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Adsorption of Textile Wastes Containing Methylene Blue & Congo Red using Activated Carbon Produced from Coconut Shell

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Abstract

The use of low-cost, locally available, highly efficient, and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from waste water. This study investigated the potential use of activated carbon produced from coconut-shell for the removal of two dyes viz: Methylene blue and Congo red from textile effluent obtained from Nichemtex Industries Ltd (NCTX) at Ikorodu, Lagos State. The coconut shells were carbonated and used to produce activated carbon using Zinc Chloride as the activating agent. The effects of contact time, pH, adsorbent dose, temperature were investigated for different particle sizes of 1nm, 50nm, and 500nm mesh-sizes for the removal of both dyes (i.e Methylene blue and Congo red) respectively, and the optimal experimental conditions were ascertained. The results showed that as the amount of the adsorbent increased, the degree of adsorption increased accordingly and equilibrium adsorption was attained in 2hrs (i.e 120mins). The optimum pH for the adsorption of dyes were 8.0, 6.0, and 4.0 for 1nm, 50nm, and 500nm mesh-sizes respectively. Maximum dye was sequestered within 30mins of the start of each experiment.

Keywords-*adsoprtion, textile waste, eco-friendly, particle size, equilibrium, activating agents, pollutants, optimum*

1. INTRODUCTION

Global village is facing many issues regarding industrial pollution. Textile, leather, food, agro industries , just to mention a few, have brought enormous atmospheric changes. The alarming question is the disposal of effluent discharged by these industries. The basis of ISO-14000 is mainly for the disposal of residual contents of these industries. But unfortunately the industries are lacking somewhere in following the procedure recommended for this purpose. The effluent from textile industries is a big question mark, which has created environmental problems around urban areas.

Industries like plastic, paper, textile and cosmetics use dyes to colour their products. These dyes are common water pollutants and they may be frequently found in trace quantities in industrial waste water. Their presence in water, even at low concentrations, is highly visible and undesirable. When these coloured effluents enter rivers or any surface water system they upset biological activity and aquatic ecosystem. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into these water bodies (e.g. streams, rivers etc). Ground-water are also affected by these pollutants because of leaching from the soil. Many dyes are difficult to degrade due to their complex aromatic structure and they tend to persist in the environment creating serious water quality and public health problems such as allergic dermatitis, skin irritation, cancer and mutation. Furthermore, these dyes are toxic to micro-organisms and may cause direct destruction or inhibition of their catalytic capabilities.

Textile industry use dyes and pigments to colour their products. There are more than 100,000 commercially available dyes with over 7x105 tonnes of dyestuff are produced annually [1]. Many types of dye are used in textile industries such as directive, reactive, acid and basic dyes. The main source of waste water generated by the textile industry originates from the washing and bleaching of natural fibres and, from the dyeing and finishing stages. Given the great variety of fibres, dyes and process aids; these processes generate waste water of great chemical complexity and diversity, which are not adequately treated in conventional waste water treatment plant.

Numerious studies have been conducted to assess the harmful impacts of colorants on the ecosystem.

The dyes present in the effluent discharged by textile industries are first to be treated for the separation of dye-stuff and then send to disposing end. In the past a number of conventional biological treatment processes have been

used which were not effective, some of which include coagulation and chemical oxidation, membrane separation process, electrochemical, reverse osmosis, aerobic and anaerobic microbial degradation but all these methods suffer one or more limitations and none of them were successful for the complete removal of dye. It has been discovered that dyes can be effectively removed by adsorption process in which dissolved dye compounds were attached to the surface of the adsorbents. Researchers have exploited many low cost and biodegradable effective adsorbents. They were obtained from natural sources which successfully removed dye from aqueous solutions [2].

Adsorption technique is by far the most versatile and widely used. Common adsorbents materials are: activated alumina, silica gel, metal hydroxides, alumina silicates (molecular sieves) and activated carbon. Activated carbon is by far the most common adsorbent used in waste water treatment. Activated carbon is produced from a wide range of agricultural waste products such as Neem (Azadirachta Indica) husk, palm shell, palm fruit fibre, egg shell, rice husk, hazelnut shell etc. One of the fastest growing areas is in environmental applications such as waste water. In the treatment of waste water, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions [3].

Activated carbon was produced from local agricultural waste which is coconut shell impregnated with an activating agent for the application and study of:

- Adsorption of pure methylene blue and congo-red dyes from textile effluent respectively, obtained from Nichemtex Industries Ltd at Ikorodu.

