Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2020, Volume 6, No. 12, pp. 1355-1362
Doi: 10.15341/mese(2333-2581)/12.06.2020/010
Academic Star Publishing Company, 2020
www.academicstar.us

Removal of Dyes from Textile Industry Wastewater Using Activated Carbon Prepared from Maize Cobs: A Case Study of Kadoma Textiles Industry, Zimbabwe

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Abstract: Water pollution is one of the fast rising global issues in need of immediate cooperation. Research has shown that textile industries have became major sources of pollution due to the dyes in their effluents which are resistant to the current treatment methods and biodegradation with their traces visibly observed in water sources and cumulative effects experienced worldwide. Adsorption method has been seen as a more effective and cheaper treatment method for dyes in wastewater especially using low cost adsorbents. In this study maize cobs were used due to their abundant availability in Zimbabwe and Zimbabwe Spinners and weavers Kadoma Textiles was used as a case study for the research and source of textile effluent. The main aim of the study was to remove dyes from industrial wastewater using maize cob activated carbon prepared by different methods. Proximate analysis and effluent characterization were carried out on the raw maize cobs and effluent respectively. Treatment with either thermal activation, Acid (HCl) activation or salt ($ZnCl_2$) activation to analyze the yielding capacity of the different activated carbon preparation methods. Continuous flow Adsorption filtration using column filters was used for the dye removal process. The results showed that maize cob activated carbon prepared by HCl activation had the greatest yield and greatest removal efficiency evidenced by around 80% decolorization followed by thermal activated AC with around 76% removal and $ZnCl_2$ activated AC with around 65% removal efficiency. TDS, pH and conductivity were also decreased significantly from the effluent.

Key words: activated carbon (AC), textile effluent, dye, adsorption

1. Introduction

Water pollution is one of the fast rising global issues in need of immediate cooperation. It is part of the United Nation's millennium sustainable development goals (MSDGs) to create a pollution free environment. Textile industries have became major sources of water pollution due to the dyes found in the effluent they discharge. The World Bank Group [17], estimates that 17 to 20 percent of industrial water pollution comes from textile dyeing and treatment applied to the fabric. The wastewater discharged from textile dyeing industry contains around a total of 72 toxic chemicals including dyes, out of which at least 30 chemicals cannot be removed by waste treatment [2], around 10% of dyes used in industries are discharged into the environment [3], because they are difficult to degrade naturally as they are resistant towards light, temperature and naturally occurring bacteria, hence,

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escape various stages of wastewater treatment plants and finally enter into the environment. (1 ppm of dye) can be extremely visible and affects the water quality (aesthetic merit and water transparency), gas solubility, and may be mutagenic or carcinogenic thereby causing severe effects to human beings such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system [4], reduce dissolved oxygen, increase COD creating odour and leading to eutrophication and bioaccumulation as well as causing toxicity affecting aquatic biota in lakes, rivers and other water bodies [5].

Manufacturing sector in particular textile industries in Zimbabwe is one of the major drivers of hazardous waste generation such as dyes disposed into the environment because of limited and inadequate facilities for treatment and safe handling mainly due to lack of financial resources causing toxicity to local water bodies such as lake chivero, Mukuvisi and Manyame Rivers etc. Zimbabwe Spinners and weavers, Kadoma textile industry is carrying out dye treatment and finishing processes using Vat and Reactive dyes which they are incapable of removing in the effluent to be discharged They are disposing a very deep colour concentrated effluent which has become a major concern to the environment and Environmental Management Agency (EMA). Traces of a strong purple to violet colour are observed at the nearby rivers affecting the water quality of the nearby communities' water sources. The last effluent quality test results at the company shows high levels of colour concentration, TDS of around 1560 mg/l an alkaline pH around 11 above the EMA and WHO standards of 6.5-8.5.

Adsorption using activated carbon (AC) has been deemed the most popular, feasible and cheapest form of dye removal technology as noted by various researchers including [6]. Mukherjee A. B. (1999) [7], described AC as a very good adsorbent used in treatment of contaminated water due to its large internal surface area (500-3,000 m^2/g), inertness, stability, lower ignition temperature, hydrophobicity, resistance to heat, hardness and attrition. However, Popuri A. K. (2016) [8], noted the need for a low-cost, renewable and easily available source of activated carbon to substitute the expensive commercially available activated carbon.

