PREPARATION AND CHARACTERIZATION OF BIOCHAR FROM CASSAVA STEM AND ITS APPLICATION FOR DYE REMOVAL

A PROJECT REPORT

Submitted by

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BONAFIDE CERTIFICATE

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ABSTRACT

Treatment of the dye house effluent is essential to minimize the environmental pollution. The main aim of this study is to investigate the feasibility of the cassava stem derived biochar for the removal of the reactive dye. Biochar is produced by slow pyrolysis under argon atmosphere at 200°C, 300°C and 400°C at varying time and their yields are compared. In this work, batch adsorption studies such as, the effect of pH, temperature, contact time, adsorbent dosage, initial dye concentration and agitation speed are investigated. The maximum dye removal is obtained at optimum pH of 3 with the initial dye concentration of 20ppm, contact time 10min and temperature 25°C with the agitation speed 75 rpm. Characterization studies like Fourier Transform-Infra Red (FT-IR), Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) are carried out for the biochar samples before and after adsorption studies. Equilibrium isotherms are analysed by Langmuir, Freundlich, Temkin and Dubin-Radushkevich isotherms along with the kinetic and thermodynamic studies. Results proved that Langmuir best fits the experimental datas with the maximum adsorption capacity of 32.258 mg/g.

Ke words: Cassava stem, Biochar, Reactive dye, Pyrolysis, Adsorption.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL

For past many years, the dyes used in the textile industry are discharged into the water. Dyes are the colored substances applied on the fabric and it has a strong affinity to the substrate. The dye house effluents not only cause pollution and environmental degradation but also harmful and hazardous effects on the living organisms. Dye treatment is done mainly to nullify or reduce the pollutants that affect the media such as water and soil. There has been a demand for an effective and cost efficient adsorbent material which will negate the effect of the pollutant dyes particularly in the textile industry. In this context, Biochar has emerged as a cost effective and a viable alternative when compared to other dye adsorbents, for the removal of the residual dye. This will result in increase the potability of ground water thereby reducing the deleterious effects of pollution.

1.1.1 Dye house effluents and their effects on environment

The colors of life in full exuberance are often exhibited through our attires. Dyes and dyestuffs play an important role in coloring of fabrics. Dyes are widely used in various industries such as textile, paper, printing, carpet and in cosmetic industries. The dye molecule consists of chromogen and auxochrome. The color of some groups associated with the organic compounds is the chromophore. The color augmented with those groups is called auxochrome.

Table 1.1 Various processes for the dye treatement.

CLASSIFICATION	PROCESSES	APPLICATION
PHYSICAL UNIT OPERATIONS	Flotation	Oil separation
	Flocculation and sedimentation	Removal of High molecular weight compounds
	Membrane filtration	Removal of colloidal and dissolved organic matter
	Ionizing radiation	Degradation of dye molecules in aqueous solution
	Ion exchange	Removal of undesirable anions and cations.
	Adsorption	Removal of effluents
	Coagulation	Clarification of suspended and colloidal solids
CHEMICAL UNIT OPERATIONS	Advance oxidation (ozonisation)	Oxidize end products to terminal end or intermediate products
	Chemical oxidation	Removal of resistant organic compounds
	Chemical precipitation	Removal of heavy metals
BIOLOGICAL UNIT OPERATIONS	Activated carbon adsorption	Removal of refractory organics in waste water
	Different organisms (*Pseudomonas* or fungi)	Removal of colour
	Wet oxidation	Removal of toxic substances

Being recalcitrant, dyes are toxic to the environment. They are synthetic colorants prepared from aromatic molecular structures such as benzene, phenol etc. In an industry, consumption pattern varies from one dye to another. The dyes are classified into three categories: cationic, anionic and non-ionic. Cationic dyes, also known as basic dyes, produce positively charged colored part when dissolved in water. These dyes are applied to silk, wool and cotton. Anionic dyes are subdivided into acid, reactive and direct dyes. Acid dyes are utilized inwool, silk, paper, leather, and synthetic fibres. Direct dyes are used to colour cotton, cellulosic and blended fibres. Reactive dyes are applied to the cellulosic fibres and cotton fabric .Non-ionic dyes are disperse dyes and they do not ionise in an aqueous medium. Disperse dyes are used in synthetic fibres (Mane 2012).

Water is one of the essential element in which each life on earth depends on. But now-a-days, it has become global garbage can because of pollutants present in water thereby finally ending in water pollution. Water pollutants causing water pollution are classified into four main categories. Firstly, organic pollutants which play an important role in the formation of photochemical smog and the emissions from the motor vehicle, incinerators into water which leads to the dangerous health hazards. Secondly, inorganic pollutants, toxic to biota, consists of mineral acids, inorganic salts, finely divided metals, trace elements, cyanides, sulphates, nitrates, organo-metallic compounds present in natural waters. Thirdly, suspended solids and sediments in water mainly comprise of silt, sand and minerals eroded from the land. Finally, radioactive isotopes or high energy particles into the water are toxic to the life forms (Bhaskaran 2011).

A dye house effluent contains heavy metals, cyanide, toxic organics, nitrogen compounds, phosphorous, phenols, suspended solids etc. These effluents are discharged either into the sewer or to the nearby river. The toxicity and the inhibitory nature of dyes are deleterious to the environment. These dyes undergo photo-chemical degradation in the water causing water pollution which is a menace to the human causing water-borne diseases such as cholera, typhoid, damage to DNA, and finally death (Senthilkumar 2015).

These synthetic dyes reduce the light penetration and decrease the efficiency of photosynthesis of aquatic plants. These dyes also affect the aquatic organisms because these organisms need light to grow. The chemicals present in the dyes evaporate in the air causing air-borne diseases. They cause severe health hazards such as kidney damage, reproductive system problems, liver, and central nervous system. These dyes are both mutagenic and carcinogenic which causes severe problems to the ecosystem. For example, Methylene blue dye is toxic to blood, reproductive system, liver, upper respiratory tract, skin, eye contact and central nervous system. Malachite green dye accumulates in the tissues, liver, thyroid gland and bladder (Raffiea 2014). This causes environmental pollution leading to land degradation, soil erosion etc (Kumar 2013).

The methods available for the treatment of dyes can be classified as given in the Table 1.1.

1.1.2 Adsorption

Adsorption is the most common method used in treatment of wastewater when compared to the other methods because it is economical, effective and simple in design. It is a surface phenomenon which reduces toxic pollutants from the effluents. Adsorption is an eco-friendly; safest and most common effective method used in the removal of dyes and heavy metal ions. Adsorption is a process in which adsorbate gets adsorbed on the surface of the adsorbent. Increasing solution pH, increases the number of hydroxyl groups thus, increasing the number of negatively charge sites and enlarges the attraction between the dye and adsorption surface. The major drawbacks of this system are product recovery, high capital cost, high equipment corrosion etc. These drawbacks can be overcome by increasing the mass transfer rate and enhancing the adsorption capacity.

There are two modes of adsorption-batch mode and continuous mode. The difference is that batch mode is time-consuming and results are difficult to interpret but in continuous mode is easy, simple to operate, and attains a high yield. Reuse of adsorbent is also possible in continuous mode (Sivakumar 2014). Based on the extent of adsorption between adsorbate and adsorbent, adsorption is classified into physisorption in which adsorption results in vanderwaals force of attraction and chemisorption in which electrostatic attraction between the adsorbate and adsorbent.

1.2 SIGNIFICANCE OF THE STUDY

India is one of the largest textile exporters in the world. In Tamil Nadu, Tiruppur is the largest contributor to textile outputs when compared to other districts such as Perundurai, Erode and Karur. Dyeing, printing and finishing processes are taking place in textile industry. The dyes are posing a great threat to the environment. There are about 700 dyeing units discharge approximately 100 million litres of effluent every day. These dyeing units in Tiruppur release the untreated effluents into the Noyyal River makes it highly polluted and dangerous causes harmful effect on the environment.

In 2011, due to the environmental degradation and pollution, the Madras High Court ordered closure of all 700 dyeing units in the area because of environmental degradation and pollution and asked them to either pay monetary compensation to farmers for causing pollution or install zero liquid discharge (ZLD) system. The need to achieve the zero waste discharge is to set up a common effluent treatment plant (CETP) in and around the textile industry area. It was a great challenge for the dyeing units as they have to spend Rs.1, 300 crores to set up this treatment plant. However, some of the large dyeing units have built CETP where as small dyeing units cannot afford to build this plant. Bringing out the solution for the deleterious environmental crisis, the project is proposed which is afforded by the dyeing units with a good intension to achieve zero liquid discharge system and to bring back the industry in correct rails.

1.3 OBJECTIVES OF THE STUDY:

The objectives of this study are:

(i) To prepare the biochar from cassava stem at different time and temperature and compare their yields

(ii) To decolorize the simulated dye effluents containing the mixed reactive dyes from the aqueous solution with the help of a prepared biochar.

(iii) To characterize the prepared biochar before and after adsorption by FTIR, SEM and XRD.

CHAPTER 2
REVIEW OF LITERATURE

2.1 GENERAL

Methylene blue dye can be effectively removed when anaerobic digestion residue, palm bark or eucalyptus is used as biochars which are prepared at limited oxygen conditions. Maximum removal of the dye can be obtained when optimum conditions like pH 7 are maintained at 40°C. About 5mg/L of adsorbent is used as optimum dose for the maximum adsorption. Monolayer adsorption capacity was found to be 9.50mg/g (Sun *et al.,* 2013).

Acid black 172 (metal-complex dye) were absorbed by using the bamboo biochar and its potential for removal was done. Maximum adsorption capacity was found to be 434.78mg/g when the pH and temperature was upheld at 1 and 40°C for the optimum adsorbent dose of 500mg/l. The adsorbent and adsorbate were kept in contact for about 100min (Yang *et al.,* 2014).

Dyes like Reactive brilliant blue and Rhodamine were removed favorably by using low cost straw based biochar. The maximum adsorption were obtained when the pH were kept optimum at 3 for reactive brilliant blue and at 6.5 for Rhodamine B (Qiu *et al.,* 2009).

Slow pyrolysis of sugar beet tailings yield biochar which are used for the removal of phosphate. Anaerobically digested and undigested raw materials were used for biochar production and each showed different removal capacity of 45.5% and 36.3%. Pyrolysis temperature was fixed at 600°C (Yao *et al.,* 2011).

Two different types of biochars are applied for the adsorption of the heavy metals from the solution. The biochars were prepared from digested dairy waste and digested whole sugar beet. These biochars were employed for the removal of the metals like Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} from the mixture. The sorption capacity of lead was found to be maximum on comparison with other metals (Inyang *et al.,* 2011).

Chen *et al.,* (2011) performed experiment for the sorption of Copper and Zinc sorption with the help of the biochars which are pyrolysed from the raw materials such as hard wood and corn straw. 1g/L was the optimal dosage and at pH 1 adsorption capacity of copper and zinc was 6.79mg/g and 4.54mg/g (hard wood as biochar). For the corn straw as biochar the adsorption capacity was found to be 12.52mg/g and 11mg/g (copper and zinc).

Cadmium and lead can be adsorbed from the aqueous solutions by using the bio-sorbent prepared from the waste agricultural residues. The sorbents are pyrolysed from the wheat straw and rape seed residues under nitrogen gas atmosphere. The sorption capacity was found to be around 31.6 (for Cd) and 85.3mg/g (Pb) (Stefusova *et al.,* 2012).

Brewers spent grain can be converted into a biochar for the removal of the pesticide pymetrozine which was experimentally proved by the work of Xi *et al.,* (2014). Yields of different pyrolysis temperature were compared (300 °C to 700°C). The biochar produced at 700°C showed the maximum adsorption capacity around 31.606mg/g at the optimum conditions like pH 4, temperature of 45°C and the contact time was 120min.

Different temperatures for pyrolysis were investigated over the adsorbent sugar cane straw for the removal of the cadmium and zinc. Optimum pyrolysis temperature was found to be 700°C among the different temperatures ranging from 400 – 700°C for maximum removal of the ions (Melo *et al.,* 2013).

The removal of the Azo dye was employed with the use of biochar. Cellulosic Municipal solid waste biochar was used as an adsorbent by Agarwal *et al.,* (2015). The pH was investigated in the range of 4-7 of which the optimum pH was found to 7. At this optimum pH the adsorption capacity was found to be 1.035mg/g.

Biochars prepared from Soy bean Stover and peanut shell was used in removal of the Trichloro ethylene. Different temperature between 400 and 700°C were employed in biochar preparation of which 700°C samples had maximum adsorption capacity of about 25.38mg/g and 30.74mg/g (Ahmad *et al.,* 2012).

The pH was optimized for the effective removal of the methyl violet which is absorbed by using different biochars. Solution pH above

8.5 gave a good response for the removal of the dye by using canola straw, peanut straw, soybean straw and rice hulls. Among the biochars the maximum adsorption capacity was shown by the peanut straw of 256mg/g (Xu *et al.,* 2011).

Kim *et al.,* (2013) used Miscanthus sacchariflorus as the biochar for the adsorption of the Cadmium from the aqueous solution. The maximum adsorption capacity was found to be 13.24mg/g.

Lead and chromium can be removed by using the biochar prepared from the municipal waste water sludge. The optimum pyrolysis temperature was 400°C for 2 hrs. The biochar produced at this optimum conditions removed the lead and chromium effectively to about 18.2mg/kg (pH 5) and 36.6mg/kg (pH 2) (Zhang *et al.*, 2013).

The adsorption of Methylene blue can be done with the help of peanut husk. Kinetic and isotherm studies were done for this type of adsorbent and adsorbate. The maximum adsorption capacity was found to be 72.13±3.03mg/g (Song *et al.,* 2011).

The dyes like Acid black 26, Acid green 25 and Acid blue 7 were absorbed into the adsorbate which was prepared from pine cone. Certain parameters were optimized for the maximal adsorption of the dyes. The removal of dyes were found to be maximum at pH 2. Adsorbent dosage varies for the dyes and the optimal was 1g/L for Acid black while 2g/L for other two dyes and the initial concentration was estimated to be 50mg/L. Acid green dye was removed to a great extent (97%) by the sorbent (Mahmoodi *et al.,* 2011).

A low cost bio-adsorbent was developed from the Swede rape straw (Brassica napus L.) by Feng *et al.,* (2013). This biochar is used for the removal of the Methylene blue. Initial concentration of the adsorbent was about 200mg/L and optimal time and adsorbent dose was 40minutes and 200mg/g. Oxalic acid treated /modified Swede rape straw can also be used as the sorbent material which has more removal capacity when compared to normal adsorbent (Feng *et al.,* 2013).

Swede rape straw can be replaced by coconut coir dust for the removal of the Methylene blue dye. Optimum pH was set as 6 in order to attain the maximum capacity. Time for the reaction was done for 20minutes as those were optimal (Etim *et al., 2012*).

