A Comparative study on removal of CU(II) using Activated carbon and low cost adsorbent from Textile wastewater

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Abstract : Copper(II) is one of the most toxic heavy metals offering significant effects on the living organisms. Removal of Cu(II) from waste water is crucial and according to World Health Organisation maximum acceptable limit of Cu(II) in drinking water is 2.0 mg/L. Present work investigate the application of sugarcane bagasse, activated sugarcane bagasse and activated carbon as an adsorbent for the removal of Cu(II) from synthetic wastewater and Textile industry wastewater. The effect of activation using sodium hydroxide and citric acid of sugarcane bagasse has been investigated.

The surface functionality of the adsorbents were studied using scanning electron microscope (SEM) and Fourier infrared spectroscopy (FTIR) respectively. FTIR analysis of unmodified and modified sugarcane bagasse revealed the presence of hydroxyl, carboxyl and carbonyl groups which participate in the adsorption of Cu(II) ion. SEM analysis showed more irregular and porous structure of chemically modified sugarcane bagasse which was responsible for high surface area, so that Cu(II) uptake capacities was increased.

The maximum removal efficiency of Cu(II) using activated carbon (AC), sugarcane bagasse (SG), acid modified sugarcane bagasse (ASG) and base modified sugarcane bagasse (BSG) was found as 98.5%, 88.9%, 96.9% and 94.8% respectively at optimum contact time 60 min, adsorbent dose 5g/L, initial Cu(II) concentration 10mg/L and pH 5 from synthetic wastewater in batch adsorption process. Adsorption isotherm of all adsorbents was performed and it was strongly correlated with Langmuir isotherm for AC, SG and ASG and Freundlich isotherm for BSG. Kinetic study established that all the experimental data for all adsorbents were found to best fit in pseudo second order kinetics. The percentage recovery of Cu(II) from industrial wastewater by batch process was found to be 83.45%, 62.53%, 81.40% and 71.77% using AC, SG, ASG and BSG respectively. The maximum Cu(II) removal obtained was 96.39 % at initial concentration of Cu(II) 11.39 mg/L, pH 5.06 and ASG dosage 8.65 g/L optimum condition. Overall, commercial activated carbon was found to be superior but from the cost analysis it seems to be too costly; however, acid modified sugarcane bagasse is an environmentally friendly, low cost, highly efficient biosorbent and can be used as alternative adsorbent for the removal of Cu(II) from textile wastewater.

Key words: Sugarcane bagasse; activated carbon; adsorption; copper; kinetics; adsorption isotherm.

I. INTRODUCTION

Contamination of the environment by heavy metals has become a major concern in recent years. Various industries produce and discharge wastewater containing heavy metals into the environment, posing a serious environmental threat to human health and the ecosystem. Wastewater treatment can be done using three methods: primary, secondary and tertiary/advanced processes. Primary treatment separates suspended solids and greases from water and a secondary treatment such as biodegradation process is used in the removal of biodegradable compounds whilst tertiary/advanced treatment methods are largely used to remove non-biodegradable wastes.

Removal of non-biodegradable contaminants (mainly heavy metal ions) wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption can be used to remove these recalcitrant wastes. Adsorption is a greatly preferred method for the removal of heavy metal ions in waste water treatment, generally due to its high efficiency, simplicity in handling, high availability of raw materials as well as its cost effectiveness.

Activated carbon is one of the most common types of adsorbent used in waste water treatment. It is highly porous (average pore diameter of 10 Å to 60 Å), therefore possessing large surface area, which ranges from 300 to 1200 m2/g. (Geankoplis, 2003), (Marsh & Rodriguez-Reinoso, 2006). The large surface area of the activated carbon will contribute to the adsorption process itself, since there are more reactive sites for the adsorbate to bind on the surface of the activated carbon.

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. The low cost agricultural waste by-products such as sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, neem bark, banana peel, orange peel etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by- product or waste material from another industry. Therefore, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail (Khan et al., 2004).

