Azo-Dye Eriochrome Black T Degradation by Heterogeneous Fenton-Like Reaction Using Olive Stones Activated Carbon-Fe Catalyst

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We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

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ABSTRACT

Chemically activated carbon K-AC was fabricated from a by-product of olive oil production (olive stones) after chemical treatment with KOH. The as-synthesized activated carbon was then used for; (1) adsorption of an azo dye, Eriochrome black T (EBT) and (2) to prepare a heterogeneous Fenton catalyst Fe-AC, for degradation of same dye using the Fenton-like process. Evaluation of the effect of pH (2-10), temperature (20-50 °C) and contact time required for adsorption was studied while effects of hydrogen peroxide concentration, EBT concentration and time on rate of degradation of EBT was also determined. Optimum conditions for both processes are reported while kinetics of EBT adsorption and degradation was also investigated. Results from the undertaken study showed that temperature and pH had a predominant impact on the adsorption of EBT by K-AC. Also, the Langmuir isotherm equation provided a better fit to experimental data than Freundlich equation implying monolayer adsorption on surface of K-AC. Maximum adsorption capacity of K-AC at 20 °C as determined using the Langmuir isotherm was 101.01 mg/g. RL (0.54-0.92) and n (1.04) values confirmed that the adsorption process is favorable while positive enthalpy ($\Delta H°$; 32.7 KJmol-1) and negative free energy ($\Delta G°$; -1.07 KJmol-1) referred to an endothermic and a spontaneous adsorption process. EBT degradation increased as time and peroxide concentration increased. However, it decreased as EBT concentration increased. Overall, degradation experiments were conducted at optimum conditions (6mM H_2O_2 and pH 4) to evaluate catalyst degradation efficiency. It was further observed that adsorption kinetics of EBT followed pseudo second order kinetic model based on R2 values. Further analysis on the regeneration of spent Fe-AC using water indicates that catalyst degradation

efficiency can be maintained even after three cycles which makes it economical to use in EBT degradation. According to results obtained in this study, both K-AC and Fe-AC can act as adsorbent and catalyst for the efficient removal of EBT dye.

ÖZ

Kimyasal K-AC aktif Karbonun, zeytinyağı üretiminin yan ürünü olan zeytin çekirdekleri kullanarak, KOH kullanılarak kimyasal olarak üretildi. Sentezlenmiş aktif karbon , daha sonra belirtilen alanlarda; (1) Azo boya absorpsiyonunda (Eriochrome Black T) (EBT) (2) Fe-AC heterojen Fenton kataliz hazırlanışında, aynı boyanın degredasyonunda kullanılan Fenton-benzeri reaksiyonlarda kullanıldı. Aktif karbon'un absorpsiyonu için gerekli olan pH (2-10), sıcaklık (20-50 derece) ve temas süresi değerlendirilip, çalışıldı. Bu çalışmalar yapılırken hidrojen peroksit konsantrasyonunun, EBT konsantrasyonunun etkisi ve zamanının EBT nin degredasyonu üzerine olan etkisi belirlendi. EBT nin absorpsyon ve degredasyon kinetiği incelenirken, her iki reaksyon için geçerli olan optimal koşullar araştırılıp, raporlanmıştır. Yapılan çalışma ve elde edilen sonuçlar, EBT'nin K-AC tarafından absorpsiyonunda sıcaklık ve pH'in öne çıkan önemli faktörler olduğunu ortaya çıkarmıştır. Bunlara ek olarak, Langmuir İzoterm denklemi deneysel verilere Freundlinch denklemine göre daha uygun sonuçlar vermesi, K-AC aktif karbon yüzeyinin tek tabaka absorpsyonuna sahip olduğu göstermektedir. K-AC'nin maksimum absorpsiyon kapasitesi, 20 derece sıcaklıkta Langmuir izoterm denklemi kullanılarak bullundu, bu değer 101.01 mg/g olarak belirlendi. RL (0.54-0.92) ve n (1.04) değerleri gösteriyor ki positif entalpi (ΔH; 32.7 Kj mol-1) ve negatif serbest enerji (ΔG; -1.07 Kj mol -1) ki bunlar sırasıyla endotermik ve spontane absorpsyon reaksyonunu simgeler; tüm bunlar aktif karbonun absorpsyonu için elverişli olduğunu gösterir. Zaman ve hydrojen peroxit konsantrasyonu artıkça, EBT degradasyonu artar. Oysa, EBT konsantrasyonu artıkça , EBT degradasyonu azalır. Sonuç olarak, kataliz degradasyonunun verimini ölçmek için degradasyon deneyleri

optimal koşullarda (6 mM H2O2 ve pH 4) uygulandı. Buna ek olarak , EBT R2 değerlerine göre EBT nin absorpsyon kinetiği, pseudo ikinci dereceden kinetik denklemine uygundur. Dahası, kullanılmış Fe-AC nin su kullanarak regenerasyonu gösteriyor ki katalizin degredasyon verimi üç döngüden sonra bile korunuyor, bu da, Fe-AC'nin EBT degredasyonu için ekonomik yönden uygun olduğunu gösteriyor. Çalışmadan elde edilen sonuçlara bakıldığında K-AC ve Fe-AC, her ikisinin de EBT boyasının verimli bir şekilde gideriminde absorban ve kataliz olarak görev yaptığı gözlenir.

Anahtar Kelimeler: Fenton Reaksyonu, adsorpsiyon, zeytin çekirdeği, Eriochrome black T

DEDICATION

This work is dedicated to my parents and siblings (THE FOLORUNSO'S) for their support in all ways. May the good Lord protect them for me.

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INTRODUCTION

1.1 Environmental problems

Rapid population growth coupled with recent advances in technology has helped the world to attain new horizons and break previously existing barriers. A major consequence of this rapid growth is environmental pollution and dwindling natural resources. One of the resources facing extinction in the future is fresh potable water.

Fresh water plays an essential role in our ecosystem but widespread pollution by industries and human activities is causing serious social and economic concerns today (Gupta et al., 2015). In fact, the detection of various environmental pollutants such as dyes, heavy metals etc. in water used for consumption has raised worldwide health concerns (Zubair et al., 2017). Estimates have shown that 15-20% of dyes and pigments used in the dyeing process by industries are disposed along with their effluents (Babaei et al., 2017). Also, the increase in demand for water by domestic, industrial and agricultural sectors has led to higher production of waste water containing several pollutants (Gupta and Suhas, 2009). All of these factors make the problem of water pollution very troubling.

Textile industries make use of a wide range of dyes which are the main source of water pollution in the environment today. Even though these industries are a source of revenue for the government of many countries, effluents produced from these

industries have been reported to contain various hazardous materials that affect public health (Otero et al., 2003). These dyes possess complex organic structures that make them inert and non-biodegradable. Many of these dyes are also carcinogenic and toxic in nature, have negative impact on photosynthesis since they reduce light penetration thereby threatening aquatic biota and can produce mutagenic compounds upon degradation (Hazzaa and Hussein, 2015). This has led to industries and governments finding ways to treat industrial effluents before discharge into the environment.

Currently, there are different chemical, biological and physical techniques proposed to treat industrial effluents containing dyes. They include but are not limited to; advanced oxidation processes (Robinson et.al 2002; Crini. et.al 2006), irradiation biodegradation (Yagub et al., 2014), ion exchange (Robinson et al., 2001), electrocoagulation (Joffe and Knieper, 2000), persulfate oxidation (Amin, 2009), adsorption (Sen et al., 2011), membrane filtration (Alventosa-deLara et al., 2014) etc. Despite all these technologies listed for waste water treatment, only very few have been applied at a commercial level because of their shortcomings such as; high operating cost, generation of harmful by products, high energy requirement, low efficiency etc. (Crini, 2006).

Adsorption process as compared to other techniques has been found to be an attractive alternative to treat industrial effluents because of its low cost and simplicity of design coupled with its ease of operation and high efficiency in the removal of dyes (Bulut and Aydin, 2006). Generally, most commercial systems make use of activated carbon to serve as an adsorbent because of its high surface area and excellent sorption ability (Crini, 2006). A major drawback of this process is the high

cost of conventional and commercial adsorbents which has led many researchers to focus on finding cheap precursors from renewable materials, agricultural and industrial wastes to prepare activated carbon.

There has also been growing attention in recent years to the use of advanced oxidation processes AOPs (especially Fenton and Fenton like oxidation) to degrade and mineralize organic compounds such as dyes. One of the driving forces behind this is that AOPs are effective in treating highly contaminated and toxic waste water (Devi et al., 2009). Among the AOPs, the Fenton reaction is very appealing because it can be carried out under moderate operating conditions and requires no specific equipment making it relatively cheap to set up (Duarte and Madeira, 2009). The classical Fenton process generates highly reactive $HO^.$ radicals from the combination of hydrogen peroxide and ferrous ions in solution. However, it poses some disadvantages such as; limited pH range, production of sludge, and deactivation. Thus, heterogeneous Fenton or Fenton-like degradation processes using solid materials containing iron appear to be a practical way to overcome these limitations (Gu et al., 2013).

Adsorption and Fenton process has been used in many studies to remove/degrade EBT dye with positive results obtained as reported in literature (Zubair et al., 2017; Khurana et al., 2017; De Luna et al., 2013; Kaur and Singhal, 2015). This confirms that both processes are suitable methods to treat effluents containing EBT.

In line with this trend, this work will focus on the use of olive stones as a precursor for preparing activated carbon and the heterogeneous Fenton catalyst. Olive stone(s), a waste product from the industrial processing of olives to form olive oil was used in

this study since it can serve as a renewable and cheap source of carbon for producing activated carbon. Eriochrome Black T (EBT) will serve as a model dye in our study to access the potential of both the activated carbon and the Fenton catalyst to degrade EBT.

Eriochrome Black T is an anionic azo dye that is widely used in the textile industries to dye silk, nylon, wool etc. It is also used to estimate the concentration of various metal cations via complexometric titration. Studies have shown that EBT is carcinogenic and toxic therefore it is of environmental importance to remove it from aquatic waste water.

A combination of heterogeneous catalysis plus adsorption technique might proffer an attractive alternative in waste water remediation.

1.2 Aim(s) and objective(s) of research work

The main focus of this research study is to synthesize activated carbon (K-AC) and Fe-modified AC (Fe-AC) using olive stones as a precursor, for the removal of EBT dye by applying both adsorption and advanced oxidative process. The AC will be used to remove the dye from aqueous solution via adsorption while the potential of Fe-modified AC will be examined using both adsorption and Fenton process under laboratory conditions via batch system.