Batch studies were done for the removal of the Congo red dye by using the low-cost adsorbent obtained from the Bengal green seed husk. The parameters like contact time, pH, initial concentration and adsorbent dosage were studied. 92% removal of the dye was obtained when the pH and time was set to 5.58 and 60min along with the initial concentration at 100mg/L and adsorbent dosage was optimized to 300mg (Somasekhara *et al.,* 2014).

Light green dye was effectually removed by using the surfactant- modified peanut husk from the aqueous solution. At pH 3 adsorption occurred to maximum of 146.2 ±2.4mg/g. The temperature was maintained at 40°C for a period of 200minutes (Zhao *et al.,* 2014).

The removal of Methyl Violet 2B from Aqueous Solution by using *Casuarina equisetifolia* Needle was done. The maximum adsorption capacity of about q = 164.99mg/g was obtained when optimized conditions were used. The optimized values were pH 6.7, contact time 120min, agitation speed 250rpm, and temperature 40°C (Dahri *et al., 2013*).

Not only barley straw, a low cost waste material almond peel also can be used for the removal of the Methylene blue which was done by Benaissa (2007). A maximum adsorption capacity was achieved to be about 113-140 mg/g when the removal process was done at pH 6.0, temperature as 60°C and the adsorbate dosage level as 0.5g. Methylene blue can also be removed by using the guava seeds as optimized carbon material. For pH of 8.1 and 45minutes of contact time the percentage removal and the maximum adsorption capacity was found to be 84.75% and 198.12mg/g.

Tamarind pod shells were used for the adsorption of the Methylene blue and amaranth. Both the adsorbates were removed at various pH, contact time and adsorbate dosage. The maximum adsorption capacity of Methylene blue was found to be 60.11mg/g at pH 6.0, 50 minutes at 1g/L of adsorbent dosage. While the maximum removal capacity for amaranth is 65.04mg/g at pH 2.0, 40 minutes and 3g/L of adsorbent dosage. Initial concentration of about 10mg/L was used for both the dye removal (Ahalya *et al.,* 2013).

Neem husk was used for the removal of various dyes. But rather than raw neem husk, when it was treated with ZnCl2, H3PO4, and KOH the adsorption efficiency was found to be increased. This adsorbent was used for adsorption of various dyes like xylenol orange, procion red, and remazole turquoise blue . at the initial concentration of 20ppm and adsorbent dosage of 0.2g the removal percentage was found to be 30%, 85%, and 35% for the above adsorbents. For the initial concentration of about 12 ppm the %R was found to be 81%, 71% and 45% while for the initial concentration of about 60ppm the %R was observed as 99%, 79%, and 68% for the same adsorbent dosage (Alau *et al.,* 2010).

The coal ash and coconut shell as carbon adsorbents were used to decolorize the textile effluents by adsorbing the Acid orange 7. The adsorption technique was done with optimized pH, contact time, and adsorbent dosage. The maximum color removal of about 85% (using coal ash) and 94% (using coconut shell) was achieved at particular pH6.0, contact time 15min, and adsorbent dosage 1.5g/100ml (Ramakrishnaiah & Arpitha 2014).

Optimization of various parameters such like pH, contact time, initial concentration, adsorbent dosage, and temperature were studied by Ponnusamy & Subramaniam (2013) for the adsorption of Congo red dye onto the cashew nut shell .at the particular pH 3.2, contact time 67 minute, the maximum removal of dye achieved was 99.99% at the initial concentration 20mg/L, adsorbent dosage 24.76g/L, and temperature 30°C. The malachite green dye was effectively removed by using the acid activated low cost carbon which acts as a adsorbent. The removal of the dye was found to be 95% at the pH 9.5, contact time 60 minutes, at temperature of about 40-60□C and the adsorbent dosage used was found to be 50mg/50ml .

Tables 2.1 and 2.2 show the selective literatures on the removal of pollutants by biochar and activated carbon produced from various agro and agro-based industrial residues.

Table 2.1. REMOVAL OF POLLUTANTS BY BIOCHAR PRODUCED FROM AGRO AND AGRO-INDUSTRIAL RESIDUES

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCES
1	(a)Anaerobic digestion residue (b)Palm bark (c)Eucalyptus	Methylene blue	pH, temperature and adsorbent dose	7 40°C 5mg/L	(a)R% = 99.5% (b)R% = 99.3 (c)R% = 86.1% (a)Q=9.50mg/g	Sun *et al.*, 2013
2	Bamboo biochar	Acid black 172	pH, temperature adsorbent dose contact time	1.0 40°C 500mg/l 100min	Q=434.78mg/g	Yang *et al.*, 2014
3	Straw based biochar	(a)Reactive brilliant blue (b)Rhodamine B	pH	(a)3 (b)6.5	--	Qiu *et al.*, 2009

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCES
4	Digested sugar beet tailing biochar	Phosphate	--	--	R% = 73%	Yao *et al.*, 2011
5	(a)Digested diary waste biochar (b)digested whole sugar beet biochar	Pb^{2+} Cu^{2+} Ni^{2+} Cd^{2+}	--	--	(a)Q=248mmol/kg (b)Q=197mmol/kg	Inyang *et al.*, 2011
6	(a)Hard wood (b)corn straw	(i)Cu (ii)Zn	pH adsorbent dose	5 1g/L	(a)(i)Q= 6.79mg/g (ii)Q=4.54mg/g (b)(i)Q=12.52mg/g (ii)Q = 11 mg/g	Chen *et al.*, 2011
7	(a)Wheat straw residue (b)Rape seed residue	Cd^{2+} Pb^{2+}	--	--	(a)Q = 36.1mg/g (b)Q = 83.5mg/g	Stefusova *et al.*, 2012

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCES
8	Brewers spent grain	Pesticide Pymetrozine	pH, contact time and temperature	4 120min 45°C	Q = 31.606mg/g	Xi *et al.*,2014
9	Sugarcane straw	Cadmium Zinc	--	--	--	Melo *et al.*, 2013
10	Cellulosic municipal solid waste	Azo dye	pH	7	Q = 1.035mg/g	Agarwal *et al.*, 2015
11	(a)soy bean stover (i)300°C (ii)700°C (b)Peanut shell (i)300°C (ii)700°C	Trichloroethylene	--	--	(a)(i)Q = 9.85mg/g (ii)Q=25.38mg/g (b)(i)Q = 7.79mg/g (ii)Q=30.74mg/g	Ahmad *et al.* 2012,

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCES
12	(a) Canola straw (b) Peanut straw (c)Soybean straw (d) Rice hulls	Methyl violet	pH	<8.5	(a) – (b) Q = 256mg/g (c) Q = 179mg/g (d) Q = 124mg/g	Xu *et al.*, 2011
13	Miscanthus sacchariflorus	Cadmium	--	--	Q = 13.24mg/g	Kim *et al.*, 2013
14	Municipal waste water sludge	(a)Pb(II) (b)Cr(II)	pH	5 2	(a) Q = 18.2mg/kg (b) Q = 36.6mg/kg	Zhang *et al.*, 2013

Table 2.2. REMOVAL OF POLLUTANTS BY ACTIVATED CARBON

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
1	Peanut husk	Methylene blue	--	--	Q = 2.13±3.03mg/g	Song *et al.*, 2011
2	Pine cone	(a) Acid black 26 (b) Acid green 25 (c) Acid blue 7	Adsorbent dosage, initial concentration, pH and temperature	(a) 1g/l (b)(c) 2g/l 50mg/l 2 65°C	(a)R%=93% (b)R%=97% (c)R%=94.5	Mahmoodi *et al.*, 2011
3	(a) Canola straw (b) Peanut straw (c) Soybean straw (d) Rice hulls	Methyl violet	pH	<8.5	(b) Q = 256mg/g (c) Q = 179mg/g (d) Q = 124mg/g	Xu *et al.*, 2011

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
4	Swede rape straw	Methylene blue	adsorbent dosage, Initial concentration and contact time	3g/l 200mg/L 40min	Q= 246.4mg/g	Feng *et al.*, 2013
5	Oxalic acid treated Swede rape straw	Methylene blue	Initial concentration contact time	300mg/L 60min	Q = 432mg/g	Feng *et al.*, 2013
6	(a) anaerobic digestion residue (b) palm bark (c) Eucalyptus	Methylene blue	Contact time pH, initial concentration and temperature	120min 7 5mg/L 40°C	Q = 9.50mg/g (a) R% = 99.5% (b) R% = 99.3% (c) R% = 86%	Sun *et al., 2013*
7	Coconut coir dust	Methylene blue	pH, adsorbent dosage and contact time	6 0.1g 20min	Q = 29.5mg/g	Etim *et al., 2012*

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
8	Bengal green seed husk	Congo red	Contact time pH, initial concentration and adsorbent dosage	60min 5.85 100mg/L 300mg	Q = 41.66mg/g R% = 92%	Somasekhara *et al.*, 2014
9	Peanut husk	Light green dye	pH, contact time and temperature	3 200min 40°C	Q = 146.2±2.4mg/g	Zhao *et al.*, 2014
10	Acacia nicotica leaves	(a) crystal violet (b) Rhodamine B	pH, initial concentration, adsorbent dosage and contact time	6 200mg/L 0.2-1g 120min	(a)Q = 33mg/g (b)Q = 37mg/g	Prasad *et al.*, 2012
11	Uncariagambir	Direct dye23	Temperature	60°C	Q = 26.67mg/g	Achmad & Kassim, 2012

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
12	Coconut husk	Acid green 25	--	--	--	Halim *et al.*, 2011
13	Sugar cane bagasse	Malachite green	adsorbent dosage, Initial concentration, contact time and temperature	1g/L 50mg/L 120min 20°C	Q = 190mg/g	Sharma & Nandi, 2013
14	(i)raw corn straw (ii)modified corn straw	(a) blue 21 (b) yellow 21	pH, Initial concentration and contact time	2 250mg/L 180min	(i) (a)R% = 4.70% (b)R% =95.67% (ii) (a)R%=58.72% b)R%= 62.54%	Umpuch & Jutarat, 2013

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
15	(a) Nut shells(GNC) (b) Eichhoria charcoal (EC)	Congo red	contact time, pH, initial concentration, adsorbent dosage and temperature	(a)30min (b)40min 2 65mg/L 1.2g 45°C	(a)Q = 1117.6mg/g (b)Q = 56.8mg/g (a)R% = 83% (b)R% = 60%	Kaur *et al.*, 2013
16	Posidoniaoceanica	Methylene blue	pH contact time	5.5 60min	Q = 0.995mmol/g	Douissa *et al.*, 2013
17	Teak tree bark powder	Methylene blue	contact time, pH, initial concentration, temperature, adsorbent dosage and agitation speed	30min 250mg/L 1g/L 7 50°C 230rpm	Q = 331.333mg/g	Patil *et al.*, 2011

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
18	(a) Neam bark (b) Mango bark	Malachite green	pH, adsorbent dosage and temperature	(a)5.0 (b)2.0 2g/50ml 40°C	(a)Q = 0.36mg/g (b)Q = 0.53mg/g	Srivastava & Rupainwar, 2011
19	Citrulluslanatus (watermelon) Rind	Crystal violet	contact time, pH, adsorbent dosage and temperature	180min 8 1.4g/L 50°C	Q = 4.82 mg/g	Bharathi & Ramesh, 2012
20	Vitexnegundo stem	Mathylene blue	pH, contact time initial concentration and adsorbent dosage	6.3 50min 25mg/L 125mg/50ml	--	Kavitha & Senthamilselvi, 2014

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
21	Pistachio nut shell	Azo dye	--	--	Q = 70.92 mg/g	Armagan & Toprak, 2013
22	Yellow passion fruit peel	Methylene blue	pH, contact time and temperature	3 56hrs 25°C	Q = 0.0068mmol/g	Pavan *et al.*, 2008
23	Raw barley straw	Methylene blue	pH, contact time, adsorbent dose and initial concentration	11 30min 50mg 5mg/L	Q = 71.8mg/g	Husseien *et al.*, 2007
24	*Casuarinaequisetifolia* Needle	Methyl violet 2B	pH, contact time, agitation speed and temperature	6.7 120min 250rpm 40°C	Q = 164.99mg/g	Dahri *et al.*, (*2013*)

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
25	Almond peel	Methylene violet	pH, temperature and adsorbent dosage	6.0 50°C 0.5g	Q = 113.140mg/g	Benaissa 2007
26	Guava seeds	Methylene blue	pH, contact time	8.10 45min	Q = 198.12mg/g	Joseph *et al.*, 2007
27	Tamarind pod shells	(a) Methylene blue (b) amaranth	pH, contact time, initial concentration and adsorbent dosage	(a) 6.0 (b) 2.0 (a) 50min (b) 40min 10mg/L (a) 1g/l (b) 3g/l	(a) Q = 60.11mg/g (b) Q = 65.04mg/g	Ahalya *et al.*, 2013
28	Kenaf (*Hibiscus cannabinus)* fiber char	Methylene blue	--	--	Q = 22.7 mg/g	Mahmoud et al 2012

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
29	Neem husk Activated with (A) $ZnCl_2$, (B) H_3PO_4 (C) KOH	(a) xylenol orange (b) procion red (c) remazole turquoise blue	initial concentration, adsorbent dosage	(a)20ppm (b)5ppm (c)12ppm 0.2g	(a) R% at 20ppm (A) 30% (B) 85% (C) 35% (b) R% at 5ppm (A) 81% (B) 71% (C) 45% (c) R% at 12ppm (A) 99% (B) 79% (C) 68%	Alau *et al.*, 2010

S.NO	ADSORBENT	ADSORBATE	PROCESS STUDIED	OPTIMUM VALUES	OUTCOMES	REFERENCE
30	Sargassumbinderi	Basic yellow11	pH, initial concentration and adsorbent dosage	5.41 100mg/L 2g	Q = 192.3077mg/g	Tan *et al* 2009
31	(a) coconut shell (b) coal ash	Acid orange 7	pH, contact time and adsorbent dosage	6.0 15min 1.5g/100ml	(a)R%=94% (b)R%=85%	Ramakrishnaiah & Arpitha 2014
32	cashew nut shell	congo red dye	pH, contact time, initial concentration, adsorbent dosage and temperature	3.2 67min 20mg/L 24.76g/L 30°C	R% = 99.99%	Ponnusamy & Subramaniam 2013
33	Kenaf (*Hibiscus cannabinus)* fiber char	Methylene blue	--	--	Q = 22.7 mg/g	Mahmoud et al 2012

CHAPTER 3
MATERIALS AND METHODS

3.1 MATERIALS:

3.1.1 Dyes and reagents

Dyes, Reactive red and Drimarene turquoise were purchased from Vanavil Dyes and Chemicals Limited, Tiruppur. Sodium hydroxide, Hydrochloric acid and Oxalic acid of analar grade, purchased from SD fine chemicals Limited, Mumbai, were used in this work.