One of the agriculture wastes that received attention in the study of this particular subject is sugarcane bagasse. It is an abandoned, readily available, low cost and cheap, environment friendly bio-material to remove harmful particles such as heavy metal ions and oil/grease particles from industrial effluents. The application of untreated sugarcane bagasse has significant drawbacks such as low adsorption capacity and high release of soluble organic compounds into the solution. (Nguyen et al., 2013).

Practically, raw sugarcane bagasse (without chemical and physical activation) can already be used as biosorbent in waste water treatment. However, studies showed that, by including activation process in the preparation of sugarcane bagasse based biosorbent, the adsorption capacity will be greatly improved due to the formation of new pores which increase the total surface

area and the adsorptive sites of the adsorbent. For these reasons it has been chemically modified by acid and base before being used in biosorption process.

Conventional methods of studying a process by maintaining other factors involved at an unspecified constant level does not describe the combined effect of all the factors involved (Ravikumar et al., 2006). In addition, it is a time consuming method and does not guarantee the determination of optimal conditions (Rajendran et al., 2007). These limitations of conventional methods can be eliminated by introducing statistical technique such as Response Surface Method (RSM). RSM regressively fits the experimental readings of the design to a model (first, second or higher order) and determines the coefficients involved. The most frequently used second order design is Box-Behnken design. The Box–Behnken design present more efficient matrices and is more economical. This design requires least number of experimental runs and hence is most economical and most suitable in case where less no. of experimental runs are performed (Kamsonlian and Shukla, 2013).

1.1.Problem Statement

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substance in aquatic environment. Industrial wastewater contains higher amount of heavy metals that can pollute the water when it is discharged to the nature. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Heavy metals are the elements that have more than 5 times the specific gravity than that of water. At least 20 metals are considered to be toxic and approximately half of these metals are emitted in the environment in quantities that are risky to the surroundings, additionally to the human health.

Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc. These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Due to their toxicity and non- biodegradability, they tend to accumulate in living organism. Therefore they cause numerous diseases and disorders.

Copper(II) as an essential element plays an important role in all living organisms. It is also widely used in industries such as high electrical and thermal conductivity, good corrosion resistance, ready availability, high recyclability and attractive appearance. Copper(II) is one of the heavy metals most toxic to the living organisms and it is one of more widespread heavy metal contaminants of the environment. Extensive intake of Cu(II) can cause hemolysis, hepatotoxic and nephro toxic effects vomiting, cramps, convulsions, or even death.

For removal of heavy metals, adsorption technique is relatively cheap and there is pressing need to replace commercial adsorbents like activated carbon, zeolite, activated alumina and silica gel with the low cost adsorbents. The method of adsorption using commercial activated carbon is costly especially for developing countries. Thus, single use adsorbent materials are undesired considering the difficulties faced during commercial activated carbon regeneration and the disposal problems posed by regeneration solutions. This calls for research efforts to develop an industrially viable, cost effective and environmentally compatible adsorbent for wastewater treatment.

In an attempt to address the cost problems associated with commercial adsorbents; the use of abundant, locally available, low cost adsorbents derived from agricultural wastes is proposed in this study. These adsorbents are cheaper and readily available. Also, these low cost adsorbents are proposed as single use materials to avoid regeneration problems. After use, the loaded adsorbent could be easily disposed off by landfilling or incineration and the metal residues could be recovered by subsequent treatment of the post-combustion ash (leaching).

II. LITERATURE REVIEW

2.1 Heavy Metals in the Environment

Due to rapid industrialization and urbanization in developing countries like India heavy metal pollution is a serious problem today and its treatment is of special concern due to their recalcitrance and persistence in the environment. Like organic pollutants, most of these heavy metals do not undergo biological degradation (Sharma et al., 2013). Toxic heavy metal ions get introduced to the aquatic streams by means of various industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. and pose a serious threat to environment. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. (Sud et al., 2008). Heavy metals are present in low concentration in wastewater and are difficult to remove from water. Pollutants in industrial wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies (Singh and Kaushal, 2013).