The following are the set objectives of this study;

    i.   To synthesize and characterize both adsorbents (i.e. K-AC and Fe-AC) produced from olive stones.

    ii.   To determine the amount of EBT adsorbed and find optimum conditions for EBT removal from simulated waste water.

    iii.   To carry out thermodynamic, kinetic studies and study the mechanism of adsorption of EBT dye by K-AC. Also, experimental data will be analysed using two common isotherms to further understand the adsorption process.

    iv.   Access the potential of the as-synthesized Fe-AC catalyst to adsorb and degrade (Fenton process) EBT dye from aqueous solutions.

    v.   Check the impact of operational parameters such as hydrogen peroxide concentration, time, and EBT concentration on the degradation process.

    vi.   Finally, the kinetics of the degradation process will also be investigated.

Chapter 2

LITERATURE REVIEW

2.1 Olive tree; history, composition and uses

Olive tree which is famous for an edible fruit called olives is a member of the *Oleaceae* family and is one of the oldest known cultivated trees in the world today. The origin of the olive tree cannot be ascertained though some believe it was first discovered 5000 years ago in ancient Persia and Mesopotamia which is present day Iran (kapellakis et al., 2008). Even though there are about 30 different species in the *Oleaceae* family, only one; *Olea europeaea* L is cultivated for its edible fruit (Anastopoulos et al., 2015). Cultivation of olives is carried out extensively in the Mediterranean regions and serves as a major source of income for rural communities and their environs. There are several nutritional benefits associated with the consumption of olives with reports obtained showing that a high amount (about 97%) of worldwide olive oil cultivation is undertaken in the Mediterranean regions while harvested olives are mostly used in olive oil production (Uylaser and Yildiz, 2014).

Industrial processing of olives in the oleic industry generates olive stone(s) as one of its by-products from the filtration after olive oil production. The main components of olive stone OS are; hemicellulose (21.9%), cellulose (31.9%) and lignin (26.5%). Other components present in small amounts include protein, moisture, free sugars and fats (Rodriguez et al., 2008). OS's have no real economic value and are

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considered as agricultural waste prompting the need to find alternative and beneficial uses for it (Calero et al., 2016).

OS is now widely used as an adsorbent to prepare activated carbon by various researchers (Alslaibi et al., 2013), producing composites or as plastic fillers (Siracusa et al., 2001), in cosmetology to aid skin exfoliation (Cosmoliva, 2007), for waste water remediation in removal of heavy metals and dyes (Hazzaa and Hussein, 2015; Baccar et al., 2010; Calero et al., 2016), as an abrasive to protect workers in the industrial sector (Dawson, 2006) etc.

2.2 Dyes; Eriochrome black T (EBT)

Dyes and pigments are an important class of organic compounds used by many industries to carry out their industrial processes. They are characterized according to their ionic charge in aqueous solution as well as their structural or functional groups (Tan et al., 2015). The discharge of coloured effluents containing dyes into natural water bodies upsets the biological processes taking place in aquatic habitats causing severe harm to aquatic communities (Gupta et al., 2006). Most of these dyes when present in water interfere with the transmission of light which hinders the photosynthetic process, are toxic, esthetically unpleasant due to colour formation and carcinogenic in nature (Moawed and Abulkibash, 2012).

Eriochrome black T EBT, ($C_{20}H_{12}N_3O7SNa$) an azo dye is a well-known textile colorant. It is also applied as an indicator in complexometric titrations to i) determine hardness of water ii) determine rare earth metals and nuclei acids (Kaur and Singhal, 2015). Excessive exposure to EBT can cause skin and eye irritation, vomiting and nausea. Similar health issues and environmental impacts associated with the use of dyes stated above are also relevant to ECT, so therefore, an efficient and cheap

method is required to treat industrial waste water that contains EBT before disposal. The structural formula of EBT is shown below:
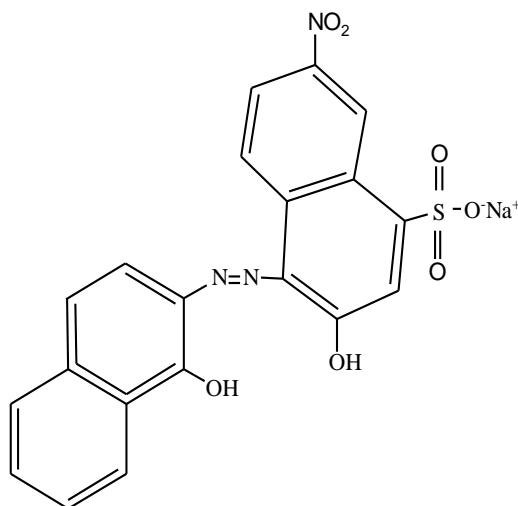
Figure 1: Structure of EBT dye

2.3 Treatment/remediation techniques

Remediation technology used for treating effluents from dye manufacturing industries can be classified into three broad categories; chemical, physical and biological treatment (Monash and Pugazhenthi 2009). All of these processes have their own advantages and drawbacks which limit their industrial application on a large scale (Crini, 2006). For example, the biological treatment of industrial effluents such as microbial degradation, fungal decolorization etc. has proven to be largely ineffective in eradicating color because almost all dyes are resistant to microbial attack and bacterial degradation. Also, by-products of biodegradation might be even more toxic than the initial substrate (Barka et al., 2013). Hence, there seems to be more focus on the use of adsorption (physical) and advanced oxidative processes (chemical) in waste water treatment.

2.3.1 Adsorption

Adsorption is a process whereby a liquid solute called the adsorbate accumulates on the surface of an adsorbent (solid) at the interphase between them. The adsorbate which can be a gas, liquid or dissolved solute creates a film on the surface of the adsorbent via adsorption. Nowadays, adsorption is considered to be one of the best and most promising methods to treat waste water effluents because it has several advantages; low cost, efficiency, flexibility in design, etc. over other treatment methods. Generally, the adsorption process can be carried out using either a batch or column technique.

The interactions between adsorbent and solvent, adsorbate and adsorbent and adsorbate and solvent are typically described either by electrostatic, physical or chemical interactions (Ersan et al., 2015). Four stages are associated with the transport process during adsorption. They are, bulk transport, film diffusion, intra particle diffusion and adsorptive attachment. Bulk transport is the first stage whereby adsorbate molecules diffuse towards the adsorbent while for film diffusion, the adsorbate molecules are transported to the surface of the adsorbent from the bulk phase. The adsorbate molecules diffuse from the adsorbent surface into its pores via intra particle diffusion before attaching to the pores in the final stage (Tran et al., 2017).

The two types of adsorption are;

1. <u>Physical adsorption</u>: occurs due to weak forces (van der Waals) between adsorbate and adsorbent at the interphase, is reversible, low enthalpy (< 80 $KJmol^{-1}$) and none or weakly specific interactions.

2. <u>Chemical adsorption</u>: chemical bonds (covalent or ionic) are formed between the adsorbent and adsorbate. It is usually selective and irreversible with high enthalpy (80-800 KJmol^{-1}).

Activated carbon AC has excellent adsorption capacity and has been used on a commercial scale for water remediation. Apart from its use in adsorption, AC has many applications in a wide variety of industries; water treatment, separation and purification (Ariyadejwanicha et al 2003), chemical and petroleum industries (Tawalbeh et al., 2005), catalysis (Azargohar and Dalai, 2006), energy storage (Kawano et al., 2008), batteries and fuel cells (Shah et al., 2006), in cooling systems and air filtering appliances (Yusufu et al., 2012) etc.

AC can be produced either through physical (use of CO_2 gas or steam) or chemical (dehydrating agents) activation. The type of precursors used, activation condition and method determines the surface chemistry of the AC and pore characteristics (Kilic et al., 2012).

Nowadays, commercially produced activated carbon is quite expensive and requires high pressure stream to regenerate it. All this adds to the overall cost of the treatment process. To overcome these drawbacks, the search for alternative adsorbents or precursors for producing AC that are efficient in removing dyes and economical to run has intensified in recent years (Crini, 2006). As earlier said, the oleic industry produces several by-products that can be used for numerous applications. In fact, residues obtained from olive oil production including OS, have also been extensively used for the removal of pollutants via biosorption techniques (Anastopoulos et al., 2015). Therefore, these by-products can serve as inexpensive alternative adsorbents.

2.3.2 Advanced oxidation process

Advanced oxidative process AOP, involves the treatment of pollutants and industrial wastes with highly reactive radicals that are capable of attacking and breaking bonds found in most organic compounds. AOPs are versatile compared to other oxidation processes since there are several ways to generate the needed hydroxyl radical *in situ* (Babuponnusami and Muthukumar, 2014). Consequently, AOP is now attracting more interest in the field of water purification because it has proven to be more efficient, with the ability to degrade recalcitrant organic pollutants as compared to other treatment techniques (Bethi et al., 2016). Since dyes are complex organic compounds that are often difficult to degrade, AOPs is widely used to effectively degrade these dyes and in some cases induce complete mineralization of the organic compound.

Ozonation, photocatalysis, Fenton, photo Fenton and Fenton like process are all examples of AOPs commonly used for water treatment.

1. Ozonation: can involve the use of O_3 alone, O_3 combined with either UV light (O_3/UV), hydrogen peroxide (O_3/ H_2O_2), catalyst (O_3/catalyst) etc.

2. Photocatalysis: use of semiconductors under UV illumination. Examples of compounds used as photocatalysts are; ZnO, TiO_2, CdS etc. In some cases, these catalysts are incorporated in solid supports to further enhance their photocatalytic properties and quantum efficiency.

3. Fenton Process: basically involves the generation of hydroxyl radicals (OH$^{\cdot}$) using a strong oxidizing agent and Fe^{2+}. Can be either; i. Fenton: Fe^{2+}/H_2O_2 ii. Photo Fenton: incorporates the use of light to accelerate the process;

$Fe^{2+}/H_2O_2/UV$ iii. Photo Fenton like: $Fe^{3+}/H_2O_2/UV$, $Fe^{2+}/(NH_4)_2S_2O_8/UV$ and $Fe^{3+}/(NH_4)_2S_2O_8/UV$.

2.4 Fenton process

The discovery of the Fenton reaction more than100 years ago (1894) by H.J.H Fenton has led to its use in treating waste water containing many hazardous organic compounds (Babuponnusami and Muthukumar, 2014). This process has been widely used to treat diverse waste water systems from many industries such as; Oleic industry (Lucas and Peres 2009), paper manufacturing factories (Amat et al., 2005), winery (Mosteo et al., 2007), refineries and fuel terminals (Aziz and Daud, 2012) etc. The Fenton reaction pathway is shown below;

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\cdot} + Fe^{3+} + OH^{-} \qquad (1)$$

$$OH^{\cdot} + RH \rightarrow R^{\cdot} + H_2 \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow {}^{\cdot}O_2H + Fe^{2+} + H^{+} \qquad (3)$$

Fenton process can be run either homogeneously or heterogeneously under varying conditions and combinations as discussed above though the classical Fenton process is homogeneous in nature.