3.2.1 Instruments and equipments

The instruments and the equipments used for this work are shown in the Table 3.1. pH pen, manufactured by the company HANNA of model H198107 was used in this work to determine the optimum pH of the solution. It was calibrated using a buffer solution of pH 4, with the help of the screw driver.

The centrifugation equipment made by the Remi manufacturers of model R8C was used for the purpose of separation of light and dense particles. When this process is done, the dense particles tend to settle at the bottom. In our study, when centrifugation was done with the dye solution and the adsorbent, they will get mixed well. The adsorbent remains at the bottom and the supernatant at the top, which was used for further evaluation of the parameters.

Table 3.1 Instruments and equipments used in this work

INSTRUMENTS/ EQUIPMENTS	MAKE	MODEL	PURPOSE
Chemical vapour Deposition	VB Ceramics,Chennai	-	Pyrolysis for the preparation of the biochar
UV/Vis Spectro-Photometer	Shimadzu	UV-1800	To determine the wavelength of the solution.
pH pen	HANNA	H198107	To determine the pH of the solution.
Scanning electron microscope (SEM)	Zeiss	Σigma	To study the surface morphology of the sample.
Centrifugation	Remi	R8C	For the separation of the dense and light particles
Hot air oven	Kemi	KOS 2	To dry the sample.
Shaker	Scigenics Biotech Private Ltd.	Orbitek-LT	For the rapid mixing of the sample at a particular agitation speed.
X-Ray Diffraction (XRD)	PANanalytical.	Netherland model	To find the presence of crystalline structure
Fourier Transform Infra Red spectrum (FTIR)	Shimadzu	IRTracer - 100	To identify the functional groups.

3.2 METHODS:

3.2.1 Optimization of pyrolysis of cassava stem for biochar production

Cassava stem of hybrid variety Htp 740/92 is obtained from Salem district, Tamil Nadu, India. The average diameter of the cassava stem particle size was determined to be 209 microns. The cassava stem is then pyrolysed to produce biochar at an optimum temperature and time. The cassava stem pyrolysis is done using an instrument named Chemical Vapour Deposition (CVD) tubular furnace with an inert argon gas atmosphere maintained at a rate of 50 ml/min. Pyrolysis is a process in which thermo-chemical decomposition of the organic materials takes place in the limited conditions or absence of oxygen.

3.2.1.1 Effect of temperature

The pyrolysis was carried out at different temperatures. The process was started from a temperature of 200^0C up to 800^0C. At 200^0C and 300^0C, it was partially carbonised. But at 400^0C, it was completely carbonised by maintaining the constant time.

3.2.1.2 Effect of time

At constant temperature 400^0C, the pyrolysis process is carried out at different time from 1h to 6h .It was found that the cassava stem was completely carbonised at 3h at this temperature. The optimum temperature and time was found to be 400^0C and 3h respectively for the production of completely carbonised cassava stem.

3.2.1.3 Activation of biochar

The completely carbonised cassava stem was then centrifuged to remove the ash matter present which results in pure biochar. This biochar was then activated with 1% (w/v) oxalic acid by keeping it in the shaker at 120 rpm for 2h.This was later filtered using Whatman No.1 filter paper and kept in hot air oven at 60^0C overnight. Now, this activated biochar was used for the adsorption and characterisation studies.

3.2.2 Adsorptive removal of simulated dye effluent by cassava stem derived biochar

The idea for the preparation of the dye solution came from our visit to Common Effluent Treatment Plant (CETP), Arulpuram. It was found that residual dye solution contained excess colours/pigments which have to be removed with the help of the adsorbent. Therefore, a simulated dye effluent was prepared in the laboratory with 1g of Reactive Red (RR) and 1g of Drimarene Turquoise (DT) in 1 litre standard measuring flask (SMF).From this prepared dye effluent,1ml of solution is taken and made up to 100 ml with distilled water in a standard measuring flask. The wavelength of this dye solution was determined with the help of Shimadzu Spectrometer.

3.2.2.1 Effect of pH

The effect of pH was determined to find the maximum dye removal percentage and adsorption capacity. It is calculated as follows:

$$Q = (C0-C_f) * V/m \qquad (3.1)$$

$$DR = (Co-C_f)*100/Co \qquad (3.2)$$

‘Q’- adsorption capacity in mg/g, ‘Co’ - initial dye concentration in ppm, ‘C_f ’-final dye concentration in ppm, ‘V’- volume of solution in mL, ‘m’- mass of adsorbent in g.

The pH was maintained at 2, 3, 4, 5, 6, and 7. The initial readings were taken. The conditions were fixed at 15 min, agitation speed 100 rpm, room temperature and adsorbent dosage of 10mg/10ml.

The centrifugation is done and supernatant is used to get the final readings. The concentration of filtered sample for each pH was inferred.

3.2.2.2 Effect of contact time

The effect of contact time was done to find the time taken required by the adsorbent to reach equilibrium time and to study adsorption kinetics. The fixed conditions are maintained at pH3, the effluent concentration 100% (v/v), the agitation speed 100 rpm, adsorbent dosage 10mg/10ml and room temperature. The time was varied from 0 to 25 min. The initial readings were noted and the final readings were taken from the supernatant obtained after the centrifugation. The samples were filtered and concentrations were determined to find the removal efficiency and adsorption capacity.

3.2.2.3 Effect of initial dye concentration

The adsorption capacity and efficient dye removal can be inferred by varying the concentration of the effluent. Isotherm studies were done with the initial dye concentration. The various conditions such as pH 3, time 10 min, the agitation speed 100 rpm, adsorbent dosage 10mg/10ml and room temperature are to be maintained. The readings initially were taken and the final readings were noted from the supernatant got from the centrifugation process. The varying concentrations of filtered samples were determined.

3.2.2.4 Effect of temperature

Adsorption thermodynamics were studied with the help of effect of temperature. The effect of temperature was carried out with certain conditions at pH3,10 min time, effluent concentration 100%(v/v),agitation speed 100 rpm and adsorbent dosage 10mg/10ml.

The concentrations of the initial solutions were taken and final solutions were found from the supernatant.

3.2.2.5 Effect of adsorbent dosage

The effect of adsorbent dosage were studied at specified conditions such as pH3, contact time 10 min, effluent concentration 100%(v/v),agitation speed 100 rpm and temperature 25^0C.This study is done to determine the maximum dye removal efficiency and adsorption capacity of the adsorbent. The readings are noted initially. The experiment was carried out for different dosages say 5 mg/10mL, 10 mg/10mL, 20 mg/10mL, 40 mg/10mL.The concentrations of final solutions were measured from the supernatant.

3.2.2.6 Effect of agitation speed

The effect of agitation speed was carried out at the optimum conditions as pH 3, temperature 25^0C, 100% (v/v) effluent concentration and 20 mg/10 ml adsorbent dosage. The initial readings were noted. The experiment was carried out for speeds 50, 75, 100,125 and 150 rpm. From the supernatant, the concentrations of the final solutions were also measured.

3.2.3 Characterization of spent biochar

3.2.3.1 FT-IR

Fourier Transform-Infra Red (FT-IR) was used for the identification of the functional groups present on biochar surface.The efficiency of adsorption is due to the chemical structure on its surface.In this technique,infra- red rays were passed through the sample.some rays gets absorbed by the sample and some were transmitted.therefore,the spectrum produced gave the molecular fringerprint of the sample.

3.2.3.2 SEM

Scanning Electron Microscopy (SEM) was performed to observe the surface morphology of biochar .In this; a small coating procedure was to be carried. At first, the sample was taken in four vials. The coating of the sample was done in the golden particle fitted chamber .As the biochar is of powdered form the colloidal gel was coated, for the good fixation of gel and sample. The colloidal cello tape will be used only if the sample is of the liquid form. Blower was used to blow away the particles which were unfixed on to the gel. The main purpose behind this coating procedure was to increase the vacuum and so the sample gets activated. Then the coated sample was placed in the SEM instrument. By turning the knob, voltage and magnification was adjusted to get the clear focus and the final image was captured.

3.2.3.3 XRD

X-Ray Diffraction (XRD) was examined mainly to detect the presence the crystalline structure and atomic spacing in the sample. In this technique,X-rays were generated in such a way that in a cathode ray tube, when the filament gets heated up, electrons were produced. These electrons get accelerated towards the target with an applied voltage leading to the bombardment of the target material along with the electrons. These X-rays produced were collimated and directed into the sample. The sample and detector were rotated to record the intensity of the reflected X-rays. This technique is based on the Bragg equation (i.e.)

$$n\,\lambda = 2d\,\sin\theta \qquad (3.3)$$

Where,'n' is the positive integer, 'λ'is the wavelength of incident X-ray ,'d'is the atomic spacing ,'θ'is the angle between the incident and reflected X-rays. Based on the equation above,the geometry of incident

X-rays will disturb the sample, thereby giving the constructive interferences and an intensity peak X-ray signal gets recorded into a detector and will be converted into peak intensity which can be produced either in a printer or computer monitor.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 MAXIMUM WAVELENGTH FOR THE SIMULATED DYE EFFLUENT:

The maximum wavelength for the simulated dye effluent was found by using UV/VIS – Spectrophotometer, for different wavelength ranging from 400 – 700 nm. From the graph obtained in Figure 4.1, it was found the dye has finest wavelength of 540 nm

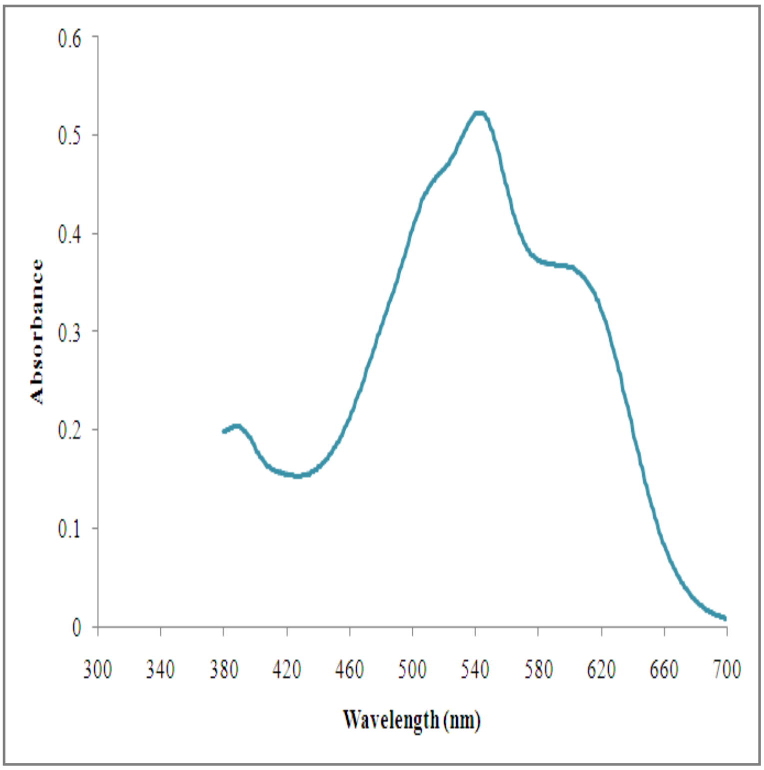


Figure 4.1 Maximum wavelength for the simulated dye effluent.

4.2 STANDARD CURVE FOR THE SIMULATED DYE EFFLUENT:

The standard curve was plotted with different concentration of dye (ppm) and absorbance at 540nm along X-axis and Y-axis respectively. The graph (Figure 4.2) was plotted to calculate the concentration of dye from its absorbance at various conditions.

Lambert-Beer's law is used to determine the concentration from absorbance, when the molar extinction co-efficient of the compound and the path length of the cuvette is known. Thus the law is expressed as Equation (4.1),

$$A = e * l * c \quad (4.1)$$

Where, 'A' is the absorbance at 540 nm, 'l' is the path length (1cm), 'e' is the molar extinction co-efficient and 'c' is the concentration of the dye (%v/v).

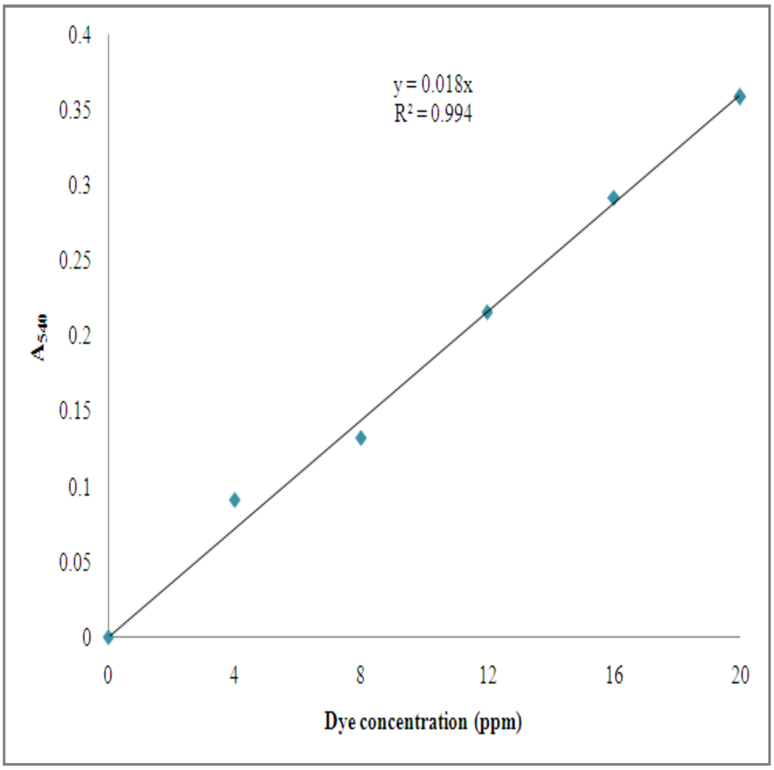


Figure 4.2 Standard curve for the simulated dye effluent.

