today*, 62, 219–229.

Cardenas, A., Higuera-Ciapara, I., Goycoolea, F. M. (1997). Rheology and aggregation of cactus (*Opuntia ficus-indica*) mucilage in solution. *Journal of the Professional Association for Cactus Development*, 2, 152–157.

Chieng, H. I., Lim, L. B. L., Priyantha, N. (2015). Sorption characteristics of peat from Brunei Darussalam for the removal of rhodamine B dye from aqueous solution: adsorption isotherms, thermodynamics, kinetics and regeneration studies. *Desalination and Water Treatment*, 55(3), 664-677.

Chowdhury, S., Chakraborty, S., Saha, P. (2011). Biosorption of Basic Green 4 from aqueous solution by *Ananas comosus* (pineapple) leaf powder. *Colloids and Surfaces B: Biointerfaces*, 84(2), 520–527.

Chowdhury, S., Misra, R., Kushwaha, P., & Das, P. (2011). Optimum sorption isotherm by linear and nonlinear methods for Safranin onto alkali-treated rice husk. *Bioremediation Journal*, 15(2), 77-89.

Clarke, E. A., Anliker, R. (1980). Organic dyes and pigments. *Handbook of Environmental Chemistry, Anthropogenic Compounds*, part A, vol. 3. New York, USA: Springer-Verlag.

Crini, G., & Badot, P. M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, 33(4), 399-447.

Crini, G. (2006). Non-conventional low cost adsorbents for dye removal: A review. *Bioresource Technology*, 97(9), 1061-1085.

Dogan, M., Ozdemir, Y., Alkan, M. (2007) Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes Pigments*, 75, 701-713.

El Haddad, M., Slimani, R., Mamouni, R., Laamari, R., Rafqah, S. & Lazar, S. (2013). Evaluation of potential capability of calcined bones on the biosorption removal efficiency of safranin as a cationic dye for aqueous solutions. *Journal of Taiwan Institute of Chemical Engineers* (44): 13-18.

Fellinger, T. P., White, R. J., Titirici, M. M., Antonietti, M. (2012). Borax-mediated formation of carbon aerogels from glucose. *Advanced Functional Materials*, 22(15), 3254–3260.

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2-10.

Forgacs, E., Cserháti, T., Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. *Environmental International*, 30(7), 953–971.

Freundlich, H. M. F. (1906). Uber die adsorption in losungen. *Zeitschrift für Physikalische Chemie*, 57, 385-470.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management*, 92(3), 407-418.

Galati, E. M., Mondello, M. R., Giuffrida, D., Dugo, G., Miceli, N., Pergolizzi, S., Taviano, M. F. (2003). Chemical characterization and biological effects of Sicilian *Opuntia ficus indica* (L.) mill. Fruit Juice: antioxidant and antiulcerogenic activity. *Journal of Agricultural and Food Chemistry*, 51, 4903–4908.

Ghaedi, M., Jaberi, S. Y. S., Hajati, S., Gupta, V. K. (2015). Preparation of iodide selective carbon paste electrode with modified carbon nanotubes by potentiometric method and effect of CuS-NPs on its response. *Electroanalysis*, 27(6), 1516-1522.

Gómez, V., Larrechi, M. S., Callao, M. P. (2007). Kinetic and adsorption study of acid dye removal using activated carbon. *Chemosphere*, 69(7), 1151–1158.

Gomez, T. R., Ramirez, R. D. A., Montoya, V. H., Petriciolet, A. B., Valle, C. J., Moran, M. A. (2012). Synergic adsorption in the simultaneous removal of acid blue 25 and heavy metals from water using a $Ca(PO_3)_2$ – modified carbon. *Journal of Hazardous materials*, 199-200, 290-300.

Gupta, N., Kushwaha, A. K., Chattopadhyaya, M. C. (2011). Application of potato (*Solanum tuberosum*) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution. *Arabian Journal of Chemistry*, 9(1), S707-S716.

Gupta, V. K., Agarwal, S., Saleh, T. A. (2011). Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. *Water Research*, 45(6), 2207–2212.

Gupta, V. K., Mittal, A., Jain, R., Mathur, M., & Sikarwar, S. (2006). Adsorption of Safranin-T from wastewater using waste materials—activated carbon and activated rice husks. *Journal of Colloid and Interface Science*, *303*(1), 80-86.

Gupta, V. K., Mohan, D., Sharma, S., & Sharma, M. (2000). Removal of basic dyes (Rhodamine B and Methylene blue) from aqueous solutions using Bagasse fly ash. *Separation Science and Technology*, 35(13), 2097-2113.

Gupta, V. K., Rastogi, A., Saini, V. K., Jain, N. (2006). Biosorption of copper(II) from aqueous solutions by *Spirogyra* species. *Journal of Colloid and Interface Science*, 296(1), 59–63.