Generally, homogeneous Fenton process is relatively simple to carry out and reagents needed for the process are safe, easy to handle and do not cause any environmental damage. However, the process has its own drawbacks such as formation of sludge, high metal concentration in effluent and low pH (process is efficient in acidic pH, usually pH3).

To find a way around these limitations, attempts have been made to recover the iron in the effluent but this process adds to the overall cost and makes the process more

complex. This has led to researchers developing new technologies to allow for a more efficient process. This is where heterogeneous Fenton catalyst systems come in to play. The Fenton catalyst is produced by using materials that contain iron or impregnating iron into numerous supports to produce efficient heterogeneous systems (Duarte et al., 2009).

Novel heterogeneous catalysts have been prepared using various supports. In selecting a solid support, the surface property and pore structure of the catalyst is important because it affects the efficiency, stability and kinetic rate of the Fenton process (Blanco et al., 2014). With this, iron leaching in the effluent is minimized, reaction can be carried out in mild conditions and the catalyst can be recovered directly after use.

2.5 Adsorption isotherms and kinetics

Isotherm and kinetic equations are useful in understanding the mechanism behind the adsorption process. Adsorption isotherms (sometimes known as equilibrium relationships) are therefore used to describe the relationship between pollutants and adsorbents. This isotherm studies are critical in the design of adsorption systems and optimization of adsorption mechanism pathway. They can also help to predict the capacity and surface properties of adsorbents under study (Rangabhashiyam et al., 2014).

Over time, many isotherms (Toth, Temkin, Flory-Huggins, Sips, Langmuir, Hill, Freundlich etc.) have been formulated and used by different researchers to better understand the mechanism of adsorption for the removal of different pollutants (Foo and Hameed, 2010).

This current study makes use of two conventional isotherms that is frequently used by researchers (Freundlich and Langmuir) to better understand the mechanism behind the adsorption process of EBT by K-AC. Both models are regarded as two parameter models.

Non-linearized and linear equations along with the graphical plots of both isotherms are shown in Table 1 below.

Table 1: Isotherms, linear and non-linear equations

Isotherm	Non-Linear equation	Linear equation	Graphical Plot	Isotherm parameters
Langmuir	$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m K_L} + \dfrac{C_e}{q_m}$	$\dfrac{C_e}{q_e}\ vs\ C_e$	K_L- maximum adsorption capacity q_m- Langmuir adsorption constant
Freundlich	$q_e = K_F C_e^{1/n}$	$In\ q_e = In\ K_F + \dfrac{1}{n} In C_e$	$In\ q_e\ vs\ In\ c_e$	K_F- related to adsorption capacity n- adsorption intensity

q_e and C_e in both equations represent the amount of adsorbate adsorbed in mgg^{-1} of adsorbent and dye concentration at equilibrium.

2.5.1 Freundlich isotherm

The Freundlich isotherm was initially developed for the adsorption study of animal charcoal but is now applied for studying heterogeneous systems (Foo and Hameed, 2010). It is regarded as the earliest known empirical relationship that described the relationship between adsorption characteristics of a heterogeneous surface and

equilibrium data (Tran et al., 2017). This model assumes that the adsorption process; represents multilayer adsorption, that sites with stronger binding energy are occupied first and binding strength decreases as site occupation increases and heterogeneous adsorbent surface with different energy for adsorption (Vijayaraghavan et al., 2006). The slope of the linear plot of the Freundlich isotherm (*1/n*), ranges from 0-1. This slope is a measure of surface heterogeneity or intensity of adsorption. If 1/n is less than 1, the adsorption is normal while a value above 1 shows co-operative adsorption. Also, according to this model, the surface of the adsorbent is regarded as becoming more heterogeneous as the slope tends towards (Mohan and Karthikeyan, 1997).

2.5.2 Langmuir isotherm

Langmuir model on the other hand indicates monolayer adsorption on homogeneous adsorbent surface. The model was originally designed to interpret the gas to solid phase adsorption by activated carbon before extending its use to empirically describing the equilibrium relationship between the liquid and solid phase (Vijayaraghavan et al., 2006). According to this model, there are no interactions between adsorbed molecules, all adsorption sites have similar/uniform energy and are identical in nature, and adsorption occurs at specific sites on adsorbent surface and once the pollutant occupies a site, no further adsorption can occur on the same site (Rangabhashiyam et al., 2014). The theoretical maximum monolayer adsorption capacity of the adsorbent q_m, sorption equilibrium constant K_L and separation factor R_L can all be determined from the Langmuir isotherm.

2.5.3 Adsorption kinetics

The uptake rate of adsorbate by adsorbents is described by carrying out a kinetic study of the adsorption process. To achieve this, two kinetics models (Lagergren

pseudo first and pseudo second order) are selected and applied in this study to describe the adsorption process. The applicability of both models to the experimental data depends on the correlation coefficient values (R^2) obtained from the linear plots and the closeness of the theoretically calculated q_e values to the experimentally obtained ones. A major difference between both models is that the pseudo first order model is based on the assumption that the rate of adsorption is proportional to the number of available sites while the second order assumes the rate to be proportional to the square of the available sites.

Table 2: Kinetic models

Kinetic model	Kinetic Equation	Graphical plot
Pseudo first order	$In(q_e - q_t) = Inq_{e,cal} - k_1 t$	$In(q_e - q_t)\ vs\ t$
Pseudo second order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e, cal^2} + \dfrac{t}{q_{e,cal}}$	$\dfrac{t}{q_t}\ vs\ t$

K_1 (min^{-1}) and K_2 (g $mg^{-1}min^{-1}$) are rate constants, q_t is adsorbent adsorption capacity (mg/g) at any time, t (minutes). From both models, the theoretical equilibrium capacity of the adsorbent can be determined.

Intra-particle diffusion on the other hand is widely applied to determine the mechanism of diffusion. It is based on a theory put forward by Weber and Morris in 1963. The hypothesis behind this theory is that q_t varies almost proportionally with the square root of contact time (Baccar et al., 2010).

$$qt = K_{ip}t^{1/2} + C \qquad (1)$$

Where, C is boundary layer thickness and k_{ip} is the rate constant for intra-particle diffusion. For intra particle diffusion to be the rate limiting step, the graphical plot of qt against the square root of time must give a linear plot that passes through the origin. If not, other mechanisms along with intra-particle diffusion are involved in the adsorption process.

Chapter 3

EXPERIMENTAL

3.1 Material and equipment

Olive stones were collected from an olive oil producing industry in TRNC. Eriochrome black T, EBT was purchased from Fluka, while potassium hydroxide used to activate the carbonized olive stones and hydrochloric acid was obtained from BDH chemicals, England. Sodium chloride and sodium hydroxide was supplied by Aldrich, Germany. Hydrogen peroxide (30%) and iron (II) sulfate heptahydrate was supplied by Merck All solutions were prepared using double distilled water.

Equipment(s): electronic balance, UV- spectrophotometer, HANNA HI 98127 water proof pH-meter, centrifuge machine (NF 815), furnace (Nabertherm GmbH model), Binder GMPH drying oven and mechanical agitator (SL350).

3.2 Synthesis of KOH activated carbon and Fenton catalyst

3.2.1 Olive stone activated carbon

A two-step procedure obtained in literature (Gazi et al., 2017) with slight modifications was used to prepare olive stone activated carbon. The olive stone(s) obtained from the factory was cleaned adequately with tap water and hot distilled water in order to remove the dirt attached to it and then dried in the oven at 80 ^{o}C for 48 hours. After drying, a known mass of the olive stones was carbonized in the furnace at 400 °C in the presence of air for 3 hours, cooled at room temperature before chemical activation. This was achieved by first crushing and milling the carbonized olive stones, sieving using a 250 μm sieve to achieve same particle size

before treating 50g of the already carbonized olive stones with 250ml of 0.1M KOH (impregnation ratio of 1:5) and stirring overnight at 40 °C. Subsequently, the solution was filtered using a filter paper and the residue was first washed with 0.1M HCl and then with water to remove impurities and unreacted chemicals until neutral pH and dried for 24 hours in the oven. The second step of the carbonization was done by weighing a known mass of the already activated olive stone into 3 separate crucibles and then carbonized in limited oxygen in the furnace for 1hour at different temperature (500 °C, 600 °C and 750 °C) respectively to determine the best carbonization temperature. The samples K-AC were cooled to room temperature and the yield was determined using equation 2 below.

$$\% \; yield = \frac{W_f}{W_i} * 100 \qquad (2)$$

Where;

   Wi: initial mass before carbonization

   W_f: mass after carbonization

3.2.2 Preparation of heterogeneous catalyst Fe-AC

Heterogeneous catalyst used for the Fenton process (AOP) was prepared using the wet impregnation method. Briefly, a known mass of the K-AC obtained from the first step of carbonization was added to 100 mL of 0.2M $FeSO_4$ solution(0.85 mL Fe^{2+} g^{-1} K-AC) and stirred for 6 hours. The produced catalyst was filtered, washed repeatedly with ethanol and water to remove un-exchanged iron before drying in the oven. The catalyst was weighed to determine the amount of iron exchanged in the K-AC before the second step of carbonization was carried out at 750 °C.

3.3 Batch adsorption study

The effect of several operational parameters on adsorption by K-AC was determined using the batch adsorption process. Influence of operation parameters such as; EBT

initial concentration (20-200mg/L), dosage (100 – 500 mg), EBT solution pH (2-10), temperature (20 – 50 °C) and time was investigated. The pH of EBT solutions was adjusted to the required pH value using 0.01M acid (HCl) or base (NaOH) solution. For the isotherm studies, EBT solutions of different concentrations containing a fixed amount of adsorbent were put in 250 mL conical flasks and agitated to allow adequate contact with K-AC until equilibrium time.

All adsorption experiments except stated otherwise was undertaken at ambient temperature (20 °C) in 250 mL conical flasks. At fixed time intervals, 3 mL was taken out, centrifuged at 3000 rpm for 15 minutes before taking the absorbance using a UV-vis spectrophotometer (1.0 cm light path quartz cell) with the wavelength set at 530 nm to determine EBT concentration. The amount of EBT absorbed at time t and removal percentage was determined using equations 3 and 4 below;

$$q_t = \frac{(c_i - c_f)V}{m} \qquad (3)$$

$$\% \ Removal = \frac{c_i - c_f}{c_i} * 100 \qquad (4)$$

C_i and C_f represent initial and final EBT concentration in mg/L, *m* is mass of K-AC and V is the volume of dye solution in Liters.