4.3 OPTIMIZATION OF PYROLYSIS OF CASSAVA STEM FOR BIO CHAR PRODUCTION:

4.3.1 Effect of temperature:

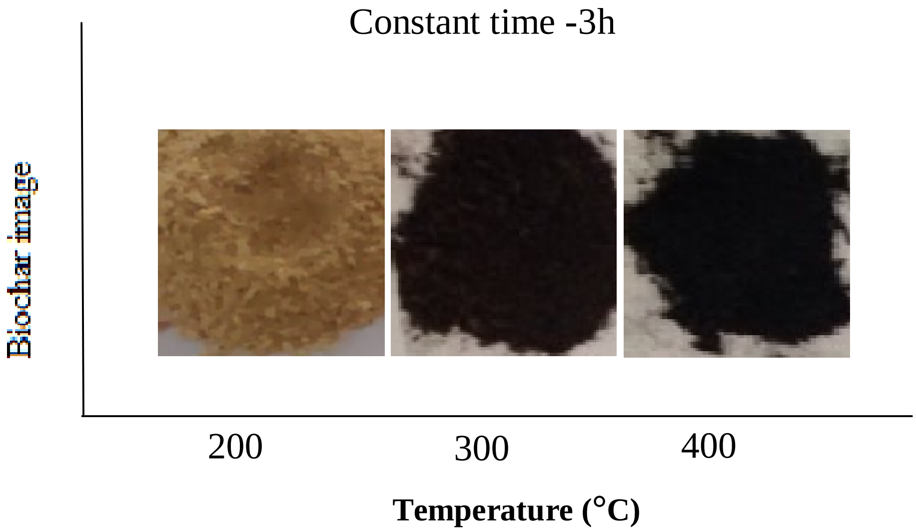


Figure 4.3 Effect of Temperature for the production of biochar

From Figure 4.3 shows that the constant time 3h was maintained to get the outcome from the pyrolysis of cassava stem for the production of biochar. It was found that at 200^0C and 300^0C, it was partially carbonised and at 400^0C, it was completely carbonised.

4.3.2 Effect of time:

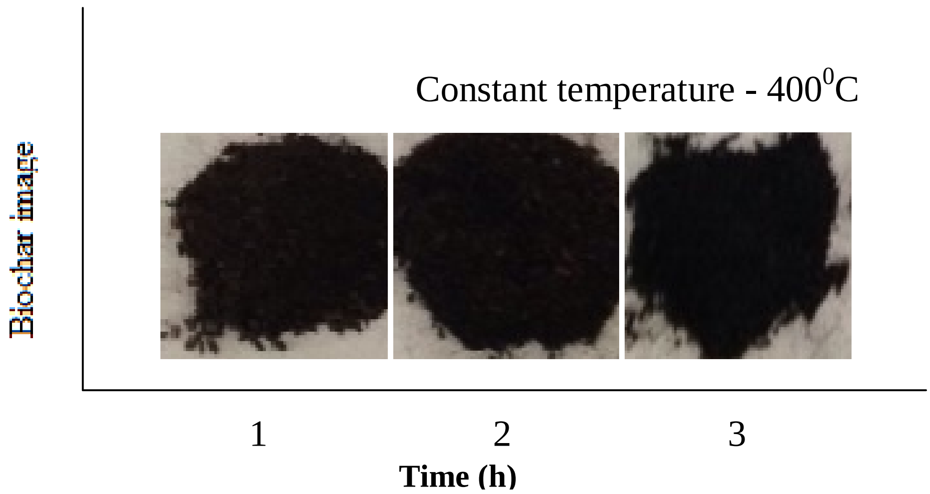


Figure 4.4 Effect of time for the production of biochar

Figure 4.4 represents that by changing the time, a constant temperature 400^0C was maintained to get the yield from the pyrolysis of cassava stem for the production of biochar. It was found that at 1h and 2h, it was partially carbonised and at 3h, the cassava stem was completely carbonised.

4.4 ADSORPTIVE REMOVAL OF SIMULATED DYE EFFLUENT BY CASSAVA STEM BIOCHAR:

4.4.1 Effect of pH:

The pH is the most influencing parameter in the adsorption process. Figure 4.5 represents that the activated biochar from the cassava stem for the maximum removal efficiency was found to be 27.626% and the adsorption capacity (Q_{max}) was obtained as 3.9445 mg/g at the optimum pH 3. . The cell wall of the cassava stem derived biochar has many functional groups on the surface. At this optimum pH, the biochar has more electrostatic attraction for dye effluent. There is a competition between the H^+ ions and the dye ions for the adsorption sites of adsorption leading to the inhibition of the dye adsorption.

The same pH was obtained as optimum for the removal of the Light green dye using peanut husk as adsorbent and Q_{max} was 146.2 ±2.4 mg/g (Zhao *et al.,* 2014). Maximum adsorption of Methylene blue was attained at 71.8 mg/g by using adsorbent raw barely straw at the pH11 (Husseien *et al.,* 2007). The Methylene blue adsorption was done with anaerobic digestion residue, palm bark, eucalyptus derived biochar at optimum pH 7 with maximum dye removal of 99.5%,99.3%,86.1% respectively and Q_{max} = 9.50 mg/g(Sun *et al.*,2013).

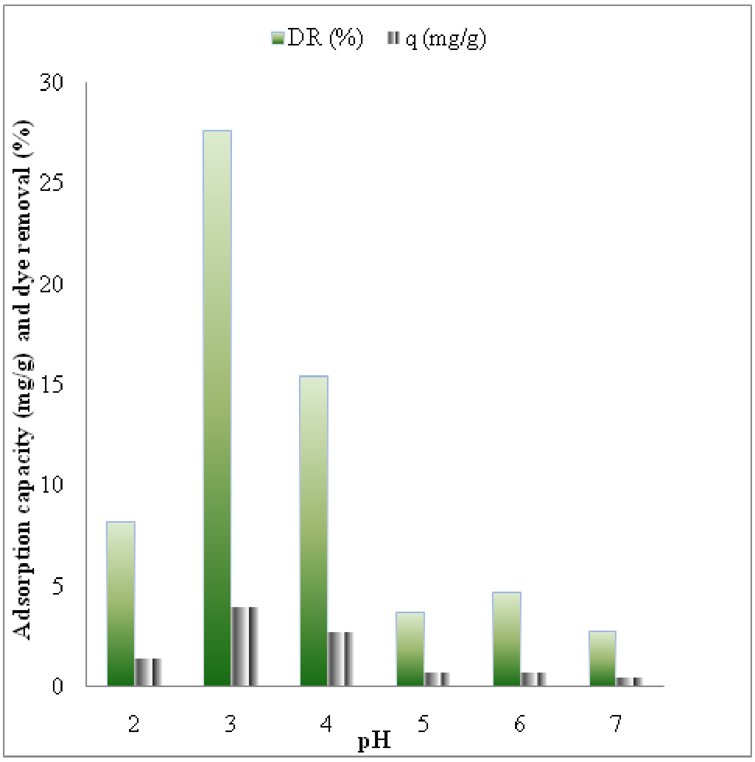


Figure 4.5 Effect of pH on removal efficiency and adsorption capacity of simulated dye effluent

4.4.2 Effect of contact time:

It was shown from Figure 4.6 at pH 3, the contact time was perceived to be optimum at 10 minutes. The efficient removal was found to be 8.1196 % and the adsorption capacity to be 1.0556 mg/g at this time. Pesticide Pymetrozine was effectively adsorbed to about 31.606 mg/g when it was in contact for 120 min with the brewers spent grain (Xi *et al.*, 2014). Acid black 172 was decolourised by using bamboo biochar at the optimum time of 100 minutes and the Q_{max} was determined to be 434.78 mg/g (Yang *et al.*, 2014).

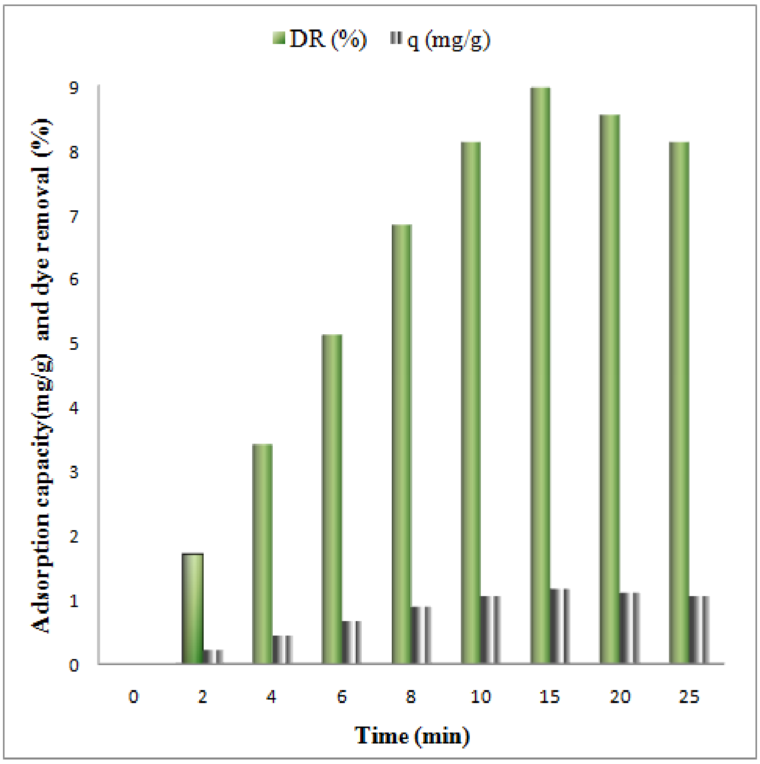


Figure 4.6 Effect of contact time on removal efficiency and adsorption capacity of simulated dye effluent.

4.4.3 Effect of initial dye concentration:

The initial dye concentration is another parameter which influences the adsorption process. It was found maximum at 4 ppm. Its efficient dye removal was attained at 33.33% and adsorption capacity at 1.555 mg/g was illustrated in Figure 4.7. Literature work shows that the effective removal of the Methylene blue was obtained for the initial dye concentration of about 200mg/L for Swede rape straw as adsorbate (Feng *et al.*, 2013). About 99.99% removal of malachite green was achieved by using cashew nut shell with optimum initial dye concentration of 20mg/L (Ponnusamy & Subramanian 2013).

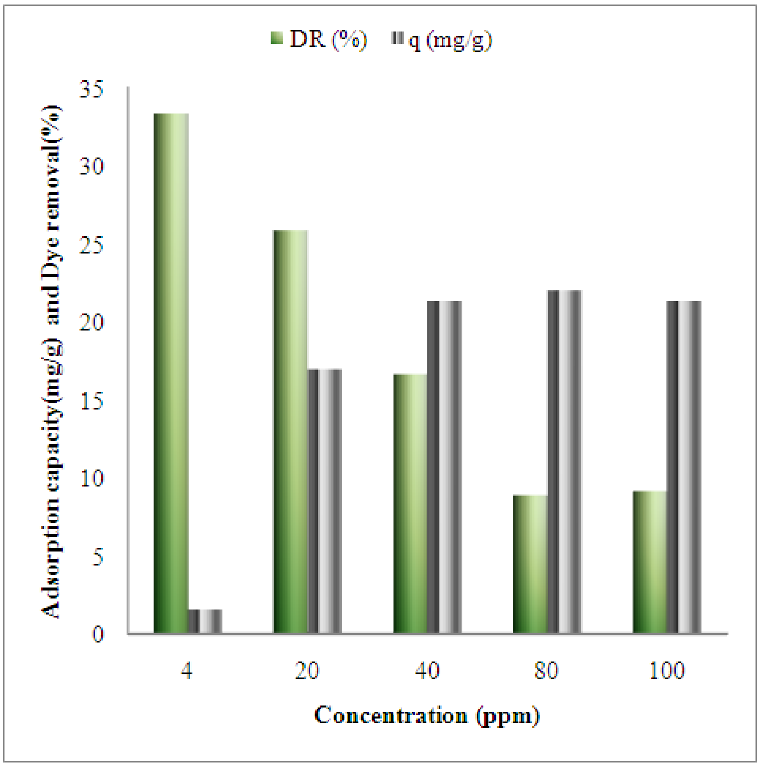


Figure 4.7 Effect of initial dye concentration on removal efficiency and adsorption capacity of simulated dye effluent

4.4.4 Effect of temperature:

The effect of temperature is another factor which influences adsorption. The maximum dye removal was observed to about 13.673 % and adsorption capacity 2.833 mg/g at an optimum temperature at 25°C in Figure 4.8. Works suggested that at 45°C, Pesticide Pymetrozine was commendably removed with the help of Brewers spent grain (Xi *et al.*,2014). With the reference to the work done by Kaur *et al* (2013), about 83 % of the Congo red dye was effectively removed by using nut shell as adsorbent. When Neem and Mango bark was used as adsorbents, it was shown from the work done by Srivastava & Rupainwar (2011) that the dye malachite green was adsorbed successfully when adsorption was carried at 40°C.

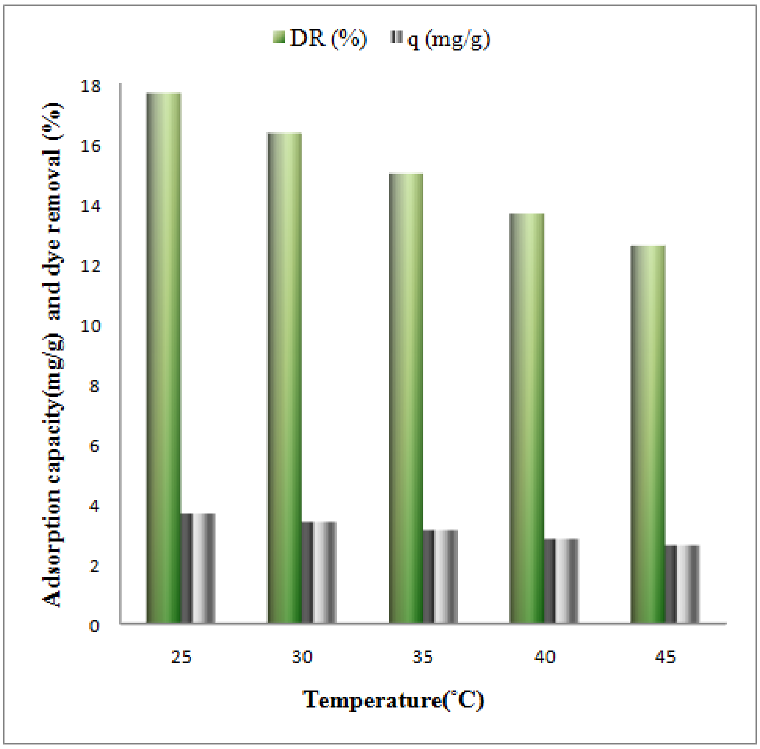


Figure 4.8 Effect of temperature on removal efficiency and adsorption capacity of simulated dye effluent

4.4.5 Effect of adsorbent dosage:

The amount of adsorbent plays a significant role in the process of adsorption. Figure 4.9 explains that, at dosage 1:2 ,it was shown that the maximum dye removal to be 13.166 % and adsorption capacity of about 2.320 mg/g. Yang *et al* (2014) achieved the adsorbent dosage to be 500 mg/l using bamboo biochar as an adsorbent for the adsorption of acid black 172 with Q_{max} = 434.78 mg/g. The Methylene blue adsorption was done using anaerobic digestion residue, palm bark, eucalyptus biochar with maximum adsorbent dosage of 5mg/l which has a dye removal of 99.5%, 99.3%, 86.1% respectively and Q_{max} = 9.50 mg/g. (Sun *et al.*,2013). At optimum adsorbent dosage of 1 g/L, effective adsorption of copper and zinc ions took place with the help of hard wood and corn straw (Chen *et al.*, 2011).