Gupta, V. K., Rastogi, A. (2008). Equilibrium and kinetic modeling of cadmium(II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase. *Journal of Hazardous Materials*, 153, 759–766.

Hameed, B. H, Din, A. T. M., & Ahmad, A. L. (2007). Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *Journal of Hazardous Materials*, 141(3), 819-825.

Hazzaa, R., & Hussein, M. (2015). Cationic dye removal by Sugarcane Bagasse activated carbon from aqueous solution. *Global NEST Journal*, 17(4), 784-795.

Ho, Y. S., McKay, G. (1999). Pseudo-second-order model for sorption processes. *Process Biochemistry*, 34(5), 451–465.

Iglesias, O., Fernandez, M. A., Rosales, E., Pazos, M., & Sanroman, M. A. (2013). Optimization of decolourization and degradation of reactive black 5 dye under electro-Fenton process using Fe alginate gel beads. *Environmental Science and Pollution Research*, 20(4), 2172-2183.

Kannan, A., & Thambidurai, S. (2008). Removal of hexavalent chromium from aqueous solution using activated carbon derived from palmyra palm fruit seed. *Bulletin of the Chemical Society of Ethiopia*, 22(2), 183-196.

Khaled, A., Elnemr, A., El-sikaily, A., Abdelwahab, O. (2009). Removal of direct N blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies. *Journal of Hazardous Materials,* 165, 100–110.

Khatabi, O., Hanine, H., Elothmani, D., & Hasib, A. (2016). Extraction and determination of polyphenols and betalain pigments in the Moroccan prickly pear fruits (*Opuntia ficus indica*). *Arabian Journal of Chemistry*, 9(1), S278-S281.

Konicki, W., Sibera, D., Mijowska, E., Lendzion-Bielun, Z., Narkiewicz, U. (2013). Equilibrium and kinetic studies on acid dye Acid Red 88 adsorption by magnetic $ZnFe_2O_4$ spinel ferrite nanoparticles. *Journal of Colloid and Interface Science*, 398, 152-160.

Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga svenska vetenskapsakademiens, *Handlingar*, 24(4), 1–39.

Liang, H. W., Guan, Q. F., Chen, L. F., Zhu, Z., Zhang, W. J., Yu, S. H. (2012). Macroscopic-Scale Template Synthesis of Robust Carbonaceous Nanofiber Hydrogels and Aerogels and Their Applications. *Angewandte Chemie International Edition*, 51(21), 5101–5105.

Lim, L. B., Priyantha, N., Tennakoon, D. T. B., Chieng, H. I., Dahri, M. K., & Suklueng, M. (2014). Breadnut peel as a highly effective low-cost biosorbent for methylene blue: Equilibrium, thermodynamic and kinetic studies. *Arabian Journal of Chemistry*, 10(2), 3216-3228.

Lorenc-Grabowska, E., Gryglewicz, G. (2007). Adsorption characteristics of Congo Redon coal-based mesoporous activated carbon. *Dyes and Pigments*, 74, 34–40.

Malekbala, M. R. Soltani, S. M., Yazdi, S. K., Hosseini, S. (2012). Equilibrium and Kinetic Studies of Safranine Adsorption on Alkali-Treated Mango Seed Integuments. *International Journal of Chemical Engineering and Applications*, 3(3), 160-166.

Mall, I. D., Srivastava, V. C., Kumar, G. V. A., Mishra, I. M. (2006). Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Colloids and Surfaces A:Physiochemical and Engineering Aspects*, 278(1-3), 175–187.

Mittal, A., Kaur, D., Malviya, A., Mittal, J., Gupta, V. K., (2009). Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents. *Journal of Colloid and Interface Science*, 337(2), 345-354.

Mohammed, M. A., Ibrahim, A., Shitu, A. (2014). Batch Removal of Hazardous Safranin-O in Wastewater Using Pineapple Peels as an Agricultural Waste Based Adsorbent. *International Journal of Environmental Monitoring and Analysis*, 2(3), 128-133.

Moawed, E.A., & Abulkibash, A. B. (2016). Selective separation of light green and safranin O from aqueous solution using Salvadora persica (Miswak) powder as a new biosorbent. *Journal of Saudi Chemical Society*, 20, 178-185.

Moussavi, G., & Mahmoudi, M. (2009) Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. *Journal of Hazardous Materials,* 168(2-3), 806–812.

Nharingo, T., & Moyo, M. (2016). Application of *Opuntia ficus-indica* in bioremediation of wastewaters. A critical review. *Journal of Environmental Management*, 166, 55-72.

Preethi, S., Sivasamy, A., Sivanesan, S., Ramamurthi, V. & Swaminathan, G. (2006). Removal of safranin basic dye from aqueous solutions by adsorption onto corncob activated carbon. *Industrial & Engineering Chemistry Research*, 45(22), 7627-7632.