3.4 Heterogeneous catalytic activity test

For the AOP process, the effect of hydrogen peroxide concentration (2-10 mM), EBT initial concentration and time was also determined. All AOP experiments were conducted in the laboratory during the day with no exposure of our sample to any other light source. The extent of degradation at pre-determined time intervals was analyzed using the UV-vis spectrophotometer with the rate of degradation calculated using equation 5. C_i and C_t represent the initial EBT concentration and EBT concentration at a time *t*. All experiments were carried out at room temperature.

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$$D(\%) = \frac{(C_i - C_t)}{C_i} * 100 \qquad\qquad (5)$$

3.5 EBT stock solution

EBT stock solution (1000mg/L) was prepared by weighing and dissolving the needed amount of Eriochrome black T in double distilled water. Sequential dilutions of the prepared stock solution were then used to prepare different EBT working solutions used in the adsorption and AOP experiments. Calibration curve of EBT dye (shown below) was obtained by plotting the absorbance of 2-10 ppm EBT solutions with the dye concentration. Using this calibration plot (Figure 2), the unknown concentrations of EBT dye during experiments can be determined.
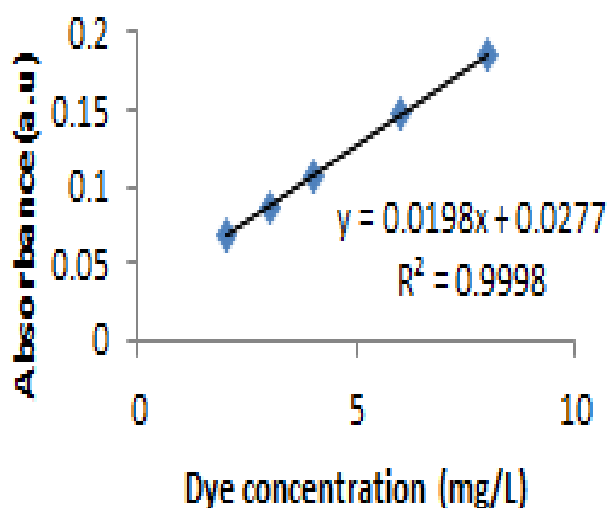

Figure 2: EBT calibration curve

3.6 Physiochemical characterization of K-AC and Fe-AC

The pH$_{pzc}$ (point of adsorbent zero charge) of both samples (K-AC and Fe-AC) was determined by agitating 25mL (0.01M NaCl) solutions with 0.1 g of both adsorbents for 24 hours using batch equilibrium technique. The pH of each solution of NaCl in the conical flasks was initially adjusted between pH 2-10 before adding the samples and agitation. After filtration, the pH was taken again and the intersection point in a

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plot of pH$_{final}$ versus pH$_{initial}$ gives us the point of zero charge (pH$_{pzc}$) of both samples. Physiochemical characterizations including moisture content, self pH (20 °C) and bulk density etc. of both adsorbents were also carried out.

3.7 Stability and reuse of heterogeneous catalyst

0.1 g of Fe-AC catalyst and the required amount of H$_2$O$_2$ as determined in section 3.4 was added to a known concentration of EBT dye and stirred until equilibrium was achieved. The already spent catalyst was then separated from the dye solution, desorbed in distilled water, filtered and dried at 80 °C before it was re-used again for the AOP. Similar cycle was repeated three times to determine the stability and reusability of the catalyst for the Fenton process.

Chapter 4

RESULTS AND DISCUSSION

4.1 Sample (K-AC and Fe-AC) characterization

Results obtained from the physiochemical characterization of K-AC and Fe-AC is depicted in Table 3.

Table 3: Physiochemical analysis of K-AC and Fe-AC

Characterization	K-AC	Fe-AC
Self pH	8.1	6.7
Moisture content (%)	1	0
Bulk density (g/cm^3)	1.46	1.63
pH$_{pzc}$	7.9	6.7
Yield % (750 °C)	62.5	72.2

The plot of initial and final solution pH of K-AC and Fe-AC is shown in Figure 3. The pH$_{pzc}$ of K-AC and Fe-AC were found to be 7.9 and 6.7 respectively. When the pH is lower than 7.9 or 6.7, the surface of AOS and Fe-AOS will be positively charged while at higher pH values the surface becomes negatively charged. Lower pH values (less than pH$_{pzc}$) of both adsorbent is expected to enhance the adsorption of EBT dye since the dye possesses a negative charge (Aksu and Tezer 2005).
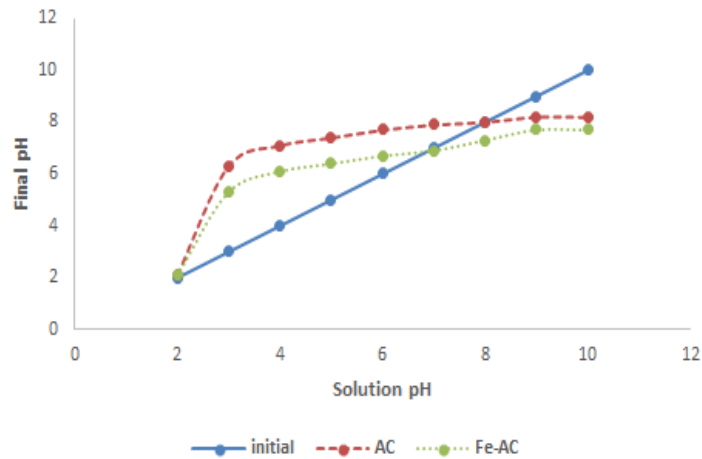
Figure 3: Point zero charge of K-AC and Fe-AC

4.2 Influence of process variables on adsorption of K-AC

4.2.1 Effect of carbonization temperature on yield and adsorption

The influence of increasing carbonization temperature from 500 – 750 °C on both the percentage yield and adsorption capacity of K-AC is shown in Figure 4. As seen from the figure, an increase in carbonization temperature led to reduction in the yield percentage from 90% to 60%. The decrease in the yield obtained could be attributed to the loss of more volatile materials from the material as the temperature increased from 500 – 750 °C (Hazzaa and Hussein, 2015).

This is in contrast to what is observed in the case of the removal efficiency of K-AC. As seen from the graph, removal efficiency of the K-AC increased dramatically as the carbonization temperature increased from 500 to 750 °C. Increasing the temperature led to the loss of volatile and organic compounds within K-AC which in turn creates a void in the AC matrix further aiding adsorption. Also, increasing activation temperature aids the development of the micropores within the AC which in turn increased the adsorption capacity of our adsorbent (Hazzaa and Hussein, 2015).
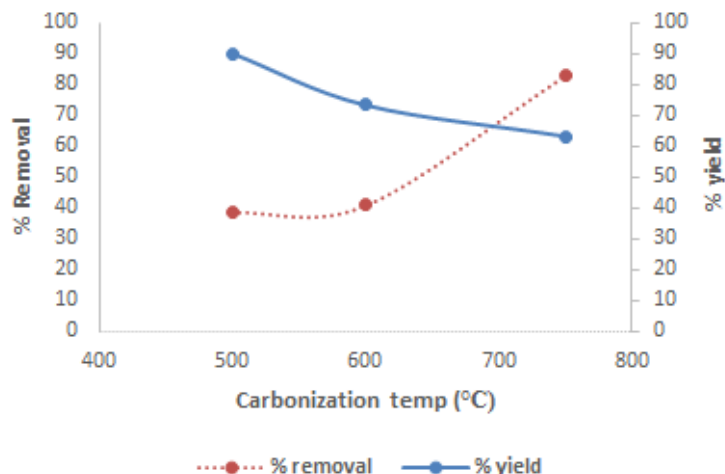
Figure 4: Effect of carbonization temperature on yield and removal %

4.2.2 Effect of pH

Solution pH plays a vital role in the dye removal process via adsorption because of the changes in dye chemistry and adsorbent surface charge as a result of pH variation (Babaei et al., 2017). Owing to this fact, the efficiency of the adsorption process was studied with respect to varying EBT solution pH values and result obtained is shown in Figure 5. The figure indicates that there is drastic reduction in the removal of EBT dye as the pH increases with only about 10% of the dye absorbed at pH 10 as compared to 95% in pH 2. This can be attributed to the surface chemistry of our adsorbent. At low pH values, the surface of K-AC is positively charged and there is a high tendency for electrostatic attraction to occur between the anionic dye and the adsorbent. Similar observations have been reported elsewhere (Khurana et al., 2018). Therefore pH 2 was taken as the optimum pH for our adsorption process.
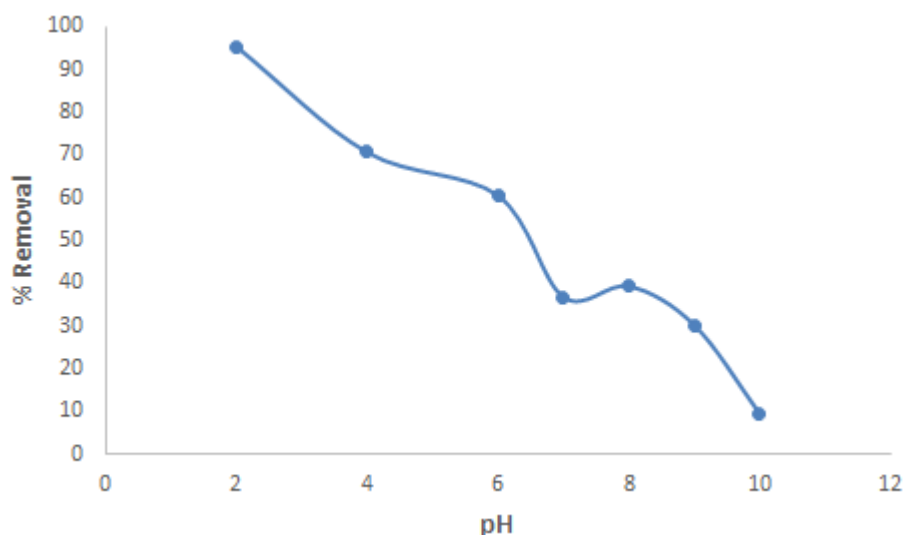
Figure 5: Effect of EBT solution pH on removal efficiency