Agro-waste was therefore, found to be one of the best sources of activated carbon due to advantages associated with the use of such materials such as low raw material cost as wastes reduction, reuse and recycling, abundant availability since the agro-wastes are being produced in large quantities globally, and sustainability due to utilization of renewable resources [9, 10]. Agro-based materials that can be used for AC preparation include rice husk, orange peels, almond shells, groundnut shells, corn stalk, maize cobs etc. [11].

This research is focusing on the use of agro-waste based activated carbon in particular maize cobs to remove dyes from textile wastewater of particular interest Spinners and weavers Kadoma textiles. It is also going to be used to compare the effect of preparing activated carbon by different processes, i.e., direct pyrolysis, acid process, and carbonization by a base. Maize cobs will be investigated in consideration that it is abundant in Southern Africa and locally in Zimbabwe on a perennial basis [9]. The effect of preparing activated carbon by different processes will be investigated on its potential and efficiency to remove dyes, by considering Color, Turbidity and pH as indicators of removal.

2. Material and Methods

Primary data was gathered through an interview with the Dyehouse and Engineering managers at Kadoma textiles whilst secondary data was obtained via desktop studies on previous literature.

2.1 Material Collection and Sampling

The maize cobs used in this work were gathered from a local farmer's produce in White city, Chinhoyi. They were washed thoroughly to remove any possible contaminants and dried at 110°C in an oven till constant weight is achieved before carbonisation.

Raw textile effluent samples containing Vat and reactive dyes used were collected at Zimbabwe spinners and weavers, Kadoma textile industry manhole in the town of Kadoma at the collection point where the effluent from the two different processes (Vat dyeing and finishing) mixed together before they are discharged to some anaerobic ponds a distance from the plant by grab sampling.

2.2 Effluent Analysis and Characterization

Effluent analysis was done at Chinhoyi University of Technology (CUT) laboratory using standard methods recommended by Ahmad A. I. (2013) [3], American Society for Testing and Materials (ASTM) D3174-3175 and [12] for the determination of various physicochemical parameters like colour, pH, temperature, turbidity and conductivity. pH was determined by the electrometric method by using a digital desktop pH meter, Turbidity was measured using the Nephelometric Method whilst the method outlined by Lenore S. C. (2005) [13], was used to determine conductivity The chromophore making up the dye and colour concentration was determined using the CECIL CE 1020 1000 series UV-VIS spectrophotometer. All experiments will be done in triplicate and an average used.

2.3 Proximate and Yield Analysis

The proximate analysis of the raw maize cobs to determine the four properties (moisture, volatile matter, fixed carbon, the nonvolatile fraction of coal, and Ash).

2.3.1 Moisture content

A sample of 1g of maize cob was measured and recorded as “wet maize cob weight” before being heated in an oven in for 1 hour at 105°C allowed to cool at ambient temperatures in a desiccator. The cooled sample is measured and recorded as “dry maize cob weight.”

Moisture content (%) = Loss in weight*100

Calculate the moisture %:

$$M_{\text{maize cob}} = \frac{w_i - w_f}{w_i} \times 100$$

Where: W_i = initial mass of maize cob (wet maize cob weight of sample)

W_f = final mass of maize cob (dry maize cob weight of sample)

2.3.2 Volatile Matter

The maize cob sample was measured and also the weight of the crucible. The maize cob sample was placed in the crucible and was placed in a muffle furnace for 8mins at 800°C. Afterwards, the crucible was allowed to cool to room temperate in a desiccator and then weighed.