To achieve these, this study was carried out with the following objectives:-

- ❖ To evaluate various operating parameters such as activation temperature and activation time for the activated carbon poroduced from coconut shell.
- ❖ To evaluate the potential application of locally produced activated carbon in textile effluents as its performance in the removal of the following dyes mentioned earlier.
- ❖ To study the effect of contact time, effect of pH, effect of adsorbent dose (concentration), effect of temperature, size and particle distribution of the activated carbon.

In recent time, special attention has been focused on the rise of natural adsorbents as an alternative to replace the conventional adsorbents based on both the environmental and economic points of view. This process attempts to put into use the principle of using waste to treat waste and become even more efficient because these agricultural by-products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost, since they are waste products.

In this work, a local agricultural coconut shell was used to prepare the activated carbon. The production of activated carbon was carried out by using chemical activation method. In this method, the carbonization and activation were accomplished in a single step by carrying out the thermal decomposition of the raw material impregnated with certain activating agents. Activating agents used are Zinc Chloride ($ZnCl_2$), Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH).

The activated carbon was used to adsorb methylene blue and congo-red dyes from model textile effluent obtained from Nichemtex Nig. Ltd. The following kinetic models viz: Langmuir, Freundlich and BET isotherms were used to study and compare the effect of contact time, effect of pH, effect of adsorbent dose , effect of temperature and to examine the kinetic behaviour of these systems reacting at the surface respectively. The results of the above specified parameters for these systems were achieved with the aid of MICROSOFT EXCEL (2007) Table 1. Summarizes various works with reference to the raw materials, methods and their application of activated carbon.

AUTHORS	YEAR	RAW MATERIALS	METHOD	APPLICATION
Lua and Guo	2001	Oil palm stones	CO_2 activation	SO_2 removal
Hu and Srivina	2001	Coconut shell & palm shell	$ZnCl_2$ activation & CO_2 activation	Phenol, Methylene blue
Hu et.al	2001	Coconut shell & palm seed	$ZnCl_2$ activation	Phenol & Dye
Mozammel et.al	2002	Coconut shell	$ZnCl_2$ activation	Iodine
Guo and Lua	2003	Palm shell	H_3PO_4 activation	Ammonia adsorption
Daud & Ali	2004	Palm shell & coconut shell	Physical activation(N_2 gas)	Nitrogen adsorption
Sodeinde	2012	Coconut shell	$ZnCl_2$ activation	Hexamine Cobalt(II) oxidation

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2.0 EXPERIMENTAL PROCEDURE

2.1 Preparation of Activated Carbon

The coconut shell samples was carbonized in the muffle furnace (model, NYC-12) at a temperature of 600^{o}C for 1hour according to the method reported [4], further crushed and separated into different mesh sizes of 1nm, 50nm, 500nm respectively according to the **IUPAC** classification of porosity reported in . The separation into different mesh sizes was achieved with the aid of mechanical sieve. The charcoal was soaked in activating agent of Zinc chloride solution with a weighed quantity of 500g of the samples for 24hrs. The samples was heated in the furnace for activation at activation temperatures ranging from 400^{o}C-500^{o}C at 20^{o} interval; at different activation times- 30-105mins at 15mins interval. After activation, the activated samples were further treated with 0.1M Hydrochloric acid (HCl) to reduce the ash and mineral content of the samples. The samples were neutralized with 1M Sodium hydroxide solution, rinsed with distill water until the pH is almost neutral (pH≈7). The resulting activated carbon was dried in the oven at 110 ± 2^{o}C for 2hours [5], and then, the activated carbon samples was packaged in well-fitted airtight containers and labelled for 1nm. 50nm and 500nm-mesh sizes respectively; ready for adsorption processes.

2.2 ADSORPTION STUDIES

Effect of Contact Time

10g of activated carbon (i.e. adsorbent) was weighed each into 6-250ml conical flasks. 100ml of the textile effluent was measured and

added to the content in each conical flask. The content was shaken rigorously and continuously for 30,60,90,120,150 and 180mins respectively. The solution was filtered with the aid of a filter paper to obtain the filtrate (i.e, the equilibrium concentration or final concentration). The final concentration (C_e(g/L)) was estimated for each sample spectrophometrically at the wavelength corresponding to maximum absorbance for methylene blue (λmax=540nm) and congo red (λmax=663nm) respectively using a spectrophotometer (UV/VIS-752). A graph of C_e (g/L) versus time (mins) was plotted for methylene blue and congo red consecutively.