4.2.3 Effect of K-AC dosage

Figure 6 shows the influence of increasing adsorbent dosage from 100 mg to 500 mg at constant EBT concentration (20 mg/L) on the removal % and adsorption capacity. The results indicated that increasing adsorbent dosage decreased the adsorption capacity of K-AC from 7.97 mgg^{-1} at 100 mg to 1.56 mgg^{-1} at 500 mg. This was ascribed to the overlapping of adsorption sites and surface area of the K-AC as the dosage increased thereby reducing the overall available sites for EBT adsorption (Jain et al., 2003; Han et al., 2007). However, there was a slight increase in removal efficiency when the dosage increased from 100 to 200 mg which is due to the increase in and availability of more adsorbent sorption sites hence, increasing dye removal though a further increase in dosage slightly reduced the removal efficiency of K-AC. Similar results have been found by other researchers (Bulut and Aydin, 2006; Sen et al., 2011). At lesser K-AC dosage, EBT is readily accessible leading to a higher removal per unit mass of adsorbent therefore 100 mg was chosen as the optimum dosage.
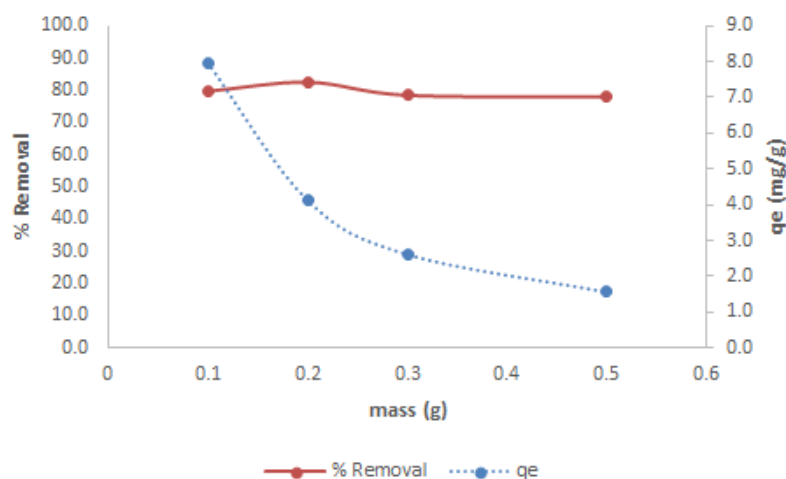
26

Figure 6: Effect of K-AC dosage on adsorption capacity and removal efficiency

4.2.4 Effect of time and temperature

To observe the effects of both contact time and temperature on EBT removal, experiments were carried out at different temperatures (20, 35 and 50 °C), varying time (0-24 hours) and constant EBT initial concentration. The adsorption capacity of K-AC for EBT dye increased as temperature and time increased as depicted in Figure 7 below. The process of dye removal with respect to time can be explained via two different steps. At the initial stage (30 minutes), there was a rapid uptake of EBT due to the presence of abundant vacant sites on the surface of K-AC. As time proceeds, the rate of adsorption reduced due to gradual occupancy of the active sites on K-AC making the adsorption process less efficient (Rani et al., 2015).After 24 hours, there was no appreciable increase in dye removal. Hence, optimum time for all adsorption experiments to attain equilibrium state was taken as 24 hours.

Entropy and enthalpy changes during adsorption process can be determined using results obtained from the changes in temperature with respect to adsorption (Alkan and Dogan, 2003). As shown below in Figure 6, the adsorption capacity of K-AC increases as temperature increases suggesting the endothermic nature of EBT adsorption by K-AC.

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Increase in temperature increases the mobility of dye molecules (in this case EBT) from the external boundary layer into the pores of K-AC (Karaca et al., 2008). Also, higher temperature enhances adsorption due to enlargement of pore size and surface area activation of adsorbents resulting in more active sites that are then available for adsorption of the EBT molecules (Senthilkumaar et al., 2006).
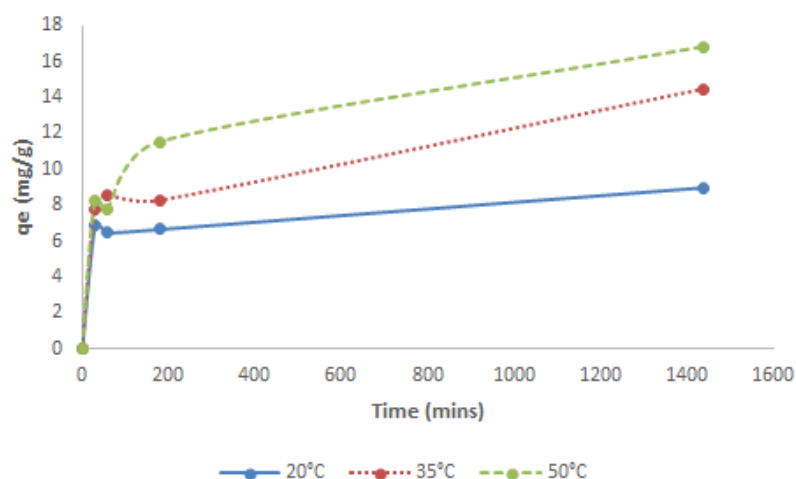

Figure 7: Effect of time and temperature on adsorption by K-AC

4.2.5 Effect of initial EBT concentration:

The concentration of dyes in waste water effluents is an important factor to consider during adsorption since a known weight of adsorbent can only remove a fixed amount of dye from its solution (Benaissa, 2005). Initial EBT concentration was varied from 20 to 200 mg/L at pH 2 and 100mg K-AC dosage to determine the effect of concentration. The influence of EBT initial concentration is shown below (Figure 8).

As seen from the plot, the adsorption capacity of K-AC increased from 1.56 mgg^{-1} to 46 mgg^{-1} as EBT concentration increased, though there was a slight decrease in its removal efficiency. Initial dye concentration provides a driving force to alleviate

mass transfer resistance between the solid medium (adsorbent) and the dye in the aqueous phase (Foo and Hameed, 2012). At low dye concentrations, the ratio of the available sites for adsorption to EBT concentration and mass transfer driving force is low which leads to lower adsorption capacity but the reverse is the case at higher dye concentrations where we have a higher mass transfer driving force resulting in higher adsorption (Hazzaa and Hussein, 2015; Bulut and Aydin 2006).
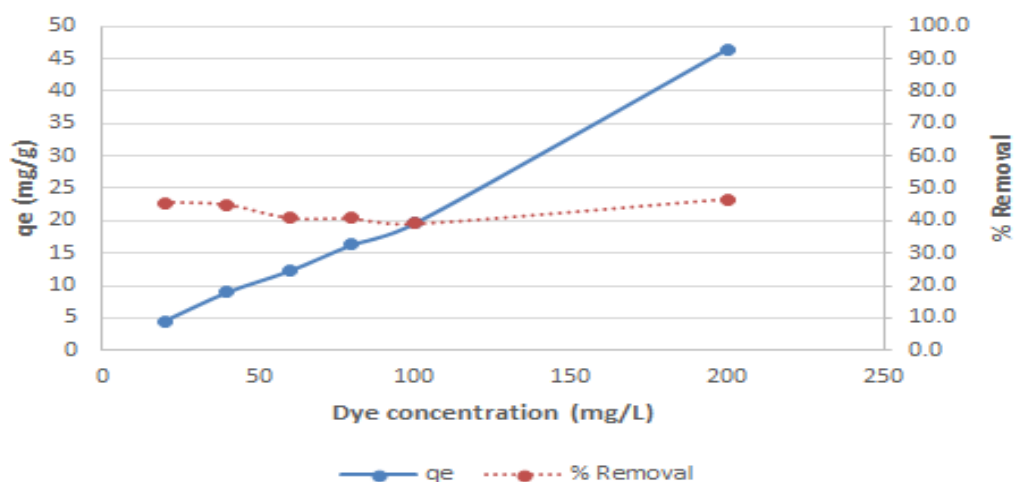

Figure 8: Effect of initial EBT concentration

4.2.6 Effect of salinity and counter ions

Industrial waste water contains several ions that can affect the adsorption process due to increase in ionic strength, so there is a need to investigate their impact on the performance of our adsorbent. The effect of varying concentrations of salinity (NaCl) and counter ions (SO_4^{2-} and NO_3^-) on removal % of EBT by K-AC is depicted in Figure 9. As seen from the graph, adding 2.5 g/L NaCl into the dye solution reduced the removal % by about 20% with further addition of sodium chloride salt having little or no effect on the adsorbent removal efficiency. Similar observations can be seen on adding nitrate and sulfate ions to EBT. This phenomenon could be either

through screening effect of the ions or preferential adsorption of ions on the active site of the adsorbent (Oladipo et al., 2014).
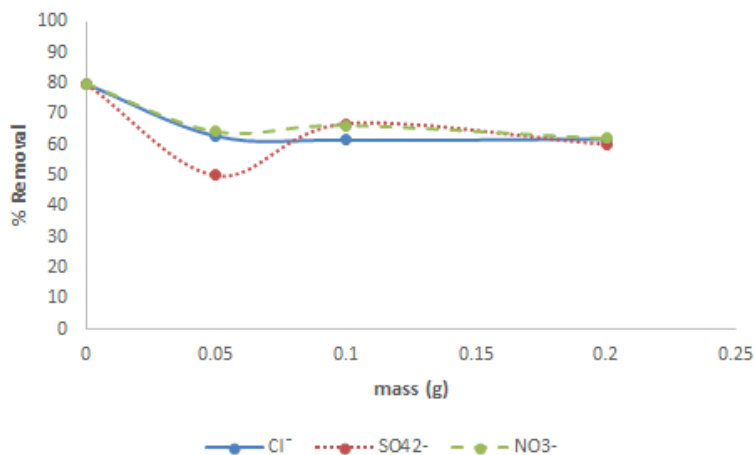