2.2 Sources and Impacts of Copper

Copper is an important engineering metal, widely used for various engineering purposes. Copper has three common oxidation states Cu(0) (metal), Cu(I) (cuprous) and Cu(II) (cupric).The main species of concern in aqueous solution is Cu(II) (Halnor et al., 2013).

Copper(II) is used for manufacture of several alloys. It is also used in ceramics and pesticides. Cu(II) is used in manufacture of wires for various industries, namely electrical, electronics, automotive, electroplating, electrical appliances, white goods, etc. and other products in copper forming industries (Shrivastava, 2009).

Copper(II) enters into the environment through natural sources, industrial sources, domestic sources, food and consumer products. Copper and its compounds are naturally present in the earth's crust. Natural discharges to air and water, such as windblown dust, volcanic eruptions, decaying vegetation, forest fires, sea spray, etc., may be significant. (TDC Environmental, 2004) Domestic sources of copper are coming from pipes and taps, metal roofing, car washes, gasoline and oil, vehicles, road surface wear etc. The contamination of air and water by copper is contributed from mining, milling, refining of copper ores, electroplating industries, fertilizer industry, pesticides industries, explosive industries, etc. (Shrivastava, 2009). The sources and pathways of copper entering into water bodies have been shown in Figure 2.1.

The effluents from these above industries usually contain a considerable amount of Cu(II), which spreads into the environment through soils and water treams and accumulates along the food chain, resulting in a high risk to human health, as high concentrations of Cu(II) will cause stomach upset and ulcer, mental retardance, liver and brain damage, anaemia; arthritis/rheumatoid arthritis, hypertension, nausea/vomiting, hyperactivity, schizophrenia, insomnia, autism, stuttering, and so on (Nalini and Nagaranjan, 2013).
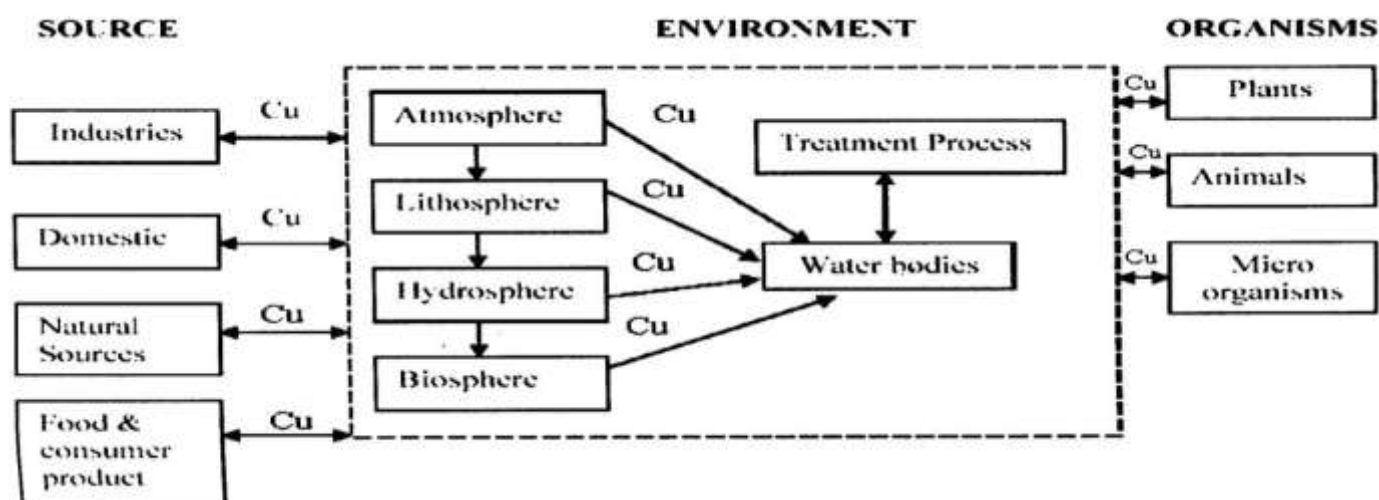