Effect of pH

100ml of the textile effluent was measured and added to 5g of the activated carbon in 6-250ml conical flasks for 1nm, 50nm, and 500nm mesh sizes respectively. The pH of the solution was adjusted using dilute 0.1M HCl and 1M NaOH solution to vary the pH of each content from 2-12 and was checked using a pH meter. The content of each flask was shaken rigorously for 10mins at room temperature. The solution in each conical flask was filtered and the final concentration was read using UV-Spectrophotometer. A plot of C_e versus initial pH was obtained for 1nm, 50nm and 500nm respectively for the adsorption of the dyes from the textile effluent.

Effect of Adsorbent Dose

100ml 0f the textile effluent was measured and added to 1,2,3,5,10 and 15g into different conical flasks. The content were shaken rigorously and filtered to obtain the filtrate. The process was conducted at room temperature. The final concentration was measured using the UV-Spectrophotometer.

The experiment was carried out for a maximum period of 120mins but was extended to 180mins to establish its equilibrium point with initial concentration of 30g/L at pH-6.0, room temperature (27±2^{o}C) and adsorbent dose-10g/100ml for the adsorption of dyes (i.e. methylene blue and congo red) from model textile waste using coconut-shell-based activated carbon. The relation between the removal of dyes (methylene blue and congo red), and reaction time was studied at pH 6.0 with increase of contact time using coconut-shell-based activated carbon as presented in Fig.4.2. At the initial stage, there was a rapid adsorption of the dyes.. It was found that 99% of the dye concentrations was removed in the first 30mins, and thereafter the rate of adsorption on the activated carbon was gradual till it became constant at 0.001 and 0.004 for methylene blue and congo red respectively from 120mins-180mins as shown in Fig.4.2. The rapid adsorption at the initial contact is attributed to the highly negatively charged surface of the activated carbon of the basic cationic dyes. The gradual rate of adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species onto the surface of the activated carbon and the available basic cationic adsorbate species in the solution, as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent (i.e saturation of the active site which do not allow further adsorption to take place). The equilibrium was attained at 120mins when the maximum dye adsorption onto coconut-shell-based activated carbon (CSAC) was reached. This shows that equilibrium was achieved in 2hours.

B. EFFECT OF pH ON THE ADSORPTION OF DYES WITH DIFFERENT MESH-SIZES

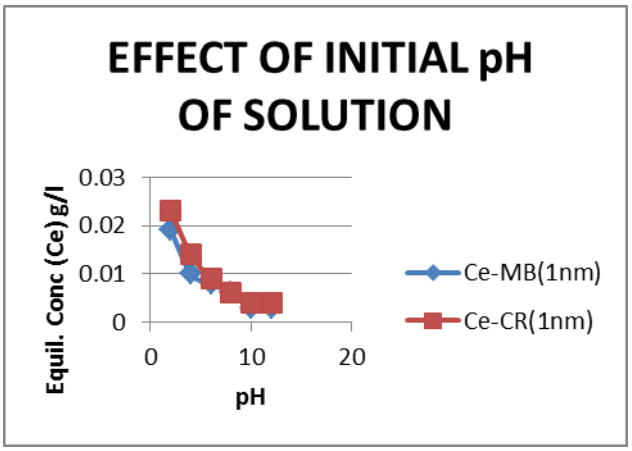

Fig.1: Effect of Initial pH of the Dye solution at Co-30 mg/L Temperature-room Temperature and adsorbent dose-5g/100ml for mesh-size of 1nm from textile effluent.

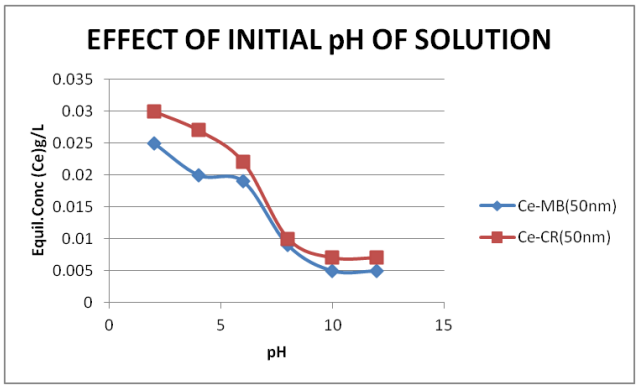

Fig.2: Effect of Initial pH of the Dye solution at Co-30 mg/L, Temperature- room Temperature and adsorbent dose-5g/100ml for mesh-size of 50nm from textile effluent.