Figure 9: Effect of salinity and counter ions

4.3 Adsorption isotherm and kinetics

Adsorption isotherms help to provide a better understanding of the interaction between K-AC and EBT dye. Equilibrium parameters obtained from these isotherms give important information that can be useful in the future designing of adsorption. To achieve this, two commonly used adsorption isotherms (Langmuir and Freundlich) were used in this study. Langmuir assumes monolayer coverage of adsorbate on the surface of adsorbent at a fixed number of identical localized sites and no interaction between adsorbed molecules while Freundlich's model on the other hand assumes multilayer adsorption occurring at sites with different energy of adsorption (Barka et al., 2013). Linearized plots of both models are shown in Figures 10 and 11 while the obtained equilibrium parameters can be found in Table 4.
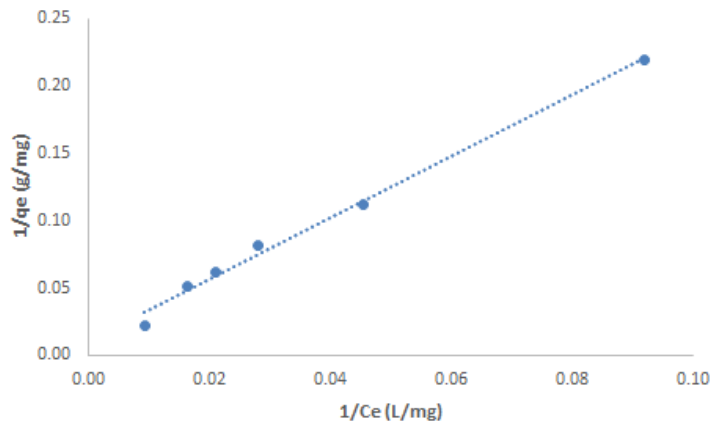
Figure 10: Langmuir isotherm plot
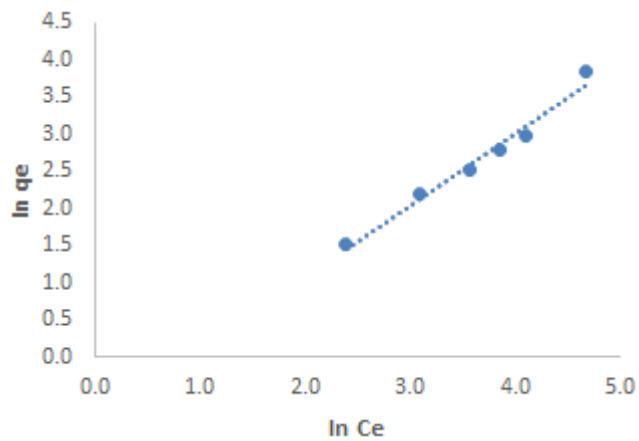
Figure 11: Freundlich's isotherm plot

As seen from the table, comparison of the correlation coefficient values (R^2) of both isotherms shows that the Langmuir isotherm (0.9928) provide a better-fit to experimental data as compared to Freundlich (0.9759). This implies that the EBT dye is absorbed on the monolayer surface of K-AC. Maximum monolayer adsorption capacity of K-AC was calculated (101.01 mg/g) for EBT dye.

R_L (separation factor) is then used to determine if the adsorption process is linear (R_L = 1), favorable (R_L values between 0 and 1), irreversible (R_L equals 0) or unfavorable

(R_L greater than 1). C_i is EBT initial concentration while K_L is gotten from the Langmuir equation.

$$R_L = \frac{1}{(1+K_L C_i)} \qquad (6)$$

All R_L values are in between 0 and 1 which suggests that adsorption of EBT by K-AC is favorable. The parameter n (calculated from slope of plot above) of the Freundlich isotherm plot is also used to verify if the adsorption process is favorable ($1 < n < 10$). n-value (1.04) obtained from the adsorption process in our study also supports that the adsorption process is favorable.

Table 4: Isotherm parameters

Langmuir Parameters	
R^2	0.9928
K_L	0.0043
q_m	101.01
R_L	0.54-0.92
Freundlich parameters	
R^2	0.9759
K_F	0.43
N	1.04

Three kinetic models (intra-particle diffusion, pseudo first and second order models) were applied in this study to help predict the rate of adsorption. The applicability of each model to the adsorption experiment is determined by their correlation coefficient values and the closeness of the experimental value to the theoretical value. Graphical plots obtained from each model and their kinetic parameters are shown in Figures 12-14 and Table 5. Pseudo second order model gives a good linear fit showing the highest R^2 values for all EBT concentration. Also, theoretically obtained values of q_e for the second order model were closer to the experimental values. This confirms that the adsorption process is pseudo second order in nature.
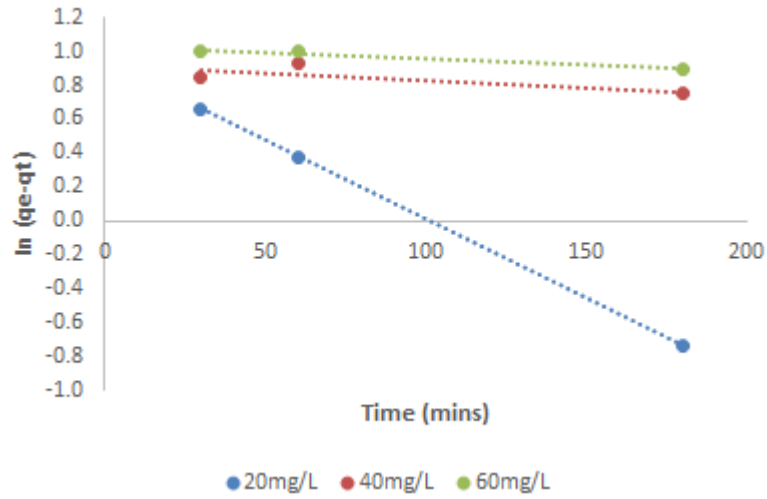
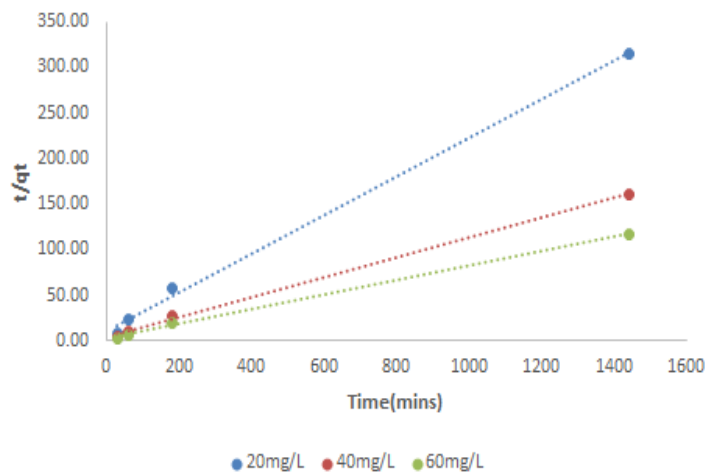Figure 12: Pseudo first order plot of EBT adsorption

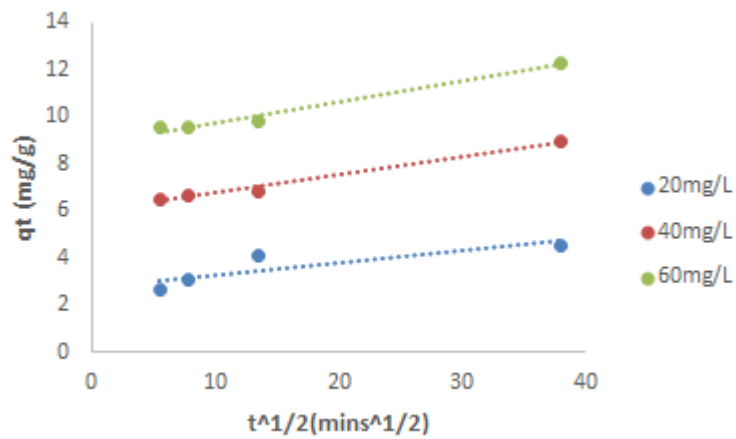Figure 13: Pseudo second order plot of EBT adsorption

Figure 14: Intra Particle plot of EBT adsorption

Adsorption process is a complex process which involves several steps (Rani et al., 2015). The Webber-Morris model was used to study the mechanism of adsorption. For intra particle diffusion to be the rate determining step in adsorption, plotting the adsorption capacity at a time t (qt) against the square root of time should give a linear plot that passes through the origin. As seen clearly from our graph (Figure 14), this is not the case hence intra-particle diffusion is involved in the adsorption process but is not the rate determining step. Similar reports have been found in literature (Priyantha et al., 2015; Baccar et al., 2010). Also, to support this, C values (boundary thickness layer) obtained from the intra particle plots were not equal to 0 and increased as concentration increased as seen in table 5. This also confirms that several processes were involved (Rani et al., 2015).

Table 5: Kinetic parameters

Kinetic Models	Parameters Obtained	EBT initial concentration (mg/L)				
		20	**40**	**60**	**80**	**100**
First order	$q_{e\,exp}$ (mgg^{-1})		12.5	21.0	30.6	40.7
	$q_{e\,cal}$ (mgg^{-1})	0.29	0.13	0.03	0.53	0.33
	k_1 (min^{-1})	0.0086	0.001	0.0008	0.011	0.0014
	R^2	0.8597	0.8745	0.9834	0.9716	0.6599
Second order	$q_{e\,cal}$ (mgg^{-1})	4.69	9.17	12.45	16.50	19.84
	k_2 (min^{-1})	0.0046	0.0033	0.0031	0.0029	0.0022
	R^2	0.9972	0.9987	0.9991	0.9992	0.9991
Intra Particle Diffusion	C	2.76	5.98	8.87	12.90	14.94
	K_{ip} (mgg^{1}min$^{1/2}$)	0.051	0.078	0.088	0.098	0.122
	R^2	0.7455	0.9908	0.9824	0.6963	0.9849

4.4 Thermodynamics of adsorption process

Thermodynamics of adsorption provides an insight into the mechanism and adsorption of an isolated system with the change in entropy regarded as the driving force behind the process (Foo and Hameed, 2012). The amount of dye adsorbed at equilibrium with respect to changes in temperature was undertaken to determine the thermodynamic parameters (using equations 7-9) of the adsorption process.

$$In\ K_c = \frac{C_S}{C_L} \qquad (7)$$

$$\Delta G° = -RT In K_c \qquad (8)$$

$$In\ K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (9)$$

K_c (equilibrium constant) can be calculated for each temperature studied by dividing C_s (EBT concentration in solid phase) with C_L (EBT concentration in liquid). T is temperature in Kelvin; R is the universal gas constant ($8.314\ Jmol^{-1}K^{-1}$).

Plot of *In Kc* (calculated using equation 7) *vs* 1/T was used to determine the values of enthalpy ($\Delta H°\ KJmol^{-1}$) and entropy ($\Delta S°$ in $Jmol^{-1}K^{-1}$) respectively. Results obtained and tabulated in Table 6 confirm the process to be endothermic in nature due to positive enthalpy value ($32.71\ KJmol^{-1}$) while positive entropy value ($114.89\ Jmol^{-1}K^{-1}$) reveals increasing randomness and disorder at the solid-liquid interphase during adsorption (Khan et al., 2013).