Figure 2.1 Copper Pollution: Source, Pathways and interaction with Organisms (Source: Shrivastava, 2009)

Standards are legally prescribed limits of pollution which are established under statutory authority. The standards for copper in drinking water and industrial or sewage effluent discharges have been given in Table 2.1. As copper(II) does not degrade biologically, the control of Cu(II) pollution has special importance for both organisms that live in waters and those that benefit from waters. It is essential that potable waters be given some treatment to remove copper before domestic supply.

III. MATERIALS AND METHODS

The adsorbents used for the experiments were sugarcane bagasse, acid modified sugarcane bagasse, base modified sugarcane bagasse and commercially available activated carbon.

Sugarcane bagasse (SG) was collected from local market. The collected sugarcane bagasse was cut washed several times with tap water and then with distilled water to remove external dirt. The wetted bagasse was kept in air for removing the water from the surface and dried in oven at 60°C for 48 hours. The dried sugarcane bagasse was grounded into powder, sieved to get size between 150 to 300μ and kept in an air tied container for experimental uses.

Acid modified sugarcane bagasse (ASG) was modified with citric acid. In this sugarcane bagasse was soaked in 0.1M citric acid solution for 24 hours and then soaked in distilled water for 4 hours to remove free citric acid. It was then dried in an oven at 60°C for 48 hours. Later it stored in air tight container.

Base modified sugarcane bagasse (BSG) was modified with sodium hydroxide. In this sugarcane bagasse was soaked in 0.1M NaOH solution for 24 hours and then soaked in distilled water for 4 hours to remove free NaOH. It was then dried in an oven at 60°C for 48 hours. Later it stored in air tight container.

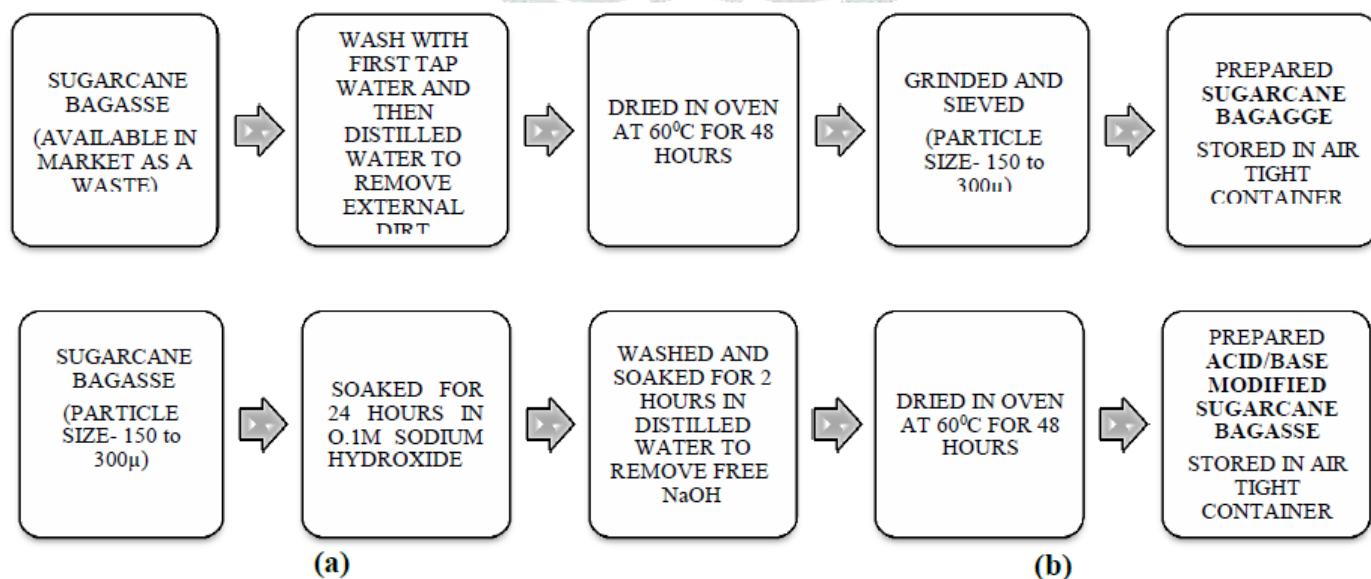Charcoal activated AR named as activated carbon was directly purchased from the market.