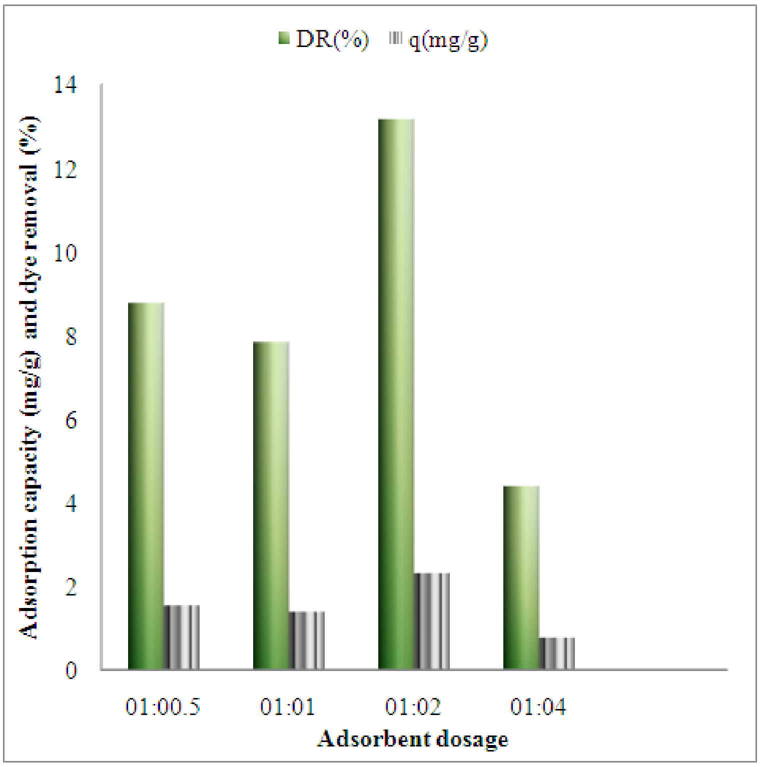


Figure 4.9 Effect of adsorbent dosage on removal efficiency and adsorption capacity of simulated dye effluent

4.4.6 Effect of agitation speed:

By maintaining the above optimum conditions, the agitation speed was observed to be 75 rpm. At this agitation speed, the removal efficiency was found to be 19.817 % and adsorption capacity to be 3.611 mg/gin Figure 4.10. Reference suggested that teak tree bark powder was kept in contact with the Methylene blue dye for about 30 minutes at the speed of 230 rpm. Due to which the dye was successfully adsorbed and its removal capacity was seen as 331.333 mg/g (Patil *et al.*, 2011). Lucrative removal of Methyl Violet 2B was done by using *Casuarinaequisetifolia* needle when they were kept in contact for 120 minutes with the optimum speed of 250 rpm.

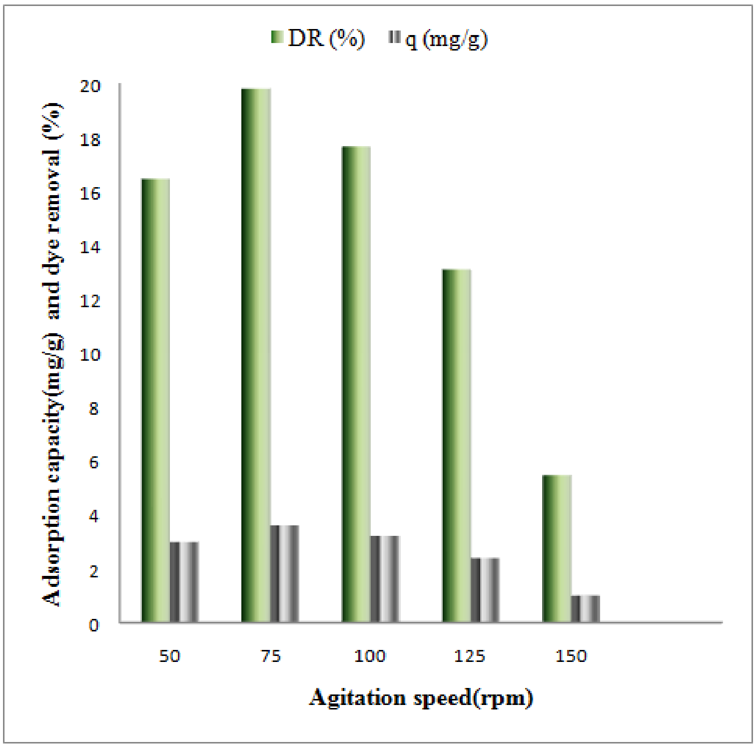


Figure 4.10 Effect of agitation speed on removal efficiency and adsorption capacity of simulated dye effluent

4.4.7 Adsorption kinetics:

Adsorption is one of the most common techniques employed in the removal of the effluents. Its kinetics studies are employed in order to assess the performance of the adsorbent. Four types of kinetics studies pseudo first-order, pseudo second-order, First order and second order were studied.

4.4.7.1 Pseudo first-order kinetics:

The pseudo first order is given by

$$\ln(Q_e - Q_t) = lnQ_e - (\frac{K_1}{2.303} * t)$$

Where, 'Q_e' is the amount of dye adsorbed per unit mass of adsorbent (mg/g), 'Q_t' is the amount of dye adsorbed per unit mass of adsorbent at a particular time (mg/g), 't' is the time (min) and 'K_1' is the constant parameter.

The intercepts and the slope are got from the graph (Figure 4.11) plotted between log (Q_e - Q_t) and time, determines the values of the Q_e and K_1 as 1.2448 mg/g and t=0.222 min^{-1}. The r^2 value for this model was found to be 0.9325 by which it is seen that the kinetics of the simulated effluent follows the pseudo first – order kinetics.

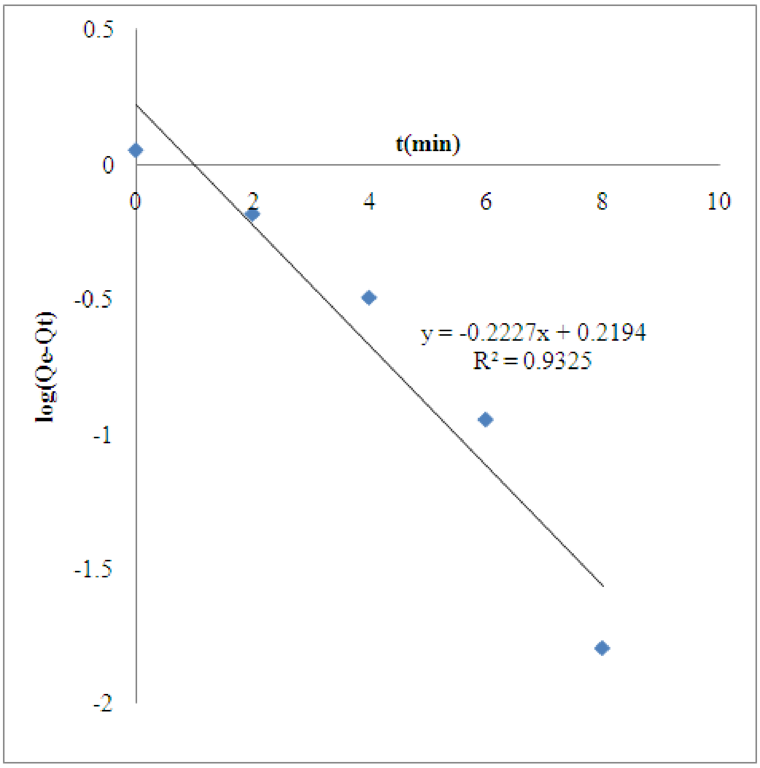


Figure 4.11 Pseudo first-order kinetics of simulated dye effluent onto activated cassava stem biochar

4.2.7.2 Pseudo second-order kinetics:

The graph between t/Q and time between Y-axis and X-axis gives the plot for pseudo second-order reaction. The values of Q_e and K_2 are determined from the intercepts and the slopes of the plot.

Pseudo second–order is given as,

$$\frac{t}{Q_t} = \frac{1}{K_2 * Q_e^2} + \frac{t}{Q_e}$$

where, 'Q_e' and 'Q_t' are the amount of dye adsorbed per unit mass of adsorbent (mg/g) and the amount of dye adsorbed per unit mass of adsorbent at a particular time (mg/g) respectively,' t' is the time (min) and 'K_2' is the rate constant of second order. From Figure 4.12, it was found that the suitable data does not fit pseudo second-order kinetics.

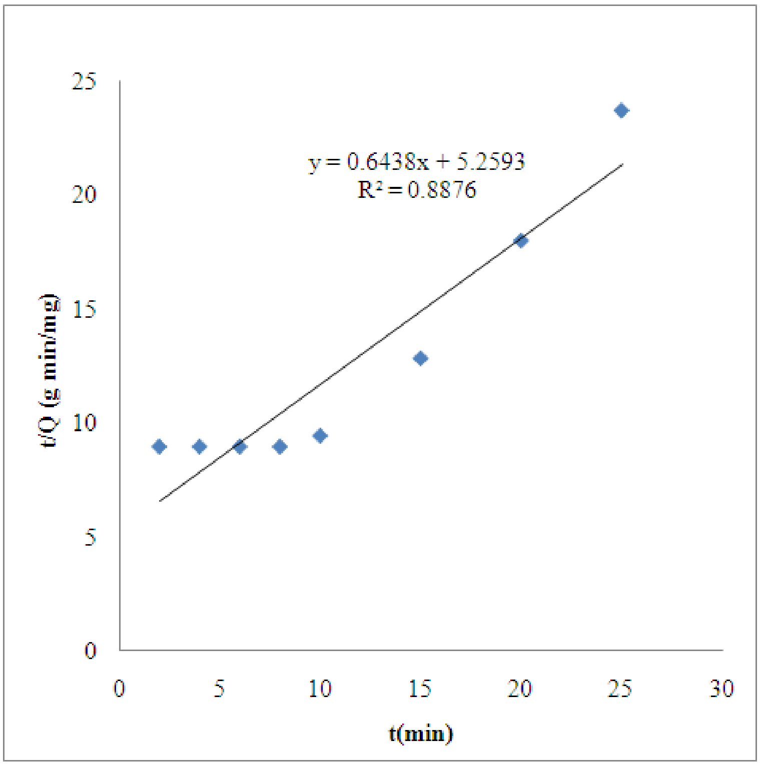


Figure 4.12 Pseudo second-order kinetics of simulated dye effluent onto activated cassava stem biochar

4.4.7.3 First order kinetics:

First order is represented as,

$$\ln\left(\frac{C_o}{C_e}\right) = k_1 * t$$

Where ,'C_e' and 'C_o' are the equilibrium dye concentration and initial concentration (%v/v), 'k_1' is the first order constant. The graph is plotted between time and $\ln(C_o/C_e)$ on X-axis and Y-axis. The constant value can be determined from the slope and the intercept.

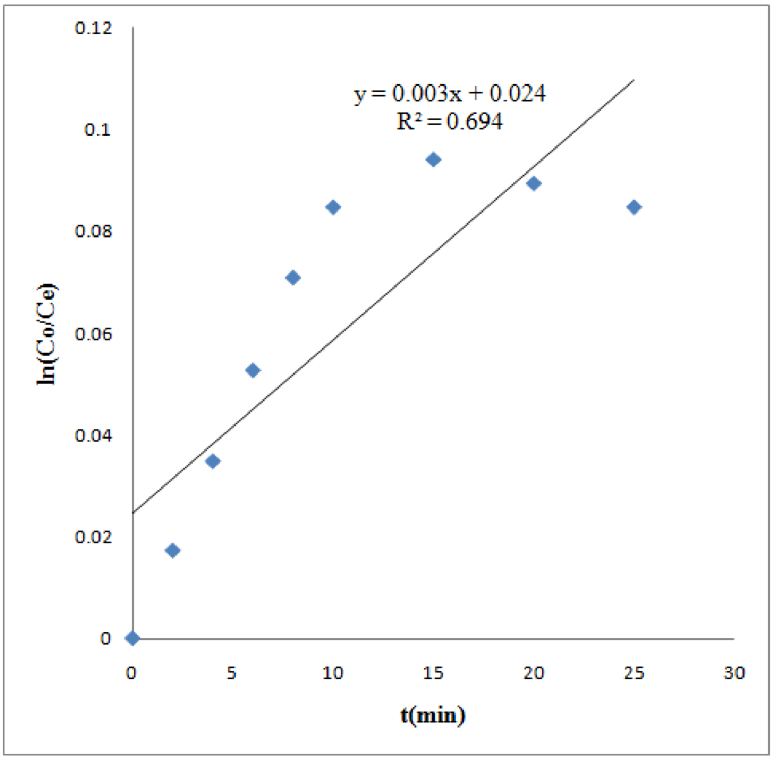


Figure 4.13 First-order kinetics of simulated dye effluent onto activated cassava stem biochar

From Figure 4.13 it is found that the r^2 value is less than 0.9, which proves that the above experimental data does not obey the first order kinetics.

4.4.7.4 Second order kinetics

Second order kinetic equation is given as,

$$\left(\frac{1}{C_o}\right) = k_2 * t + \frac{1}{C_e}$$

Where 'C_e' and 'C_o' are the equilibrium dye concentration and initial concentration (%v/v), 'k_2' is the second order constant. From Figure

4.14, the graph plotted against 1/Co and t showed that the datas doesn't obey the second order kinetics.