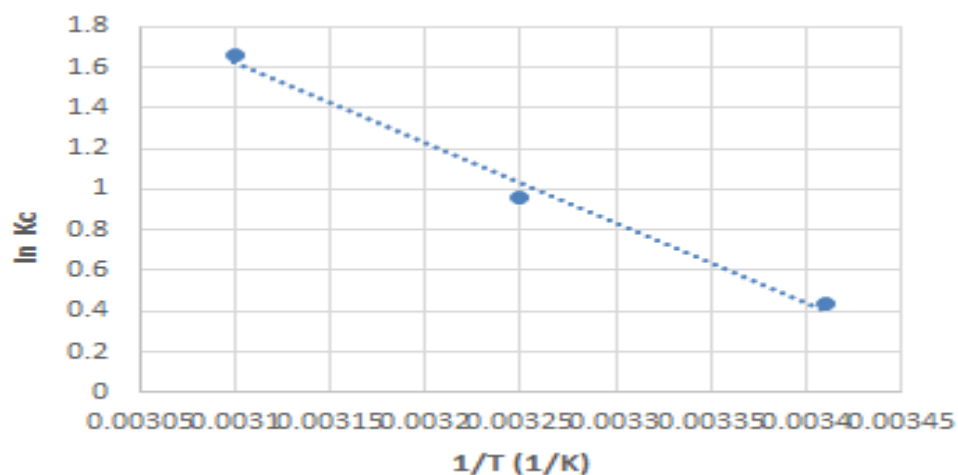Figure 15: Thermodynamic plot of *In K_c* versus 1/T for EBT adsorption

Gibb's free energy $\Delta G°$ (KJmol^{-1}) was calculated using equation 8. Negative $\Delta G°$ values obtained for all temperatures under study dictate the spontaneity and feasibility of the adsorption process. Also, the decrease in $\Delta G°$ values(from -1.07 to 4.46 KJmol^{-1}) as temperature increases shows that the spontaneous nature of the process increases as temperature increases.

Table 6: Thermodynamic parameters

C$_o$ (mg/L)	Temp (K)	*In K_c*	$\Delta G°$ (KJmol^{-1})	$\Delta S°$ (Jmol^{-1}K^{-1})	$\Delta H°$ (KJmol^{-1})
40	293	0.439	-1.07		
40	308	0.959	-2.46	114.89	32.71
40	323	1.661	-4.46		

4.5 Fenton-like process using Fe-AC

Heterogeneous Fenton catalyst Fe-AC using wet impregnation process was synthesized according to section 3.5 and used to degrade EBT dye. The amount of iron impregnated in the K-AC was 17.5mg Fe/g K-AC. All experiments conducted to determine the catalytic activity of the Fe-AC were carried out during the day without exposing the samples to any other light source (e.g. UV, sunlight etc.). To achieve this, optimum conditions for dye removal (pH and dosage) of Fe-AC was first

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determined using batch adsorption process. The impact of hydrogen peroxide concentration, time and EBT concentration on dye degradation was then investigated.

4.5.1 Effect of pH and dosage on adsorption of EBT by Fe-AC

Adsorption is the first step involved in developing a heterogeneous catalyst since it has an important role to play in the heterogeneous Fenton oxidation process (Jafari et al., 2017). The degradation of some dyes occurs on the surface of the photocatalyst (i.e. depends on their adsorption efficiency) making adsorption to be a crucial step in the degradation process (Kazeminezhad and Sadollahkhani, 2014). So therefore, a study of the effect of adsorption was undertaken to;

1. Confirm that there was no degradation of EBT via adsorption.

2. Access the adsorptive potential of Fe-AC.

3. Determine the effect of pH and dosage to confirm optimum conditions for use in the Fenton process.

The pH of the dye solution as earlier said is a vital factor when considering the oxidation of pollutants in the AOP. Hydrogen peroxide is more stable at acidic pH and unstable in basic conditions because it decomposes to form water and oxygen thereby reducing its oxidation ability (Blanco et al., 2014). The Fenton process is therefore more effective in acidic conditions so our study focused on the effect of pH on the adsorption capacity of our catalyst Fe-AC under acidic conditions (pH 2 - 4).

Under strong acidic conditions i.e. pH 2, there was 50% dye removal as compared to pH 4 where we achieved 69% EBT removal via adsorption. Since Fe-AC provides active sites for the Fenton reaction to take place by adsorbing and decomposing the hydrogen peroxide thereby producing OH· radicals near the surface of Fe-AC that

will immediately degrade the EBT dye in its vicinity, hence we chose the pH where we obtained maximum removal efficiency.

Optimum dosage required for the Fenton process was also determined by varying adsorbent dosage (100-300 mg). Results obtained showed (graph not included) that 100 mg had the highest adsorption capacity for EBT which is in line with what was obtained using K-AC. Optimum conditions for AOP was 100 mg and pH 4.

Preliminary studies undertaken on adsorption using the catalyst showed that it displayed lower adsorption capacity when compared to the K-AC so our work focused on the use of the catalyst in the Fenton like degradation of the azo dye EBT. We also found that Fe-AC cannot degrade EBT dye alone.
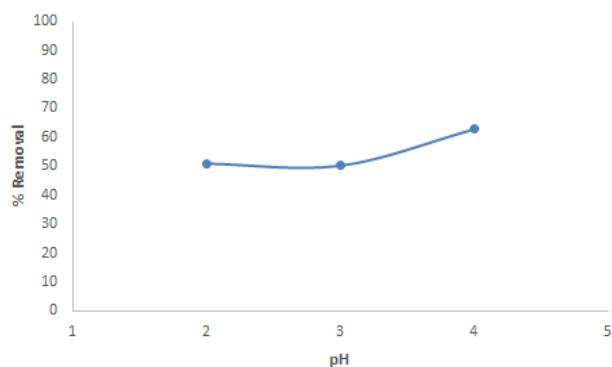
Figure 16: Effect of pH on removal of Fe-AC

4.5.2 Effect of H_2O_2 concentration

H_2O_2 plays an important role as the oxidizing agent in the Fenton process. Therefore, the effect of H_2O_2 concentration on the catalytic activity of Fe-AC was investigated for EBT removal and shown below in Figure 17. A blank run was carried out using only hydrogen peroxide. The samples were kept in the dark for 24 hours and the

absorbance of EBT was taken. There was no observable color change in the dye showing that the peroxide alone could degrade the azo dye.

On adding the catalyst (100mg), concentration of H_2O_2 was varied from 2-10 ppm (constant volume of 10 mL) at constant EBT concentration (20 mg/L). The addition of 2-8 ppm H_2O_2 reduced the residual concentration of EBT before additional increase in peroxide concentration i.e. 10 ppm led a slight increase. This is due to the scavenging effect caused by excessive amount of peroxide in solution as shown in the chemical reactions 4 and 5 (Gu et al., 2013).

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (10)$$

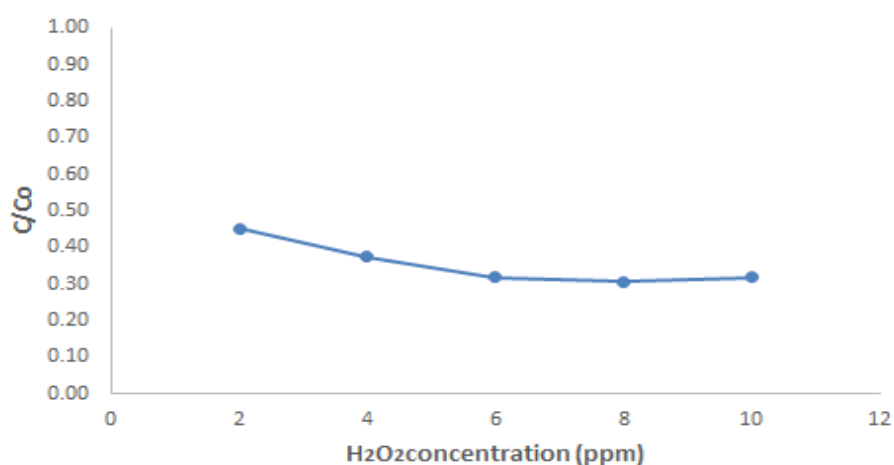$$HO_2^{\cdot} \rightarrow O_2^{\cdot} + H^{+} \quad\quad\quad (11)$$

Figure 17: Effect of H_2O_2 concentration

An image of both processes is shown in Figure 18. This confirms that the AOP led to decolorization of EBT. On applying AOP to EBT, the intense black blue color of the dye reduced dramatically. Optimal H_2O_2 concentration was 6ppm.
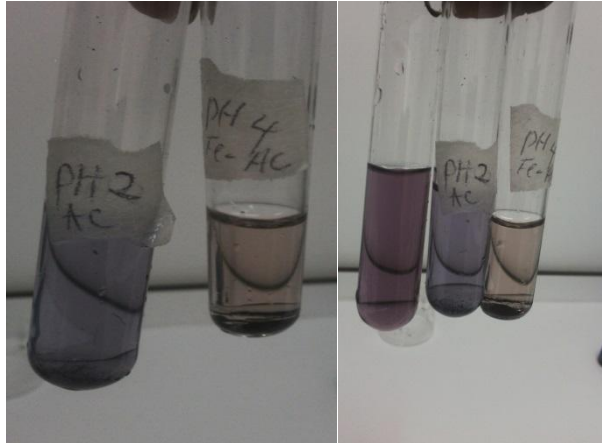
Figure 18: Fenton *vs* adsorption process

4.5.3 Effect of initial EBT concentration on dye degradation

Degradation efficiency of a dye is highly dependent on its initial concentration in solution. Better degradation was observed at lower EBT concentration as seen from Figure 19. Degradation efficiency of Fe-AC dropped from 80% to 40% as EBT concentration increased from 40-80 mg/L. This is attributed to the insufficient amount of oxidizing agent (H_2O_2) as EBT concentration increased since hydroxyl radicals generated did not increase proportionally as EBT concentration and there was also a fixed catalyst concentration (Devi et al., 2009).
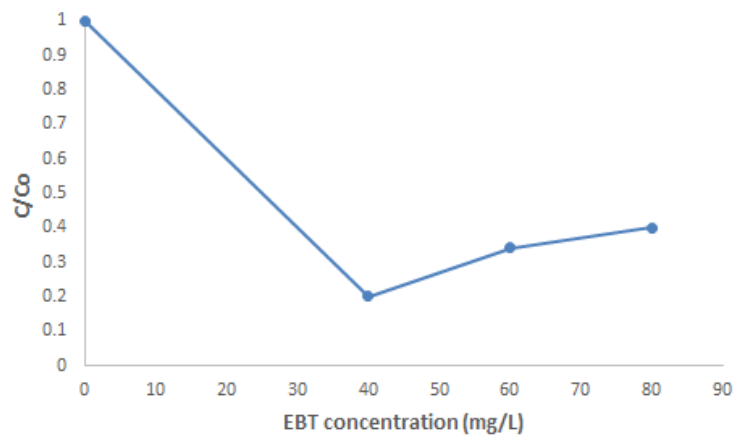