Figure 3.2 Preparation of Adsorbents (a) Sugarcane bagasse, (b) Acid/ Base modified sugarcane bagasse

3.1 Characterization of Adsorbents

The functional groups of adsorbents before and after sorption were determined using Fourier Transform Infrared Spectroscopy (FTIR), at wave number range of 400-4000 cm-1. The sample disk was prepared by mixing KBr powder with dried biosorbent, then ground and compressed into pellet before it was analysed. The surface morphology of adsorbents was studied using Scanning Electron Microscope (SEM).

3.2 Adsorbate Solution

Synthetic wastewater of copper was prepared from copper sulphate salt. The stock solution of Copper (1000 mg/L) was prepared by dissolving 3.929 g of copper sulphate ($CuSO_4.5H_2O$) in 1L of distilled water and used for all experiments with required dilution.

Real wastewater sample used was collected from the effluent discharge point of chemical industry in Vapi (Gujarat), which manufactures mainly copper sulphate and iron sulphate. It was carefully bottled in a plastic container and was taken to the laboratory for analysis.

3.3 Batch Studies

A series of batch experiments was conducted to determine the equilibrium conditions for removal of Cu(II) using sugarcane bagasse, acid modified sugarcane bagasse, base modified sugarcane bagasse and commercially available activated carbon as an adsorbent. Equilibrium conditions were contact time (0-180 min), initial Cu(II) concentration (10-30 mg/L), pH (3-9), and adsorbent dosage (1-10 g/L). All experiments were carried out at room temperature. A known desired quantity of the adsorbent was added to 50mL of the Cu(II) solution of known concentration. pH of solution was adjusted using either 0.1M NaOH or 0.1M HCl. The contents in the flasks were shaken at 150-160 rpm in water bath shaker. Samples and duplicate samples were drawn as per experiment required, first filtered coarse filter paper and then with Whatman No. 42 filter paper and concentration of Cu(II) in the filtrate was analysed by UV-Vis Spectrophotometer using cuprethol method for Cu(II).

IV. RESULTS AND DISCUSSION

4.1 Characterization of the Adsorbents

The biosorbent was characterized by Fourier transform infrared spectrometer (FTIR) and Scanning Electron Microscopy (SEM).

4.12 Effect of Contact Time:

The result showed that the adsorption of Cu(II) ion increases with time up to 60min and then it becomes almost constant at the end of the experiment. After 15min, the removal efficiency of Cu(II) ion using AC, SG, ASG and BSG were 84.4%, 46.8%, 71.4% and 68.8% respectively and a maximum removal efficiency after 60min were 98%, 85.7%, 96.5% and 91.8% respectively.

4.3 Effect of Adsorbent dose

maximum removal of Cu(II) was found to be 98%, 85.7%, 96.5% and 91.8% of AC, SG, ASG and BSG respectively at the optimum adsorbent dosage of 5g/L.

4.4 Effect of initial concentration of Copper(II) ion

The maximum removal of Cu(II) was found to be at the optimum initial Cu(II) concentration of 10mg/L.

4.5 Effect of pH

pH influences the surface charge of the adsorbent, degree of ionization and the species of adsorbate. So the pH of the aqueous solution is an important controlling parameter in heavy metal adsorption process *(Huang et al., 2012)*. The influence of pH on Cu(II) biosorption by AC, SG, ASG, BSG was investigated in the pH range 3–9 at constant adsorbent dose 5g/L, initial Cu(II) concentration 10mg/L and equilibrium time 60min as shown in Figure 4.6.