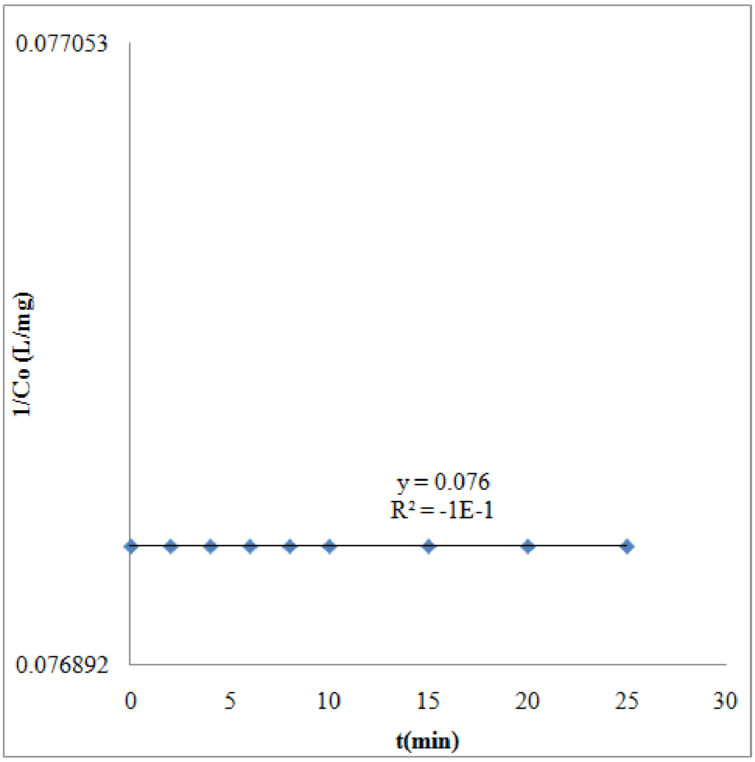


Figure 4.14 Second-order kinetics of simulated dye effluent onto activated cassava stem biochar

4.4.8 Adsorption isotherms:

To optimize the adsorption design, the isotherm model studies are carried out for the removal of the dye effluent with the adsorbent biochar. The adsorption isotherm gives the better understanding of adsorption efficiency and characteristics of the mixed dye effluent on the surface of the biochar. This sorption characteristics was determined based on the coefficient of correlation (r^2) emphasizes the strong affinity between adsorbent and the dye effluent

4.4.8.1 Langmuir isotherm:

Langmuir isotherm model is the adsorption model which is based on the homogenous surface. Langmuir isotherm model is given by

$$\frac{1}{Q} = \frac{1}{(Q_{max} * b) * Ce} + \frac{1}{Q_{max}}$$

where, 'C_e' is the equilibrium dye concentration (%v/v), 'Q' is the amount of dye adsorbed per unit mass of adsorbent called adsorption capacity(mg/g), 'Q_{max}' is the maximum adsorption capacity (mg/g), 'b' is the adsorption intensity Langmuir constant.

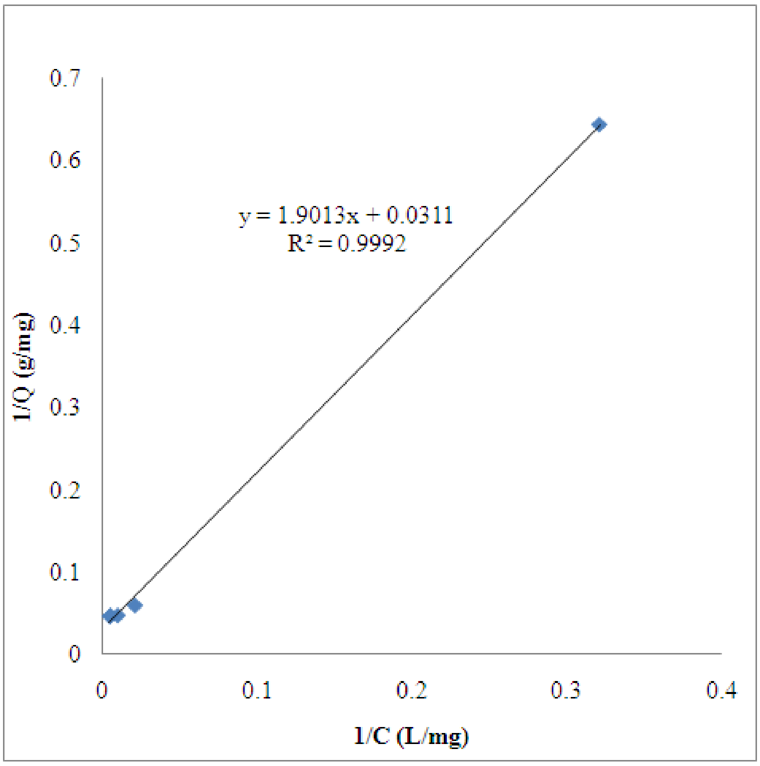


Figure 4.15 Langmuir isotherm model of simulated dye onto activated cassava stem biochar

The cassava stem derived biochar is then activated, used for the decolourisation of the mixed dye shows a linear plot by plotting 1/C and1/Q along the X-axis and Y-axis respectively with the regression value r^2 = 0.9992. So this model exactly fits the data for all solutions, say from diluted solution to the concentrated solution. Maximum adsorption capacity (Q_{max}) of our work was a 32.258 mg/g and the constant b = 0.0163 L/mg. Yang *et al* (2014) work supported that the bamboo derived biochar was used for the adsorption of acid black 172, has a Q_{max} = 434.78 mg/g and K_L = 0.049. The biochar derived from anaerobic digestion residue palm bark, eucalyptus used in the work done by Sun *et al* (2013), for the removal of methylene blue dye has Q_{max} = 9.77mg/g, 2.95 mg/g, 2.00 mg/g and K_L= 0.099, 0.63, 0.21 respectively following this model. Thus, it is found that biochar from cassava stem has higher efficiency for the dye adsorption

4.4.8.2 Freudlich isotherm:

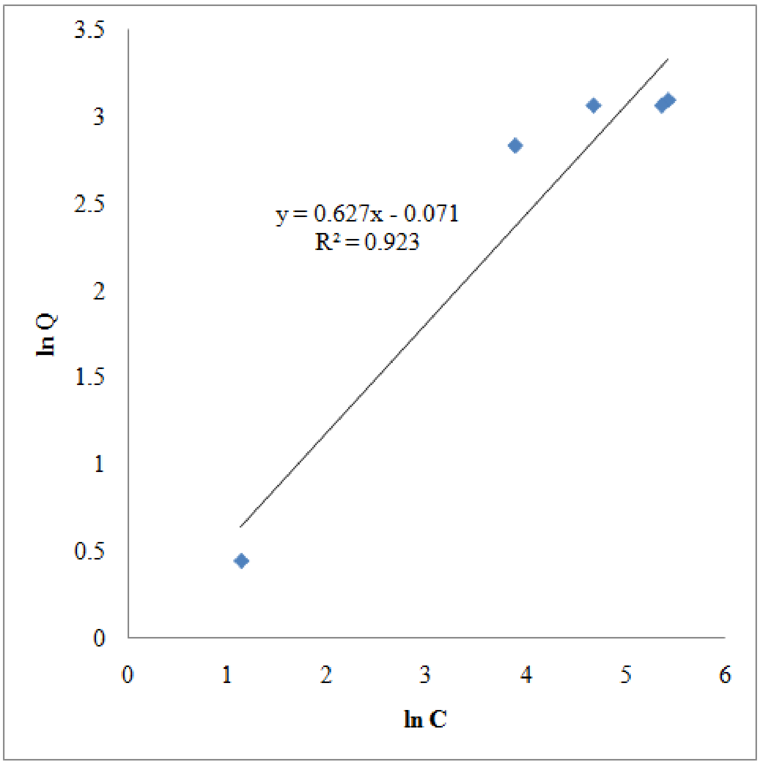


Figure 4.16 Freundlich isotherm model of simulated dye onto activated cassava stem biochar

Freundlich isotherm model is the adsorption based on heterogeneous surface and the equation is:

$$\ln Q = \ln K_f + \left(1/n\right) \ln C_e$$

Where, 'C_e' is the equilibrium dye concentration (%v/v), 'Q' is the amount of dye adsorbed per unit mass of adsorbent (mg/g), 'K_f' is the maximum adsorption capacity (mg/g), 'n' is the Freundlich constant related to adsorption intensity

The biochar derived from cassava stem is modified and used for the removal of the simulated effluent shows a linear plot by plotting ln C and ln Q along the X-axis and Y-axis respectively with the regression value r^2 = 0.923 thereby following the freundlich model with n = 1.5948 and K_f = 0.9314 L/mg. Yang *et* al (2014) achieved the decolourisation of acid black 172 with bamboo derived biochar and constant values were found to be K_f = 37.61 L/g, 36.09L/g, 48.54L/g and n = 2.69, 2.52, 2.26 respectively. Sun *et al*(2013) reported that by using the biochar obtained from anaerobic digestion residue, palm bark, eucalyptus for the adsorption of Methylene blue dye showed K_f = 3.39 $(L/mg)^n$, 1.32mg/g, 0.34mg/g and n = 5.74, 5.68, 5.39 respectively, thus the first two follows this model but biochar from eucalyptus does not fit this model. Thus the activated biochar adsorption characteristics follow the above two isotherm models at equilibrium dye concentration.

4.4.8.3 Temkin isotherm:

The equations of Temkin isotherm are:

$$Q = B * ln\, A + B * \ln C_e$$

$$B = RT/b$$

Where, 'C_e' is the equilibrium dye concentration (%v/v), 'Q' is the adsorption capacity (mg/g), 'A' is Temkin isotherm binding constant at equilibrium (L/g), 'b' is the Temkin constant(J/mol), 'B' is heat of adsorption constant .

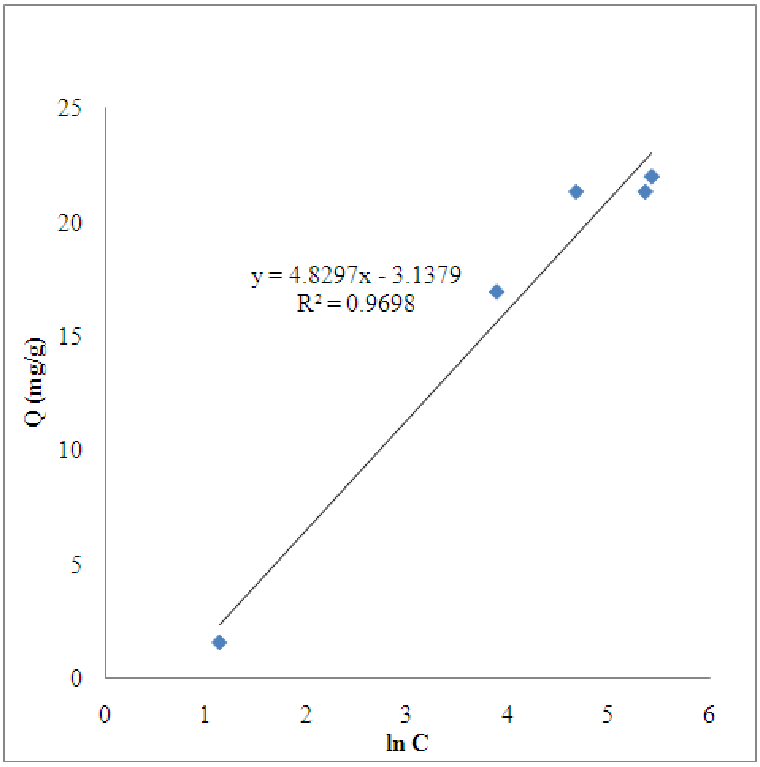


Figure 4.17 Temkin isotherm model of simulated dye onto activated cassava stem biochar

The constants A = 0.5222 L/g and b=513.06 J/mol, the heat of adsorption, B = 4.829 were procured from Figure 4.17, by plotting ln C and Q along the X-axis and Y-axis respectively with the regression value r^2 = 0.9698 following Temkin isotherm model for simulated dye effluent removal using cassava stem derived activated biochar. Elmorsi (2011) proposed that constants of this isotherm were found to be b= 0.101 kJ/mol and K_T = 0.161 L/mg for the deduction of Methylene blue dye using Miswak leaves.

4.4.8.4 Dubin –Radushkevich(D-R) isotherm:

The D-R isotherm equation is given by:

$$ln\,Q = ln\,Q_m - K\,\varepsilon^2$$

where, ‘Q’ is the adsorption capacity (mg/g), ‘Q_m’ is the D-R saturation constant (mg/g), ‘K’ is the adsorption energy constant(mol^2/kJ^2) and ‘ε’ is the Polanyi potential.

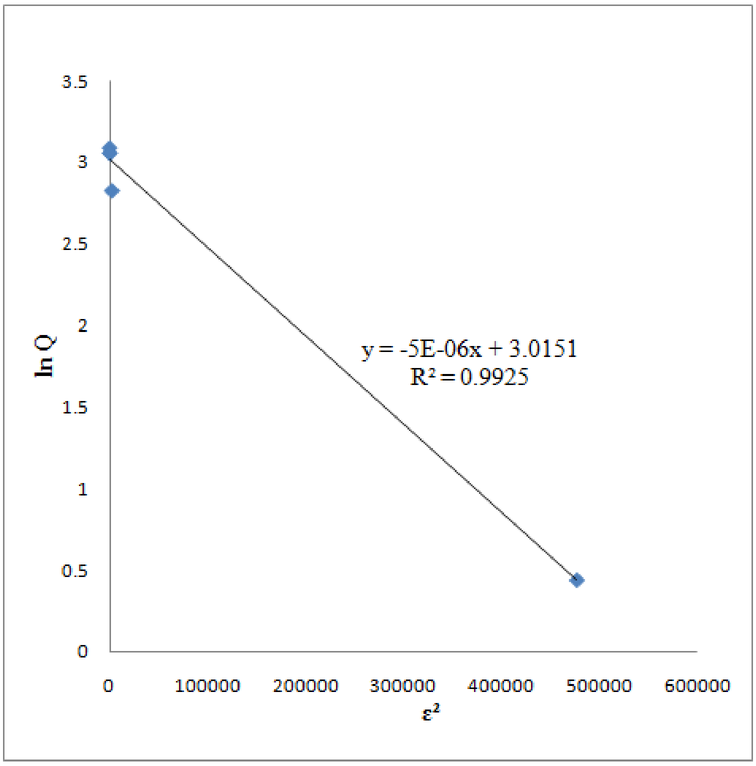


Figure 4.18 D-R isotherm model of simulated dye onto activated Cassava stem biochar

In Figure 4.18, a linear graph is obtained from the experimental data by plotting between ε^2 along the X-axis and ln Q along the Y-axis with r^2=0.9925 thus fitting D-R isotherm, and their constants were found to be K = 5*10 $^{-6}$ mol^2/KJ^2 and Q_m = 20.381mg/g.

4.4.8.6 Separation factor R_L :

Separation factor R_L is presented as:

$$R_L = \frac{1}{1 + (b * Ce)}$$

Where, 'C_e' is equilibrium dye concentration (%v/v), 'b' is the separation factor constant. From the above Figure 4.19, it is evident that the type of isotherm is favourable as the values of R_L lies between 0 and 1.