Figure 19: Effect of EBT concentration on degradation

4.5.4 Effect of time on EBT degradation

Figure 20 shows the influence of contact time on EBT degradation efficiency. As seen from the graph, equilibrium degradation was achieved after 6 hours for higher concentrations of EBT dye (60 and 80 mg/L) as compared to that of 40 mg/L which took 24 hours. The high EBT concentration increased the driving force behind the adsorption of the dye on the surface of the catalyst which aided the degradation process as compared to low EBT concentration.
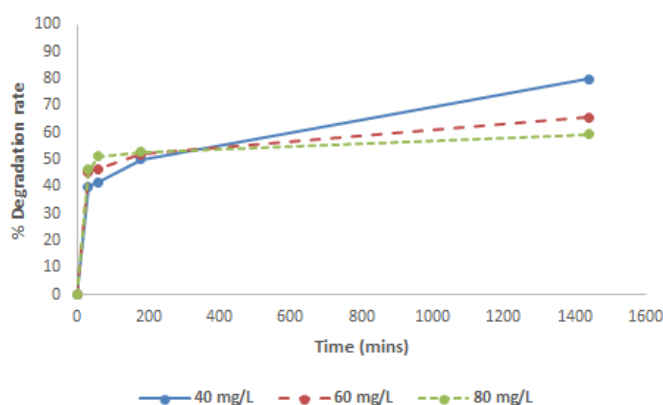
Figure 20: Effect of time on degradation rate

4.5.5 Effect of adsorption plus Fenton process

It was observed that using the Fe-AC catalyst alone (i.e. adsorption) led to less than 40% dye removal (EBT concentration of 40 mg/L) after 24 hours with no decolorization (Figure 18) while on using both adsorption (for 24 hours) followed by Fenton process (24 hours) increased the removal percentage of the heterogeneous catalyst to about 81%. This removal obtained by incorporating adsorption first before the Fenton process was only just slightly higher than that obtained when we use both adsorption and Fenton process simultaneously (about 79% after 24 hours). This shows that it is more favorable and economic to apply both processes simultaneously.

4.6 Kinetic analysis of the Fenton process

Degradation process of EBT dye was examined using two models i.e. zero and pseudo first order kinetic models according to the kinetic model expressed below;

$$r = dC/dT = K_{deg} C^n \qquad (12)$$

Figures 21 and 22 represent the plots for each kinetic model while the kinetic parameters obtained are tabulated in Table 6.
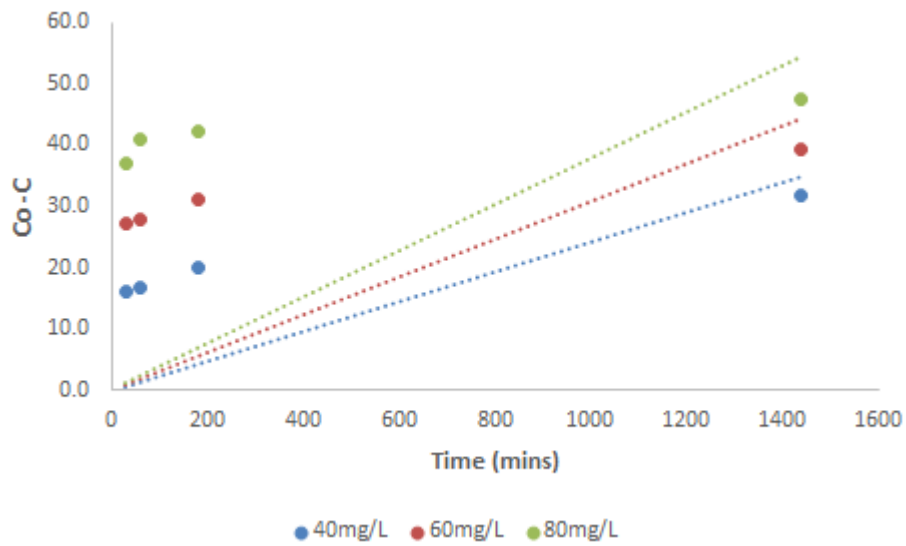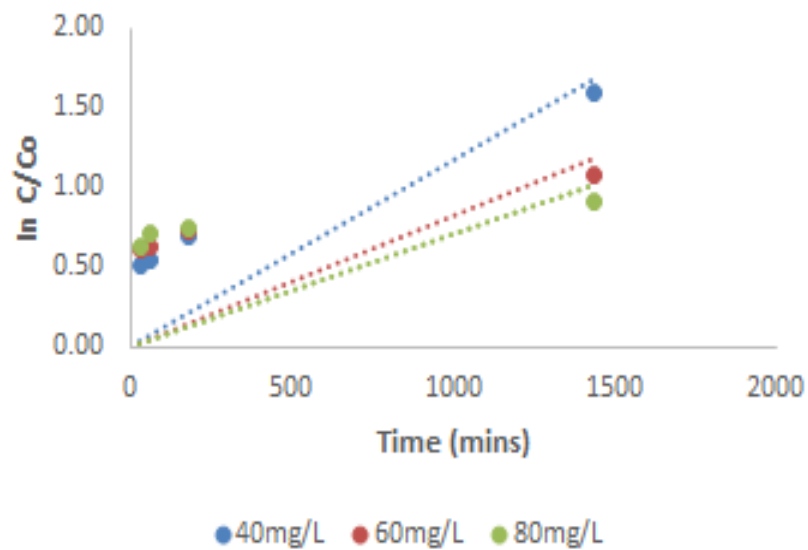

Figure 21: Zero order plot

Figure 22: First order plot

First order kinetic model exhibited higher R^2 value for all concentrations under study which confirms the model to provide a best fit for the degradation process of EBT. The table shows that the calculated rate of degradation for the pseudo first order model reduces from $5.0*10^{-5}$ to $3.0*10^{-5}$ as EBT concentration increases. This is in line with the effect of EBT concentration already discussed above. Similar observations have been reported elsewhere (Jafar et al., 2017; Kaur and Singhal, 2015).

Table 7: Degradation kinetics

Kinetic model	Kinetic parameters	EBT initial concentration (mg/L)		
		40	60	80
Zero order	K_{f0} (min^{-1}) * 10^{-4}	2.0	3.0	3.0
	R^2	0.9782	0.9513	0.8106
First order	K_{f1} (min^{-1}) * 10^{-4}	5.0	4.0	3.0
	R^2	0.9959	0.9702	0.8454

4.7 Fe-AC catalyst regeneration and reusability

In practice, it is important when using a heterogeneous catalyst for the Fenton-like process to determine the stability and reusability of the catalyst under study. To achieve this, spent Fe-AC catalyst was desorbed in water for 6 hours, dried at 80°C and then used for another degradation process under previously determined optimum conditions for 3 cycles. As depicted from the graph (Figure 18), there was an initial reduction in catalyst performance (from 80-70% color degradation) in the first cycle before it became constant. This result shows that the catalyst can be reused for repeated degradation of EBT with minimal loss in catalytic activity.
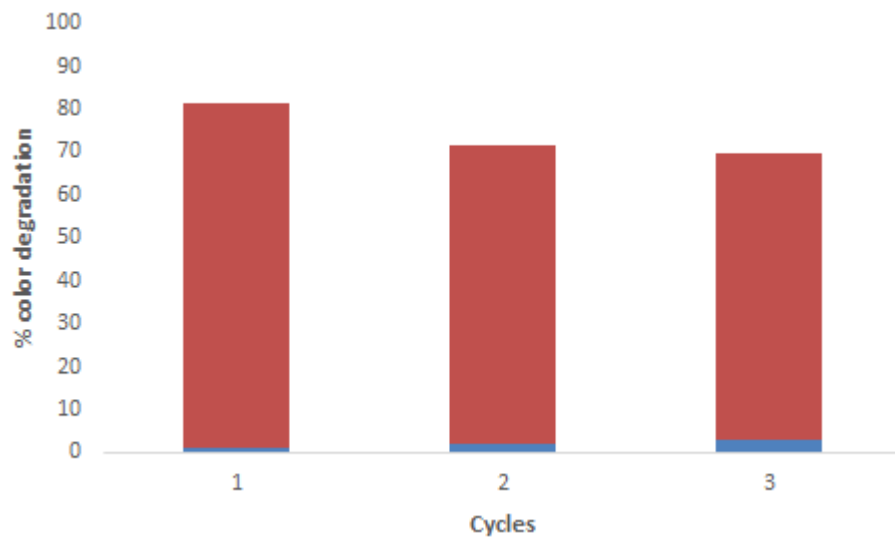
Figure 23: Regeneration of Fe-AC

Chapter 5

CONCLUSION

Potassium hydroxide Activated carbon K-AC and Iron exchanged potassium hydroxide Activated carbon Fe-AC was synthesized and used for removal of an azo dye EBT, via adsorption and advanced oxidative process in this thesis work. Both materials were characterized extensively and the effects of changing several experimental conditions were meticulously investigated.

In the case of K-AC, optimal operating conditions were found to be pH 2, 100 mg and 24 hours for pH, adsorbent dosage and contact time. Increasing adsorbent dosage led to reduced adsorption capacity though there was higher dye removal as dosage increased. Adding counter ions led to a marked decrease in removal efficiency of K-AC while removal efficiency increased steadily with increase in temperature. The Langmuir model provides a better-fit to the experimental data with a higher R^2 value than the Freundlich isotherm. Maximum monolayer adsorption capacity of K-AC as determined using the Langmuir isotherm was 101.01 mg/g which is quite good with R_L (0.54 − 0.92) and n (1.04) values confirming a favorable adsorption process. Adsorption system obeys pseudo second order kinetic model while the mechanism of adsorption was found to be a complex process with intra particle diffusion playing a role in the overall process. Positive enthalpy (114.9 $Jmol^{-1}K^{-1}$) and entropy (32.7 $KJmol^{-1}$) values pointed to the endothermic nature of the adsorption process while

negative Gibbs free energy (-1.07 – -4.46 KJmol^{-1}) confirmed the adsorption process to be spontaneous and feasible.

Heterogeneous catalyst Fe-AC was used in the Fenton process to degrade EBT. The effect of peroxide concentration, EBT concentration and time was investigated. Degradation rate and process efficiency was strongly influenced by EBT and peroxide concentration. EBT degradation followed pseudo first order kinetic with higher R^2 values (0.8454 – 0.9959) compared to zero order model. Results obtained revealed that Fe-AC can act as a suitable catalyst for degrading EBT dye. Furthermore, Fe-AC can be reused in successive cycles though a better desorbing agent needs to be found to improve the catalyst effectiveness.

In conclusion, both K-AC and Fe-AC can be suitable adsorbents for the remediation of waste water containing EBT dye from industries using either adsorption or advanced oxidative processes.

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