Figure 4.6 Effect of pH
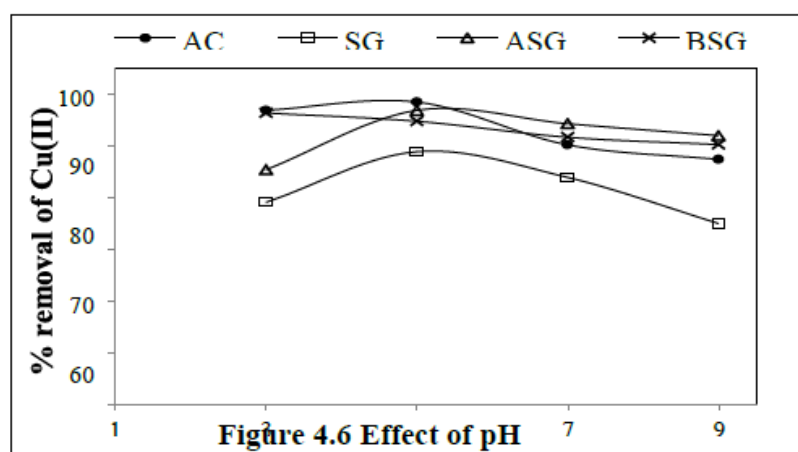
(Equilibrium time= 60min, initial concentration Cu(II)= 10mg/L, Adsorbent Dose= 5g/L Temp.=25 °C)

4.6 Optimum condition

A series of batch experiments was conducted to determine optimum conditions for removal of Cu(II) by varying different parameters using AC, SG, ASG and BSG. Contact time varied from 0-180 min, initial Cu(II) concentration varied from 10-30 mg/L, pH varied from 3-9 and adsorbent dosage varied from 1-10 g/L. The optimum conditions obtained after a detailed laboratory study are; contact time 60 min, pH 5, adsorbent dose 5 g/L and initial Cu (II) concentration 10 mg/L and the percentage removal of Cu(II) at these optimum conditions, using AC, SG, ASG and BSG were 98.5%, 88.9%, 96.9% and 94.8% respectively, from synthetic wastewater. It indicates that ASG has the almost same efficiency as commercially available AC has and ASG can be act like AC so that it used in industries to remove heavy metals from wastewater. This optimum condition was shown in Figure 4.
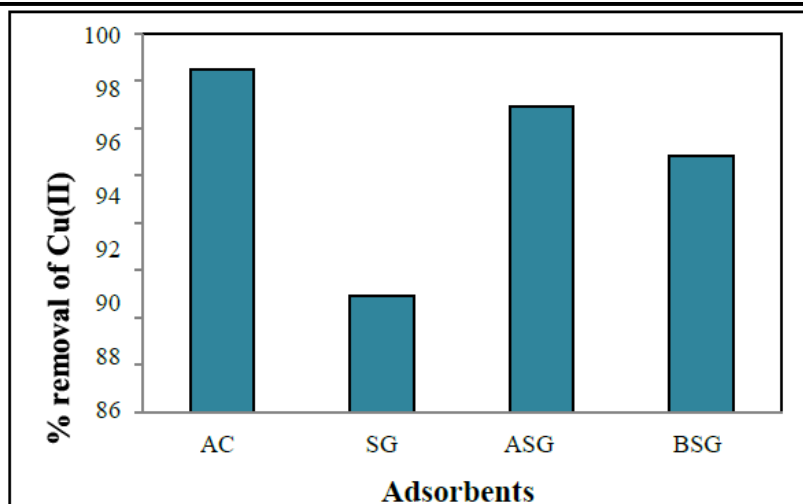
Figure 4 Cu(II) uptake capacities at optimum condition
(contact time-60min, adsorbent dose-5g/L, initial Cu(II) conc.-10mg/L, pH-5)

4.7 Adsorption Isotherms

An adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution (mass/volume) and its sorbed concentration (mass adsorbate/mass adsorbent) *(Sawyer et al., 2012).* Adsorption isotherms described by several mathematical relationships such as Langmuir, Freundlich and Tempkin models.