Calculate volatile matter by using the equation:

$$Volatile\ Matter\ Content\ \% = \frac{W_i - W_f}{W_i} \times 100$$

Where: W_i = $initial\ weight$ of sample

W_f = $final\ weight$ of sample

2.3.3 Ash Content

The maize cob sample and crucible were weighed and recorded. The sample was placed in the crucible and heated in a furnace at 800°C for 1 hour. Thereafter the sample was allowed to cool to room temperature in a desiccator and then weighed.

$$Ash\ content\ (\%) = \frac{W_2 - W_o}{W_1 - W_o} \times 100$$

Where: W_0 = Weight of the crucible

W_1 = Weight of the crucible + sample before incineration and

W_2 = Weight of the crucible + sample after incineration

2.3.4 Carbon Content

The fixed carbon was determined by:

Fixed carbon% = $100 - (of ash + of volatile matter + Moisture Content)$

2.4 Yield Analysis

The yield of activated products after complete activation was determined from raw materials by weighing 100 g of each raw material and activate separately before reweighing the resultant product and calculate using the formula:

$$Y_{\text{maize cob activated carbon}} = \frac{w_f}{w_i} \times 100$$

Where: W_i = initial mass of raw material before activation

W_f = final mass of products after activation (Dada, 2012)

2.5 Activated Carbon Preparation From Maize Cobs

Thermal treatment method was employed for AC1 by directly subjecting the carbonised cobs to activation temperature of around 500°C before washing in distilled water and drying at 110°C.

Secondly, Acid process activation was done for AC2 using 5.5 M concentrated HCl and allowed to mix for 24 hrs before washing with 1%(w/v) $NaHCO_3$ solution overnight to remove any residual acid. Rinsing was done by double distilled water until the pH rose above 5.0. It was dried at 80°C for almost 6 hrs.

Activation by 10% $ZnCl_2$ solution was the third method used for AC3 at an impregnation ratio of 1.00 between ($ZnCl_2$) and (maize cobs) solution. The carbon was activated in a muffle furnace at 800°C for a period of 10 minutes before being washed sufficiently with 4N HCl and later distilled water to remove the residual $ZnCl_2$.

2.6 Dye Adsorption Studies

For the treatment of the textile wastewater, 3 continuous flow standard bio-adsorption columns containing the prepared activated carbons packed beds with standard design parameters such as radius, depth and flow rate. The adsorption process between the prepared activated carbons and raw textile effluent was allowed to proceed with operating conditions such as pH, temperature constant but varying contact time.

2.7 Analysis of Removal Efficiencies

The removal efficiency was determined by the following equation

$$Removal = \frac{(initialvalue - finalvalue)}{initialvalue} x100$$

Quantification of dye solution removed from the effluent was done by spectral analysis in the wavelength range of 400-800 nm with quantification done based on the decrease of the chromophore peak identified before and after reaction.

$$Decoloration = \frac{(initialabsorbance - finalabsorbance)}{initialabsorbance} x100$$

3. Results and Discussion

3.1 Proximate Analysis

The proximate analysis carried out on the raw maize cobs showed that ash content, volatile matter and fixed carbon were found to be 5.79 wt%, 63.01 wt% and 17.2 wt%, respectively. Since our raw maize cobs were dry, moisture content was negligent. The high volatile content in maize cob proves that corn cob is a suitable feedstock for the thermochemical conversion process. The ash content fell in the range of < 7% defined by Manyuchi M. M. (2015) [14], and other researchers to be a good source for A.C production.

From Table 2, it can be noted that thermal treatment process produced the lowest (AC1) yield compared to other methods. This is because of high temperature used above 400°C which reduced the yield by progressive loss of organic matter. It is deduced that as the activation time increased gradually, the surface area also increased while the AC percentage yields decrease.

In the activation process using $ZnCl_2$, the optimum impregnation ratio used was capable of inhibiting the release of volatile matter, hence leading to higher

Table 1 The results of maize cob proximate analysis.

Characteristic	wt% content
Ash content	5.79
Volatile matter	63.01
Fixed carbon	17.2

Table 2 The yielding capacity of the 3 activated carbon preparation methods.

Activated carbon	Initial weight (w_i)	Final mass (w_f)	Percentage yield (Y)
AC 1	100g	41.20g	41.2%
AC 2	100g	45.22g	45.22%
AC 3	100g	44.82g	44.82%

yields (AC3). Retention of a greater proportion of low molecular weight scission products in the carbon residue has also been considered as the reason for the enhanced yield of carbon in the case of Zinc chloride activation.