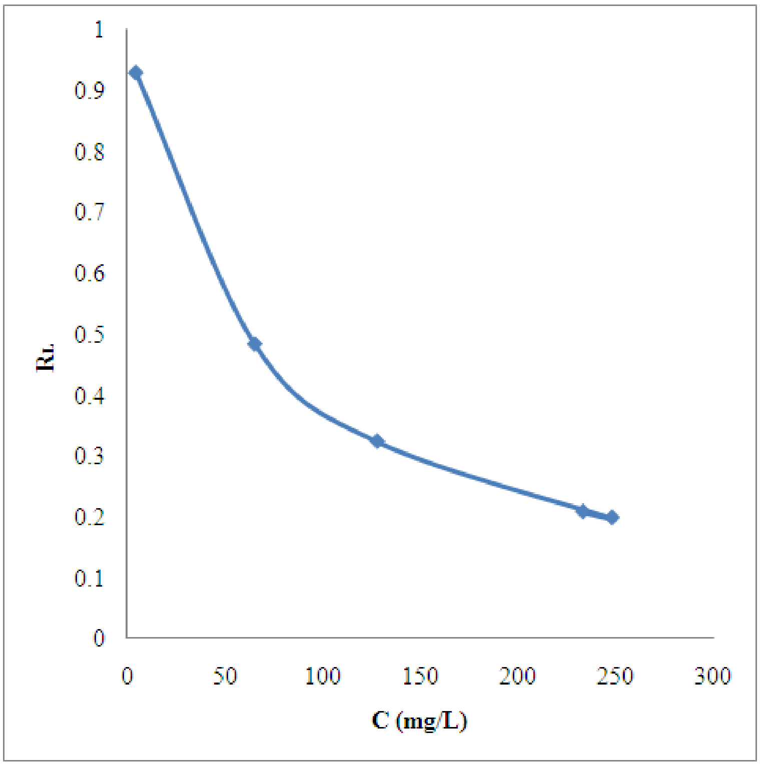


Figure 4.19 Separation factor R_L of simulated dye onto activated Cassava stem biochar.

The conditions for the separation factor R_L are as follows:

Table 4.1: Conditions for the separation factor R_L

R_L	Unfavorable	Linear	Favorable	Irreversible
$R_L > 1$	X			
$R_L = 1$		X		
$0<R_L<1$			✓	
$R_L = 0$				X

4.4.9 Adsorption thermodynamics:

4.4.9.1 Van't Hoff 's equation:

The Van't Hoff equation, proposed by Jacobus Henricus Van't Hoff a Dutch chemist has been utilized in order to find the changes in the state functions in a thermodynamic system

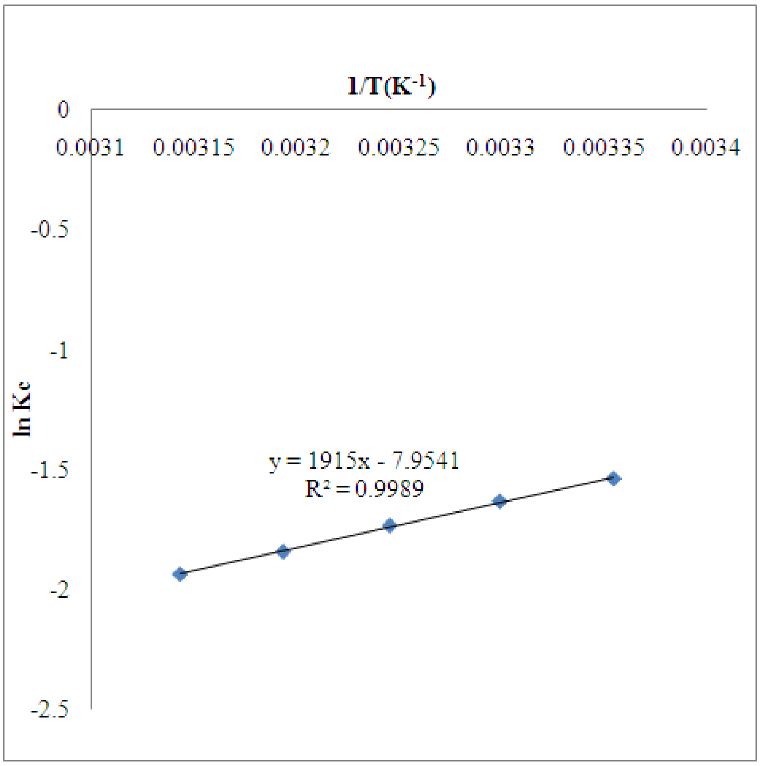


Figure 4.20 Adsorption thermodynamics of simulated dye onto activated cassava stem biochar

The Van't Hoff equation is described as,

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Where, $k_c = \frac{C_{Ae}}{C_e}$, 'C_{Ae}' is the adsorbed dye concentration at equilibrium (%v/v) and 'C_e' is the equilibrium concentration of dye in the solution (%v/v). ΔH° and ΔS° are constants.

Table 4.2: Constants calculated from various isotherms, kinetics and thermodynamics

S.No	Adsorption	Name	Parameters	R^2
1	Isotherms	Langmuir	Q_{max}=32.258mg/g b = 0.0163 L/mg	0.9992
2		Freundlich	n = 1.5948 K_f = 0.9314 $(L/mg)^n$	0.923
3		Temkin	A = 0.5222 L/g B = 4.829 J/mol	0.9698
4		D-R	K=$5*10^{-6}$ mol^2/KJ^2 Q_m= 20.381mg/g.	0.9925
5	Kinetics	Pseudo first-order	Q_e = 1.2448mg/g k_1 = 0.222min^{-1}	0.9325
6	Thermodynamics	Van't-Hoff	ΔS° = -66.1295 J/mol.K ΔH° = -15921.31J/mol.K	0.9989

From Figure 4.20, thermodynamic parameters were evaluated and was found that the change in entropy ΔS° and change in enthalpy ΔH° as -66.1295 J/mol.K and -15921.31 J/mol.K respectively. The negative value of the enthalpy signifies that the process is exothermic. The negative sign of entropy represents the reaction is non-spontaneous.

4.5 CHARACTERIZATION OF SPENT BIOCHAR

4.5.1 FT-IR

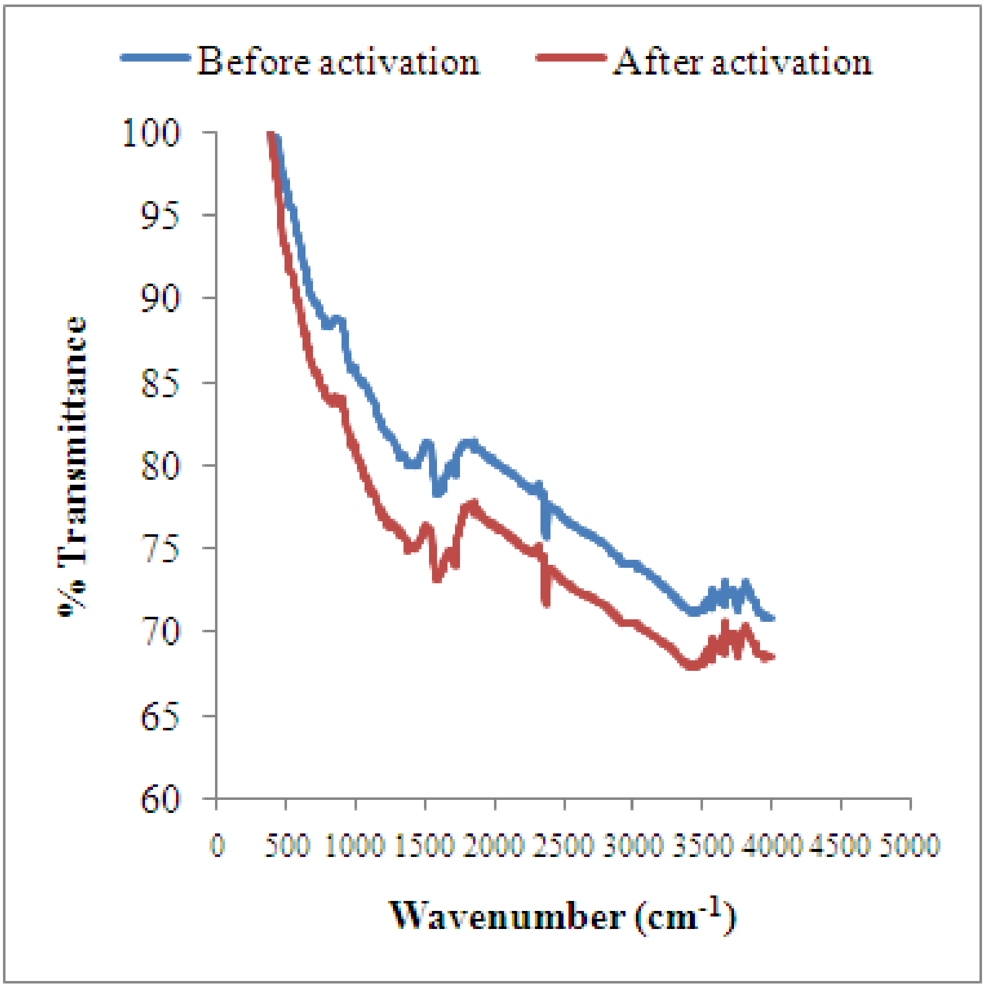


Figure 4.21 FT-IR spectra of activated cassava stem biochar before activation (blue line) and after activation (red line)

Figure 4.21, shows the presence of functional groups on the surface of the activated biochar in the range from 4000 cm^{-1} to 390 cm^{-1}.These functional groups were obtained at these specified wavenumber (cm^{-1}) as shown in the Table 4.3 before activation and after activation as shown in Table 4.4. From these findings, it is reported that both activated and non-activated biochar had similar functional groups that remained intact when activated with oxalic acid at a pyrolytic temperature of 400^0C

Table 4.3: The functional groups present for the corresponding wavenumber - before activation

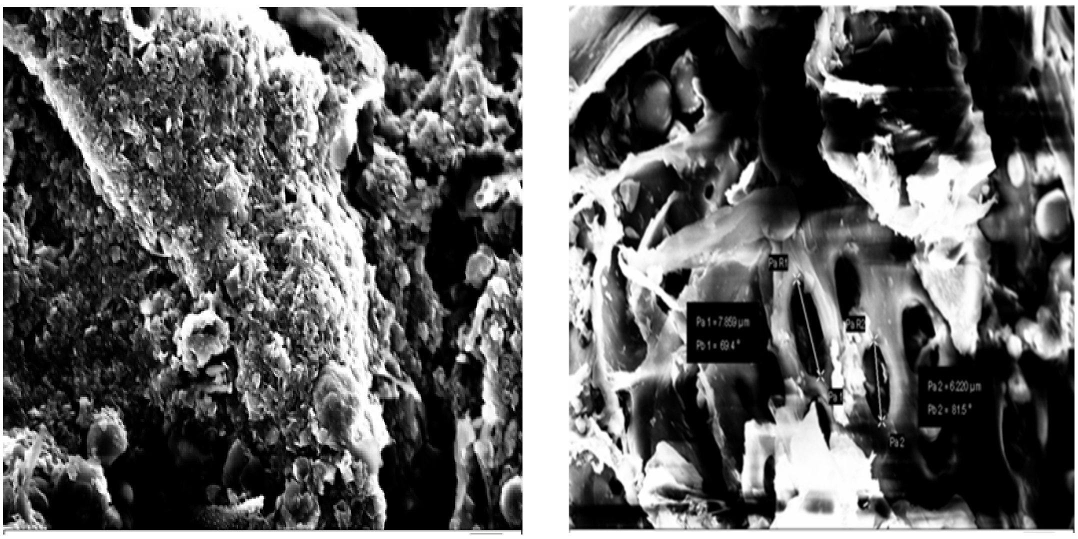
Wavenumber (cm^{-1})	Functional groups
3371.57	N-H group
2931.80	Methylene C-H asym./sym.
1975.11	Aromatic combination bands
1921.10	Aromatic combination bands
1720.50	Aromatic combination bands
1381.03	*gem*-Dimethyl or ‘‘iso’’- (doublet)
1327.03	Skeletal C-C vibrations
1249.87	C-N group
1041.56	Cyclohexane ring vibrations
964.41	Skeletal C-C vibrations
786.96	Skeletal C-C vibrations

Table 4.4: The functional groups present for the corresponding wavenumber - after activation

Wavenumber (cm^{-1})	Functional groups
1975.11	Aromatic combination bonds
1897.95	Aromatic combination bonds
1720.50	Aromatic combination bonds
1581.63	C=C region
1381.03	C-H region
1319.31	C-N region
1172.72	C-O-C region
1033.72	Cyclohexane ring vibrations
964.41	Trans- C-H out of plane band
810.10	1,4-Disubstitution (para)
763.81	Monosubstitution (phenyl)

4.5.2 SEM

The scanning electron microscope was employed to examine the surface physical morphology of the cassava stem derived biochar sample. From Figure 4.22(a), it is seen that the fresh cassava stem derived biochar sample was flat in its surface morphology without any pores . After activation of the sample with the oxalic acid, many pores were observed through which the adsorption of the dye has taken place. This is evident from Figure 4.22(b)



(a) **(b)**

Figure 4.22 SEM images of activated cassava stem biochar (a) before activation and (b) after activation

4.5.3 XRD

XRD technique is based on Bragg equation explained under 3.3, the constructive interferences and intensity peaks will be produced when incident X-rays affect the sample. This intensity peaks detect the presence of crystalline structure in the sample. But in Figure 4.23, it confirms that cassava stem derived biochar is completely amorphous in nature and not crystalline.