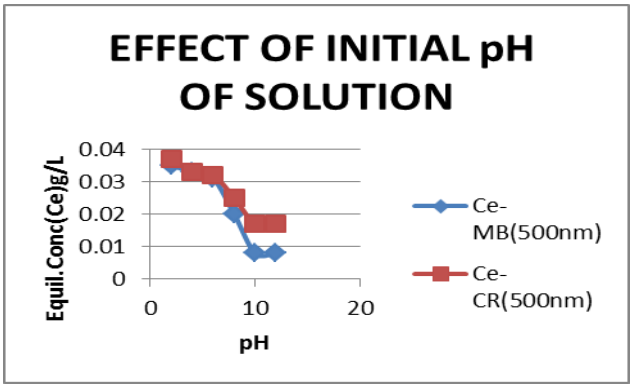

Fig.3: Effect of initial pH of the Dye solution at Co-30 mg/L, Temperature- room Temperature and adsorbent dose-5g/100ml for mesh-size of 500nm from textile effluent.

The experiment for the adsorption process of the dyes was conducted at room temperature with initial concentration of 30g/L and adsorbent dose-5g/100ml for mesh-sizes of 1nm, 50nm, and 500nm respectively.. A graph of equilibrium concentration vs pH was plotted as presented in Fig.4.3a, 4.3b and 4.3c respectively. A comparative study of the effect of initial pH was carried out for the adsorption of methylene blue and congo red for mesh-size of 1nm to determine the pH value where optimum adsorption is attained. The adsorption process of methylene blue showed that there was a sharp fall from pH-2.0 to pH-4.0 and continued in that fashion till it became constant at pH10.0-12.0. From Fig4.3a, optimum adsorption for methylene blue was attained at pH-8.0.

The adsorption process for congo red showed a significant decrease in the results obtained with increase in pH. The resultant effect produced a curve and the optimum adsorption for congo red was attained at pH-8.0. The optimum point coincided for both dyes presented in Fig 4.3a. The adsorption process for methylene blue and congo red for mesh-sizes of 50nm and 500nm respectively also showed a significant decrease in their values with increase in pH. The optimum adsorption for methylene blue is pH-6.0 with equilibrium concentration of 0.019g/L and the optimum adsorption for congo red is pH-6.0 with equilibrium concentration of 0.022g/L for 50nm mesh-size while for 500nm mesh-size; the optimum adsorption for methylene blue and congo red is pH-4.0 with equilibrium concentration of 0.033g/L as presented in Figs.4.3b and 4.3c respectively. The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. Hence, the availability of negatively charged groups at the adsorbent surface is necessary for the adsorption of basic cationic dyes.

C. EFFECT OF ADSORBENT DOSE

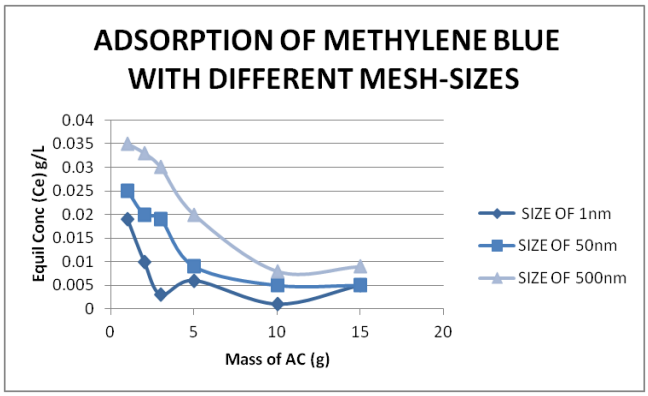

Fig.4.: Effect of the amount of Activated carbon on the adsorption of Methylene blue dye for different mesh-sizes, from model textile effluent at Co-30g/L, Temp-room temperature (i.e.. particle size distribution).

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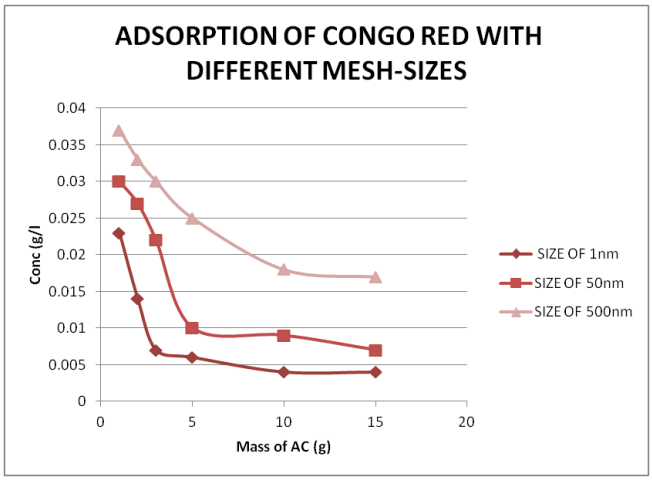

Fig.5: Effect of the amount of Activated carbon on the adsorption of Congo red dye for different mesh-sizes, from model textile effluent at Co-30g/L, Temp-room temperature (i.e. particle size distribution).