In acid activation the percentage of yield was highest producing AC2 due to retention of a greater proportion of low molecular weight scission products in the carbon residue.

3.2 Effluent Characterization

A pH of 11.2 was observed in the effluent fitting in the range of 6.95-11.8 reported by Kehinde F. A. (2014) [15], who concluded that this strong alkali pH is a result of caustic and other detergents of alkali nature used in large quantity. This study validates the presence of reactive dye having the main chromophore 1.4 diamino anthraquinone whereby the auxochrome amino (NH) group which is a strong base.

TDS were found to be 2,300 mg/l which can be attributed to the dyeing and finish process as well as the detergents and other reagants being used which in turn dissolves in the water.

Conductivity was found to be 1,560 µs. This is most probably because of the dyeing and fixation process whereby high conductive ions are derived from dissolving of detergents and other reagants in the water. This is also attributed to the presence of salts such as Glauber's salt or common or vacuum salt used in the dyeing process to improve the dye affinity to the fabric it is applied and this shows that low salt dyeing is used at Kadoma Textiles.

The color observed was between purple, violet and indigo. This is because of the main dyes being used at Kadoma textiles which are anthraquinones and

Table 3 Effluent characterization and treatment.

Parameter	Concentration
pH	11.2
TDS	2300 mg/l
Conductivity	1560 µs
Colour	Purple to violet Peak absorbance 2.4 at 550 nm wavelength

indigoids, hence their mixture in the effluent is the cause of the effluent color observed. The colored effluents is also due to inadequate dye exhaustion by the electrolyte used in exhaust and pad application. The color can also be attributed to the properties exhibited by the main parent chromophore in the dyes which is the 1.4 diamino anthraquinone.

3.2.1 Treatment and Removal of Dye in Textile Effluent Using Maize Cob AC

Effectiveness of the maize cob activated carbon in the textile effluent dye removal was confirmed in the adsorption filtration experiment using a continuous flow activated carbon packed column filter setup. Significant color removal was observed after 1 hour of contact time by all the three ACs. The increase in contact time from 1-4 hours enhanced the removal of the dye from the effluent by all the three adsorbents with AC1, AC2 and AC3 reaching 76.29%, 83.42% and 69.58% respectively. The absorbance value at the maximum wavelength of 550 nm after 4 hours of phase contact was reduced from 2.4 to 0.569 for AC1, 2.4 to 0.398 for AC2 and 2,4 to 0.398 for AC3. Hence in general the maize cob activated carbon was efficient

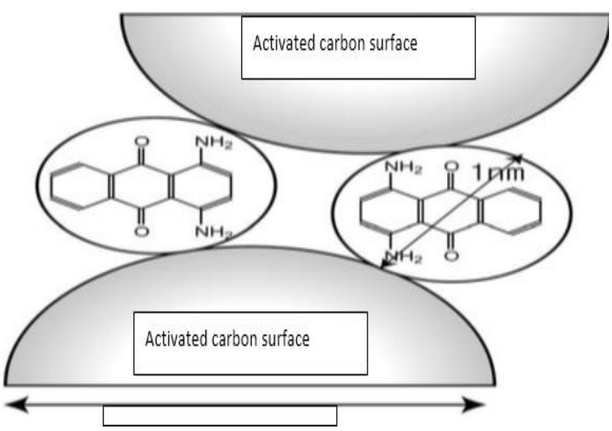

Fig. 1 The theory of adsorption of the 1.4 diamino anthraquinone by maize cob activated carbon.

in removing dye in wastewater, with AC 2 being the most efficient.

3.2.2 Effect of Adsorption on Effluent pH

There was a progressive decrease in pH with increased contact time in all the 3 filter columns with final pH values of 6.8, 5.7 and 7.2 for AC1, AC2 and AC3 respectively showing a pH decrease of 39.3%, 49.1% and 35.7% respectively after 4hours contact time, this was mainly due to the adsorption of the 1,4 diamino anthraquinone on to the activated carbon leading to the disintergration of the basicity causing amine and probably the formation of weak organic and inorganic acids as degradation products of adsorption.