Ramírez-Montoya, L. A., Hernández-Montoya, V., & Montes-Morán, M. A. (2014). Optimizing the preparation of carbonaceous adsorbents for the selective removal of textile dyes by using Taguchi methodology. *Journal of Analytical and Applied Pyrolysis*, *109*, 9-20.

Ramsay, J. A., & Nguyen, T. (2002). Decoloration of textile dyes by *Trametes versicolor* and its effect on dye toxicity. *Biotechnology Letters*, 24(21), 1756–1760.

Rani, S., Sumanjit, K., & Mahajan, R. K. (2015). Comparative Study of Surface Modified Carbonized Eichhornia crassipes for Adsorption of Dye Safranin. *Separation Science and Technology*, 50(16), 2436-2447.

Reife, A., & Fermann, H. S. (1996). *Environmental Chemistry of Dyes and Pigments*; New York, USA: Wiley.

Rejniak, L., & Piotrowska, H. (1966). Effect of Malachite Green, Congo red and Safranin on Cell Division in Gemmae of Allium cepa. *Nature*, 209(5022), 517 – 518.

Robinson, T., Chandran, B., & Nigam, P. (2002). Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Research*, 36(11), 2824–2830.

Robinson, T., McMullan, G., Marchant, R., Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77(3), 247–255.

Scalbert, A., Williamson, G. (2000). Dietary intake and bioavailability of polyphenols. *The Journal of Nutrition*, 130(8), 2073S–2085S.

Sen, K.T., Afroze, S., & Ang, H. M. (2011). Equilibrium, kinetics and mechanism of removal of Methylene Blue from aqueous solution by adsorption onto Pine Cone Biomass of *Pinus radiata*. *Water, Air, & Soil Pollution*, 218(1-4), 499-515.

Shah, K. M. (1998). *Handbook of Synthetic Dyes and Pigments*, 2nd ed. Bombay, India: Multitech Publishing Company.

Shawabkeh, R. A., Tutunji, M. F. (2003). Experimental study and modeling of basic dye sorption by diatomaceous clay. *Applied Clay Science*, 24, 111-120.

Shore, J. (1996). Advances in direct dyes. *Indian Journal of Fibres and Textile Research*, 21(1), 1–29.

Song X., Zhang M., Zhang Y., Huang S., Geng B., Meng R., Yang Y., Zhong Y., liu H. (2013). Surface modification of coconut based activated carbon by SDS and its effects on Pb2+ adsorption. *Journal of Central South University of Technology* 20: 1156-1160.

Srinivasan, A., Viraraghavan, T. (2010). Decolorization of dye wastewaters by biosorbents: A review. *Journal of Environmental Management*, 91(10), 1915-1929.

Stawinski, W., Freitas, O., Chmielarz, L., Wegrzyn, A., Komedera, K., Blachowski, A., & Figueiredo, S. (2016). The influence of acid treatment over vermiculite based material as adsorbent for cationic textile dyestuffs. *Chemosphere*, 153, 115-129.

Stintzing, F. C., Scheiber, A., Carle, R. (2003). Evaluation of color properties and chemical quality parameters of cactus juices. *European Food Research & Technology*, 216(4), 303–311.

Vasanth Kumar, K., Ramamurthy, V., Sivanesan, S. (2005). Modelling the mechanism involved during the sorption of methylene blue onto fly ash. *Journal of Colloid and Interface Science*, 284(1), 14-21.

Wang, J., Chen, M., Wang, C., Wang, J., Zheng, J. (2012). A Facile method to prepare carbon aerogels from amphiphilic carbon material. *Material Letters,* 2012, 68(1), 446–449.

Weber, W. J., Morris, J. C. (1963). Kinetics of adsorption on carbon from solutions. *Journal of the Sanitary Engineering Division*, 89, 31-60.

White, R. J., Brun, N., Budarin, V. L., Clark, J. H., & Titirici, M. M. (2014). Always look on the "light" side of life: sustainable carbon aerogels. *ChemSusChem*, 7(3), 670-689.

White, R. J., Budarin, V., Luque, R., Clark, J. H., Macquarrie, D. J. (2009). Tuneable porous carbonaceous materials from renewable resources. *Chemical Society Reviews*, 38(12), 3401–3418.

Wu, X. L., Wen, T., Guo, H. L., Yang, S., Wang, X., & Xu, A. W. (2013). Biomass-derived sponge-like carbonaceous hydrogels and aerogels for supercapacitors. *ACS nano*, *7*(4), 3589-3597.

Yagub, M. T., Sen, T. K., & Ang, M. (2014). Removal of cationic dye methylene blue from aqueous solution by ground raw and base modified pine cone powder. *Environmental Earth Sciences*, 71(4), 1507-1519.

Zeldowitsch, J. (1934). Über den mechanismus der katalytischen oxydation von CO an MnO2. *Acta Physicochimica U.R.S.S.*, 1, 449–464.