COMPARATIVE STUDY OF THE ADSORPTION OF METHYLENE BLUE AND CONGO RED.

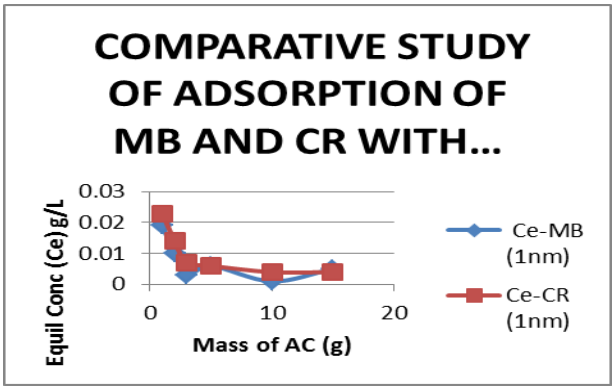

Fig.6: A comparative adsorption study of Methylene blue and Congo red for 1nm mesh-size.

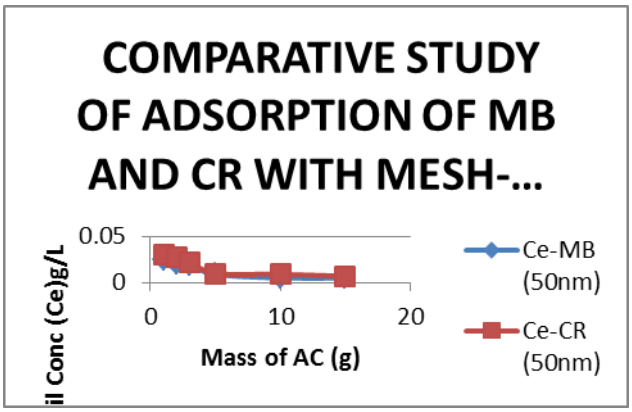

Fig.7: A comparative adsorption study of Methylene blue and Congo red for 50nm mesh-size.

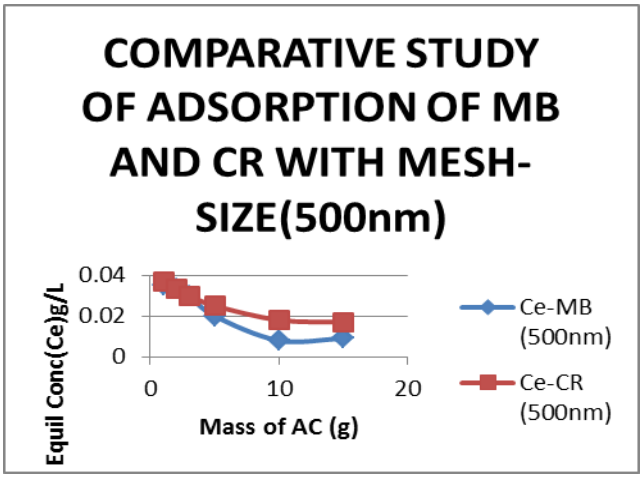

Fig.8: A comparative adsorption study of Methylene blue and Congo red for 500nm mesh-size.

The experiment was conducted for masses of 1,2,3,5,10, and 15g/100ml respectively for a contact time of 2hrs with initial concentration (Co) of 30g/L at room temperature (27±2^{o}C) and pH-6.0. The study carried out for the adsorption of methylene blue and congo red alone for different mesh-sizes and the respective comparative studies as presented in Figs.4.4a,4.4b,4.5a,4.5b, and 4.5c showed that 99% of the dyes was adsorbed from the model textile waste and the quantity left is just a trace amount of the dye. In other words, the rate of adsorption of the dyes is high with the increase in the amount of coconut-shell-based activated carbon. The best adsorption took place with the amount of 10g/100ml and 15g/100ml for both adsorption cases (i.e the adsorption of methylene blue and congo red) as presented in the graphical comparative study of methylene blue and congo red in Figs.4.5a,4.5b and 4.5c respectively.

2.0 CONCLUSIONS

This prepared activated carbon from coconut shell has proved to be effective in the removal of textile wastes containing methylene blue and congo red dyes. It was more effective for removal of methylene blue than congo red.The optimum parameters are 1 nm particle size, contact time of thirty minutes and equilibrium time of two hours.

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