3.2.3 Effect of adsorption on effluent Conductivity and TDS

There was a progressive decrease in conductivity and TDS in all the three filter columns. This is probably due to the fact that the adsorption process removed the dissolved salts, i.e., (Glauber's/vacuum or common salt) added to the solution to increase or improve the dye affinity to the fabric. The degradation of the dye also reduced alkalinity and salinity of the solution hence decreased conductive ion concentration and eventually solution electrical conductivity and TDS.

3.2.4 Decolorization of the Effluent

Direct observation of the treated effluents shown above can show that there was a significant color change and removal of the initial purple to violet color of the initial dye. This can be attributed to the degradation of the main dye chromophore, i.e., the 1.4 diamino anthraquinone of the reactive dye by the adsorption process. Direct observation cannot quantify the removal efficiency but shows the color removal or changing trend. And it can be noted that AC1 and AC2 were more efficient on color removal.

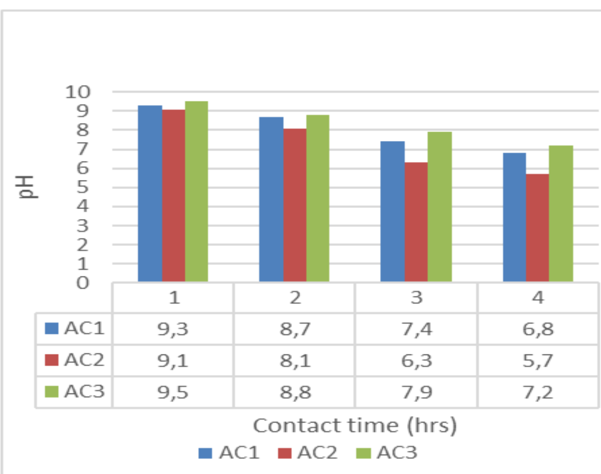

Fig. 2 Graph showing effect of adsorption on solution pH.