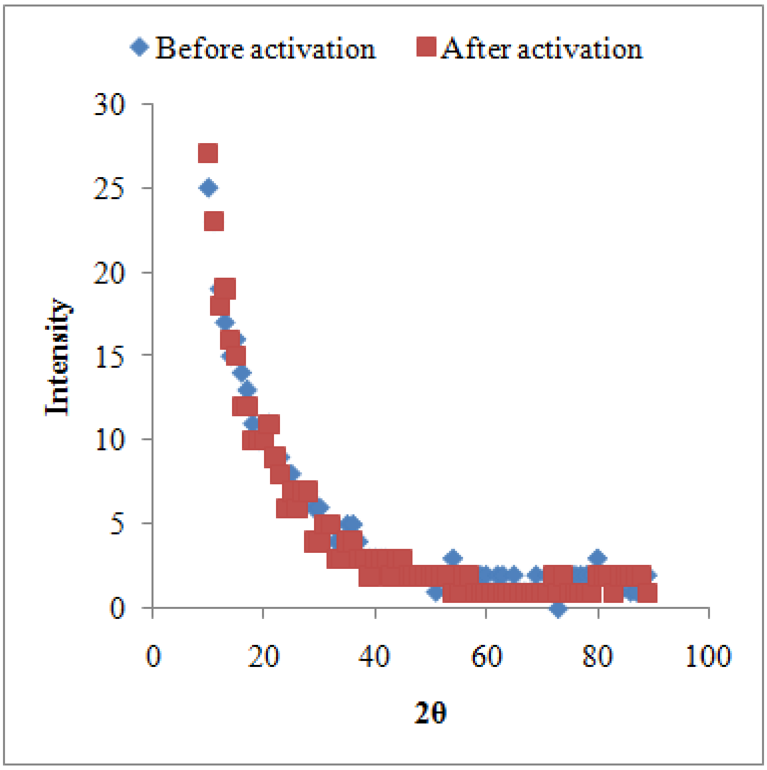


Figure 4.23 XRD spectra of activated cassava stem biochar before activation (blue line) and after activation (red line)

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CHAPTER 5

CONCLUSION

In this current analysis, the pyrolytic temperature is considered to be major parameter that affects the adsorption efficiency of the dye removal on the surface of the biochar. The results were concluded that at pyrolysis was attained at 400^0C for 3h.Higher efficiency of dye removal increased when biochar was activated. The batch adsorption studies such as pH, contact time, temperature, adsorbent dosage and agitation speed were performed varyingly to get the optimum conditions for the removal efficiency of the dye by biochar. The results exhibited that maximum dye removal and adsorption capacity was achieved at pH 3, time 10 min, temperature 25^0C, adsorbent dosage in the ratio 1:2 and agitation speed 75 rpm. The activated biochar fitted the adsorption isotherms mainly Langmuir, freundlich, temkin, D-R model which has regression value (R^2>0.90) and indicated the strong affinity between the biochar and simulated dye effluent. The adsorption kinetics and thermodynamics were performed in which the pseudo first-order kinetics and Van't-Hoff's equation suited the experimental data generated. The separation factor R_L proves that the system is a favourable one. The characterization techniques were also observed in which X-Ray Diffraction confirmed that biochar is amorphous in structure.SEM showed the surface morphology of biochar before activation to be linear and after activation to be porous. FT-IR proved the presence of functional groups on the biochar surface. Thus from this study, it is concluded that cassava stem derived biochar can be considered as the low cost adsorbent for the decolourization of simulated dye from the wastewater.

REFERENCES

Achmad, A., Kassim, J., suan, T.K., Amat, C. and Seey, T.L. (2012) ' Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Direct Dye onto a Novel Green Adsorbent Developed from *Uncaria Gambir* Extract', Journal of Physical Science, Vol. 23, No. 1, pp. 1-13.

Agarwal, M., Tardio, J. and Mohan, V.S. (2015) 'Pyrolysis Biochar from Cellulosic Municipal Solid Waste as Adsorbent for Azo Dye Removal: Equilibrium Isotherms and Kinetics Analysis', International Journal of Environmental Science and Development, Vol. 6, No. 1, pp. 67-72.

Ahalya, N., Chandraprabha, M.N., Kanamadi, R.D. and Ramachandra, T.V. (2013) 'Adosrption of Methylene blue and Amaranth on to tamarind pod shells', Journal of Biochemical Technology, Vol. 3, No. 5, pp. S189-S192.

Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.K. and Yang, J.E. (2012) 'Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water', Bioresource technology, Vol. 118, pp. 536–544.

Alau, K.K., Gimba, C.E. and Kagbu, J.A (2010) 'Removal of Dyes from Aqueous Solution Using Neem (*Azadirachta Indica*) Husk as Activated Carbon', Archives of Applied Science Research, Vol. 2, No. 5, pp. 456-461.

Armagan, B. and Toprak, F. (2013) 'Optimum Isotherm Parameters for Reactive Azo dye onto Pistachio Nut Shells: Comparison of Linear and Non-Linear Methods', Polish Journal of Environmental Studies, Vol. 22, No. 4, pp. 1007-1011.

Benaïssa,H. (2007), 'Equilibrium study of methylene blue sorption from aqueous solutions by a low-cost waste material: almond peel', Eleventh International Water Technology Conference, pp. 895-909.

Bharathi, K.S. and Ramesh, S.T. (2012) 'Biosorption of crystal violet from aqueous solution by C*itrullus lanatus* (watermelon) rind', Journal of Environmental Research and Development, Vol. 7, No. 1A, pp. 321-329.

Bhaskaran, P.K. (2011) Removal of heavy metals and dyes from aqueous solution by adsorption on acid treated activated carbon. Ph.D. thesis, Bharadhidasan University.

Chen, X., Chen, G., Chen, Y., Lehmann, J., McBride, M.B. and Hay, A. (2011) 'Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution', BioResources Technology, Vol. 102, pp. 8877-8884.

Dahri, M.K., Kooh, M.R.R. and Lim, L.B.L. (2013) 'Removal of Methyl Violet 2B from Aqueous Solution using *Casuarinaequisetifolia* Needle', ISRN Environmental Chemistry. Available from: 'http://dx.doi.org/10.1155/2013/619819'.

Douissa, N.B., Bergaoui, L., Mansouri, S., Khiari, R. and Mhenni, M.F. (2013) 'Macroscopic and microscopic studies of methylene blue sorption onto extracted celluloses from Posidonia oceanica', Industrial Crops and Products, Vol. 45, pp. 106-113.

Elmorsi, T.M (2011) 'Equlibrium Isotherms and Kinetic Studies of removal of Methylene Blue by Adsoption onto Miswak leaves as a natural adsorbent', Journal of Environmental Protection, Vol. 2, pp. 817-827.

Etim, U.J., Umoren, S.A. and Eduok, U.M. (2012) 'Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution', Journal of Saudi chemical society.

Feng, Y., Dionysiou, D.D., Wu, Y., Zhou, H., Xue, L., He, S. and Yang, L. (2013) 'Adsorption of dyestuff from aqueous solutions through oxalic acid-modified swede rape straw: Adsorption process and disposal methodology of depleted bioadsorbents', Bioresource Technology, Vol. 138, pp. 191-197.

Feng, Y., Zhou, H., Liu, G., Qiao, J., Wang, J., Lu, H., Yang, L. and Wu, Y. (2012) 'Methylene blue adsorption onto swede rape straw (Brassica napus L.) modified by tartaric acid: Equilibrium, kinetic and adsorption mechanisms', Bioresource Technology, Vol. 125, pp.138-144.

Halim, H.N.A. and Yatim, N.S.M. (2011) ‘Removal of Acid Green 25 from Aqueous Solution using Coconut Husk as Adsorbent’, Proceedings of the International Conference on Environment and Industrial Innovation, Vol. 12, pp. 268-272.

Husseien,M., Amer,A,A., Azza, El-Maghraby, Taha,N,A., (2007) ‘Utilization of Barley Straw as a Source of a Activated Carbon for Removal of Methylene Blue from Aqueous Solution’, Journal of Applied Sciences Research, Vol. 3, No. 11, pp. 1352-1358.

Inyang, M., Gao, Bin., Xue, Y., Zimmerman, A.R., Pullammanappallil, P. and Cao, X. (2011) ‘Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass’, BioResources Technology, Vol. 110, pp. 50-56.

Joseph,C,G., Bono,A., Krishnaiah,D. and Soon,K,O., (2007), ‘Sorption Studies of Methylene Blue Dye in Aqueous Solution by Optimised Carbon Prepared from Guava Seeds (*Psidiumguajava L.*)’, ISSN Material Science, Vol. 13, No. 1, pp. 1392–1320.

Kaur, S., Rani, S. and Mahajan, R.K. (2013) ‘Adsorption Kinetics for the removal of Hazardous Dye Congo Red by Biowaste Materials as Adsorbents’, Journal of Chemistry, pp.1-12.

Kavitha, K. and Senthamilselvi, M.M. (2014) ‘Adsorptive removal of methylene blue using the natural adsorbent-*Vitex negundo Stem’,* International Journal of Current Reseach and Academic Review, Vol. 2, No. 9, pp. 270-280.

Kim, W.K., Shim, T., Kim, Y.S., Hyun, S., Ryu, C., Park, Y.K. and Jung, J. (2013) ‘Characterization of cadmium removal from aqueous solution by biochar produced from a giant *Miscanthus* at different pyrolytic temperatures’, BioResourse Technology, Vol. 138, pp. 266-270.

Kumar, R. (2013) Preparation, characterization and adsorption studies of adsorbent for dyes removal. Ph.D. thesis, Aligarh Muslim University.

Mahmoodi, N.M., Hayati, B., Arami, M. and Lan, C. (2011) ‘Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies’, Desalination, Vol. 268, pp. 117-125.

Mahmoud, DK., Salleh, MAM., Karim, WAWA., Idris, A. and Abidin, ZZ. (2012) 'Batch adsorption of basic dye using acid treated Kenaf fibre char: Equlibrium kinetic and thermodynamic studies', Chemical Engineering Journal, Vol. 181-182, pp. 449-457.

Mane, V.S. (2012) Study of decolourization of brilliant green and Congo red dye bearing water by adsorption, coagulation, electro-coagulation and electrochemical techniques. Ph.D. thesis, University of Lonere.

Melo, L.C.A., Coscione, A.R., Abreu, C.A., Puga, A.P. and Camargo, O.A. (2013) 'Influence of pyrolysis temperature on cadmium and zinc sorbtion capacity of sugar cane straw-Derived biochar', BioResources, Vol.8, No. 4, pp. 4992-5004.

Parvathi, C., Maruthavanan, T., Sivamani, S. and Prakas, C. (2011) 'Biosorption Studies for the Removal of Malachite Green from its Aqueous Solution by Activated Carbon Prepared from Cassava Peel', E-Journal of Chemistry, Vol. 8, No. 1, pp. 61-66.

Patil, S., Renukdas, S. and Patel, N. (2011) 'Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (*Tectona grandis*) bark powder', International Journal of Environmental Sciences, Vol. 1, No. 5, pp. 711- 726.

Pavan, F.A., Mazzocato, A.C. and Gushikem, Y. (2008) 'Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent', Bioresource Technology, Vol. 99, pp. 3162-3165.

Ponnusamy, S.K. and Subramaniam, R. (2013) 'Process optimization studies of Congo red dye Adsorption onto cashew nut shell using response surface methodology', Industrial journal of Industrial Chemistry, Vol. 4, No. 17.

Prasad, A.L. and Santhi, T. (2012) 'Adsorption of hazardous cationic dyes from aqueous solution onto *Acacia nilotica* leaves as an eco friendly adsorbent', Sustainable Environmental Resource, Vol. 22, No. 2, pp. 113-122.

Qiu, Y., Zheng, Z., Zhou, Z. and Sheng, D.G. (2009) 'Effectiveness and mechanisms of dye adsorption on a straw-based biochar', BioResource Technology, Vol.100, pp. 5348-5351.

Raffiea, B.J. (2014) Comparative studies on the adsorption of textile dyes from aqueous solutions using activated carbon and polymer coated sawdust. Ph.D. thesis, Anna University.

Ramakrishnaiah, C.R. and Arpitha, D.N. (2014) 'Removal of Colour from Textile Effluent by Adosrption Using Low Cost Adsorbents', International Research Journal of Pune and Applied chemistry, Vol. 4, No. 5, pp. 568-577.
Senthilkumar, T. (2015) Adsorption of textile dye effluent Using activated carbon obtained From biomass. Ph.D. thesis, Anna University.

Sharma, N. and Nandi, B.K. (2013) ' Utilization of Sugarcane Baggase, an Agricultural Waste to Remove Malachite Green Dye from Aqueous Solutions', Journal of Materials and Environmental Science, Vol. 4, No. 6, pp. 1052-1065.

Sivakumar, P. (2014) Adsorptive removal of textile dyes from aqueous solution using a nonconventional low cost adsorbent. Ph.D. thesis, Anna University.

Somasekhara, M.C., Nirmala, V. and Ashwini, C. (2014) 'Bengal Gram Seed Husk as an adsorbent for the removal of dye from aqueous solutions – Batch studies', Arabian Journal of Chemistry.

Song, J., Zou, W., Bian, Y., Su, F. and Han, R. (2011) 'Adsorption characteristics of methylene blue by peanut husk in batch and column modes', Desalination, Vol. 265, pp. 119-125.

Srivastava, R. and Rupainwar, D.D. (2011) 'Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (*Tectona grandis*) bark powder', Indian Journal of chemical Technology, Vol. 18, pp. 67-75.

Stefusova, K., Lovas, M., Zubrik, A., Matik, M. and Vaclavikova, M. (2012) 'Removal of Cd^{2+} and Pb^{2+} from aqueous solutions using biochar residues', Nova Biotechnological at Chimica, Vol. 11, No. 2, pp. 139-146.

Sun, L., Wan, S. and Luo, W. (2013) 'Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: Characterization, equilibrium, and kinetic studies', Bioresource Technology, Vol. 140, pp. 406-413.

Sun, Lei., Wan, S. and Luo, W. (2013) 'Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: Characterization, equilibrium, and kinetic studies', BioResource Technology, Vol.140, pp. 406-413.

Tan, P.L., Wong, C.L., Ong, S.T. and Hii, S.L. (2009) 'Equilibrium and Kinectic Studies for Basic Yellow11 Removal by *Sargassum binderi*', Journal of Applied Sciences, Vol. 9, No. 17, pp. 3005-3012.

Umpuch, C. and Jutarat, B. (2013) 'Adsorption of Organic Dyes from Aqueous Solution by Surfactant Modified Corn Straw', International Journal of Chemical Engineering and Applications, Vol. 4, No. 3, pp.134-139.

Xi, X., Yan, J., Quan, G. and Cui, L. (2014) 'Removal of the pesticide Pymetrozine from Aqueous solution by Biochar Produced from Brewer's Spent at Different Pyrolytic Temperatures', BioResources, Vol. 9, No. 4, pp. 7696-7709.

Xu, R., Xiao, S., Yuan, J. and Zhao, A. (2011) 'Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues', Bioresource Technology, Vol. 102, pp. 10293-10298.

Yang, Y., Lin, X., Wei, B., Zhao, Y. and Wang, J. (2014) 'Evaluation of adsorption potential of bamboo biochar for metal –complex dye: equilibrium, kinetics and artificial neural network modeling', International Journey of Science and Technology, Vol. 11, pp. 1093-1100.

Yao, Y., Gao, Bin., Inyang, Mandu., Zimmerman, A.R., Cao, X., Pullammanappallil, P. and Yang, L. (2011) 'Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential', BioResource technology, Vol. 102, pp. 6273-6278.

Zhang, W., Mao, S., Chen, H., Huang, L and Qui, R. (2013) 'Pb(II) and Cr(II) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions', Bioresource Technology, Vol. 147, pp. 545-552

Zhao, B., Xiao, W., Zhu, H. and Han, R. (2014) 'Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode', Arabian Journal of chemistry.