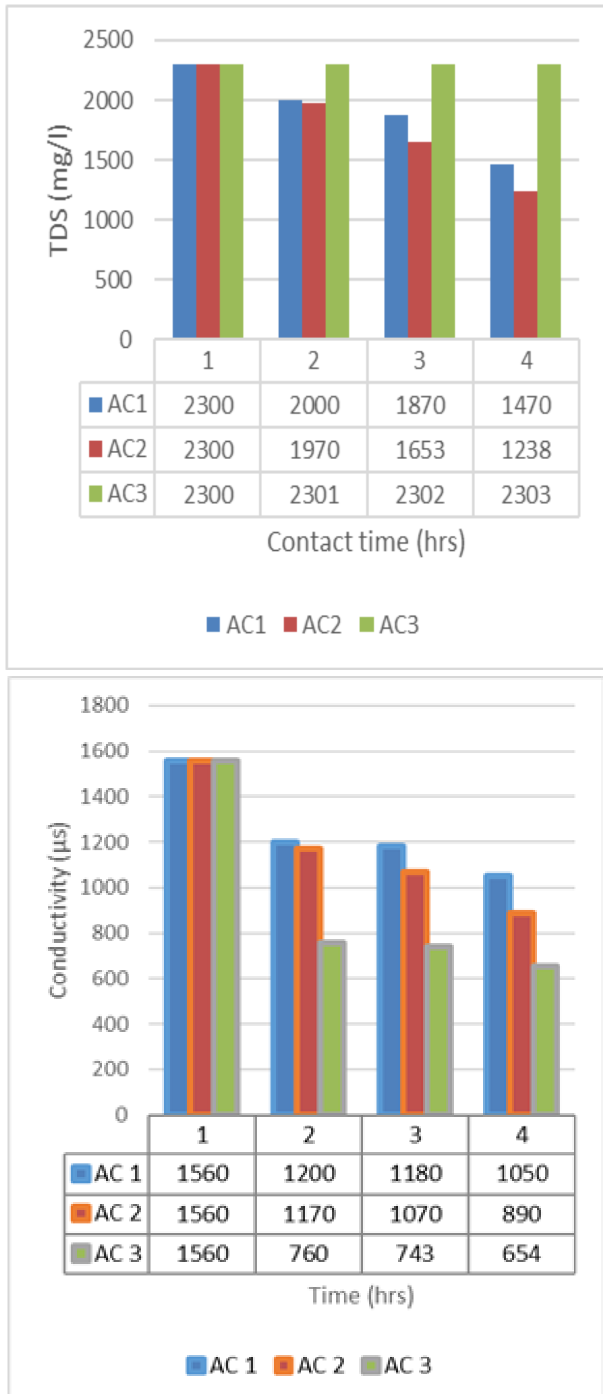

Fig. 3 Graph showing effect of adsorption on solution conductivity and TDS.

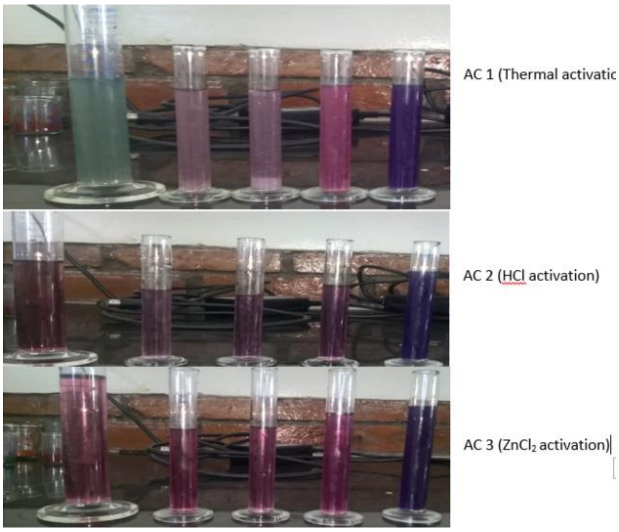

Fig. 4 Decolorised effluent samples collected from the 3 different activated carbon adsorption filter columns.

Table 4 shows that all the three ACs were effective in decoloration of the effluent. This is because of substitution and degradation of the color helping auxochrome amine as well as disruption of the conjugated system of the 1.4 diamino anthraquinone in the dye. AC3 was more efficient as it showed upto 83% decoloration of the dye. This is because AC3 was of of higher quality and higher surface area such that there was enough surface area for the adsorption process. AC1 showed quite a good result with removal efficiencies upto 76%. This is because of a very high surface area which offers enough area for adsorption despite its lower yield. AC2 had a lower removal efficiency than AC1 and AC2, this may be due to the fact that AC 1 had a smaller surface area such that it got filled up with increasing adsorption time hence limiting the adsorption process and in turn decreasing removal efficiency and performance.

Variation in contact time of the adsorption process showed an increased removal efficiency with increase in contact time. All the adsorbents reached equilibrium at 3 hours contact time with AC2 having the highest removal efficiency followed by AC1 and AC3. At equilibrium the rates of adsorption are equal to the rate of desorption and it is influenced by nature and properties of the adsorbent and its available sites for sorption. The high adsorption rate at the initial stage was due to the concentration gradient between dye in solution and the dye adsorbed in the adsorbents because of a high affinity of the dye by the adsorbent which has a number of vacant sites available at the beginning.

Table 4 Table showing the absorbances of the treated effluent using AC1, AC2 and AC3 adsorbents and decoloration percentage.

Activated carbon used	Contact time for sample collection (hrs)	Initial effluent absorbance	Final effluent absorbance	Decoloration (%)
AC 1	1	2.4	0.798	66.75
	2	2.4	0.708	70.5
	3	2.4	0.64	73.3
	4	2.4	0.569	76.29
AC 2	1	2.4	0.752	68.6
	2	2.4	0.543	77.38
	3	2.4	0.463	80.71
	4	2.4	0.398	83.42
AC 3	1	2.4	0.966	59.75
	2	2.4	0.935	61.04
	3	2.4	0.85	64.58
	4	2.4	0.73	69.58

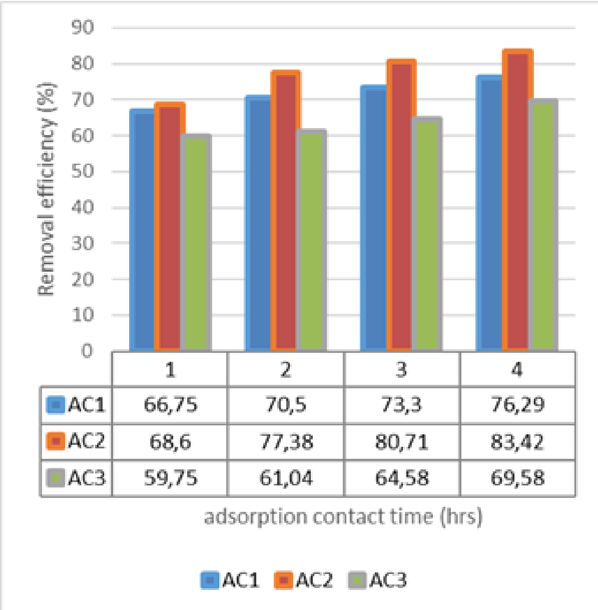

Fig. 5 Graph showing the removal efficiency of the three adsorbents.

4. Conclusion and Recommendations

It can be concluded that agricultural solid waste (maize cobs) can be used to prepare Activated carbon especially by HCl acid treatment which can effectively remove and decolorise dyes in wastewater.However it can be recommended to use multi-treatment methods for AC production to enhance the yield and quality of the activated carbon produced.

References

[1] World Bank Group, Pollution Prevention and Abatement Handbook, 1998.

[2] K. A. Adekoge, Dye sequestration using agricultural wastes as adsorbents, *Water. Resour. Ind.* 12 (2015) 8-24.

[3] A. I. Ahmad, Organic dye adsorption on activated carbon derived from solid waste, *Desalin Water Treat* 51 (2013) (13–15) 2554-2563.

[4] A. A. Adekola, Adsorption of lead (II) Ion from aqueous solution of activated carbon from coconut coirpith, *J. Chem. Soc. Nigeria* 36 (2011) (2) 134-138.

[5] H. X. Nan Liua, Catalytic activity of a composite metal electrode catalyst for the degradation of real dyeing wastewater by a heterogeneous electro-fenton process, *Journal of Environmental Chemical Engineering* (2019).

[6] S. L. G. Sivamani, Removal of dyes from wastewater using adsorption — A review, *IJBST* 2 (2009) (4) 47-51 .

[7] A. B. Mukherjee, Separation of dyes from cotton dyeing effluent using cationic polyelectrolytes, *Am. Dyestuff Rep.* 88 (1999) 25-28.

[8] A. K. Popuri., Color removal from dye wastewater using adsorption, *International Journal of Pharmaceutical Sciences Review And Research* (2016).

[9] M. Manyuchi et al., Utilization of agro waste bio adsorbents in textile wastewater treatment, in: *International Conference on Industrial Engineering and Operations Management*, Pretoria, Johannesburg, South Arica, 2018.

[10] H. W. Zhang, Oxidation and coagulation removal of COD from landfill leachate by Fered-Fenton process,. *Chemical Engineering Journal* 210 (2012) 188-194.

[11] S. A. Hashemian, Synthesize and characterization of Sawdust/Mnfe2o4 nano composite for removal of indigo carmine from aqueous solutions, *Oriental Journal of Chemistry* 30 (2014) (4) 1753-1762.

[12] R. K. G. Trivedy, Chemical and Biological Methods for Water Pollution Studies, Environmental Publications, 1984.

[13] S. C. Lenore, *Standard Methods for Examination of Water & Wastewater*, Washington, DC: American Publihealth Association, American Water Works Association, and The Water Environment Association, 2005.

[14] M. M. Manyuchi, Potential for production of activated carbon from jatropha carcus fruit shells, Article in Chemical Science, 2015.

[15] F. A. Kehinde, Textile waste water and the advanced oxidative treatment process — An overview, *Int J. Innovat Res Sci Eng Technol* 3 (2014) 15310-15317.