Langmuir isotherm was obtained from the linear expression of Langmuir equation as represented in Table 2.3. The values of q_{max} and b were computed from the slope and the intercept of Langmuir plot of C_e/q_e versus C_e as shown in Figure 4.8. The higher the b, the higher is the affinity of the adsorbent for metal ions, q_{max}, can also be interpreted as the total number of binding sites that are available for adsorption and q as the number of binding sites that are in fact occupied by the Cu(II) ions at the concentration C_e. According to the above data, the affinity order of adsorbents to adsorb Cu(II) are AC>ASG>SG. Langmuir isotherm represent the monolayer of Cu(II) ions are formed on adsorbent *(Kumar et al., 2011).*

4.8 Application to Textile waste water

The adsorption batch process for the real wastewater was done at the optimum conditions which were found in batch process of synthetic wastewater. The optimum conditions were pH-5, contact time-60min and the adsorbent dose-5g/L. The removal efficiency of Cu(II) ion was 83.45%, 62.53%, 81.40% and 71.77% using AC, SG, ASG and BSG respectively in real wastewater. It also indicates that the acid treated sugarcane bagasse (ASG) has almost same efficiency as the activated carbon (AC) has. So the ASG may be treated and used like AC in the industries to removal of heavy metal.

Table 4.5 Removal of Cu(II) from Textile wastewater

Adsorbent	Initial Cu(II) Conc. (mg/L)	Final Cu(II) Conc.(mg/L)	Percentage removal (%)
AC		8.73	83.45
SG	52.4	19.76	62.53
ASG		9.81	81.40
BSG		14.89	71.77
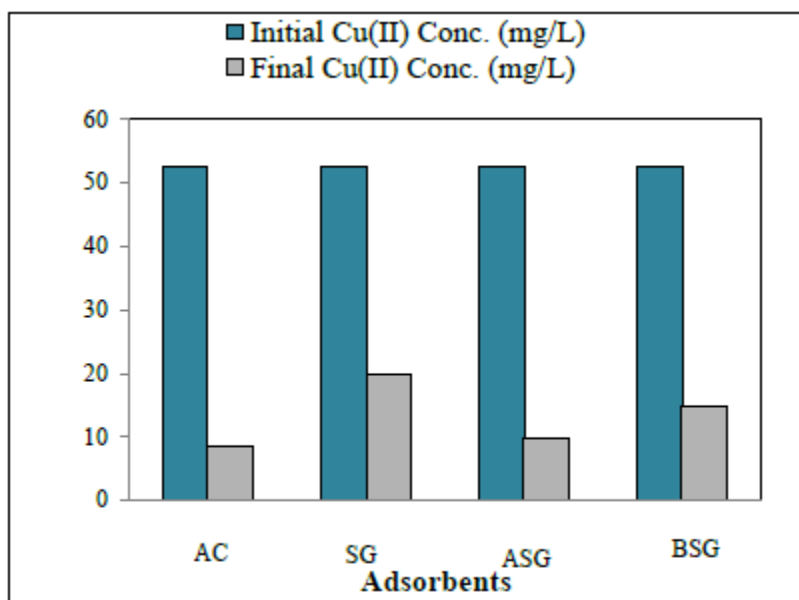
Figure 4.14 Cu(II) concentration before and after adsorption in Textile wastewater

V. CONCLUSION

- In this study, the efficiency of using sugarcane bagasse as an adsorbent and as a substitution to activated carbon has been studied. Also the comparison between activated carbon and sugarcane bagasse treated with citric acid and sodium hydroxide has been made to remove Cu(II) from synthetic wastewater and chemical industry wastewater. Additionally, response surface methodology was used to investigate the interactive effect of the operating parameters. Based on the data from the present investigation, the following conclusions are made:

- Low cost adsorbents prepared from locally available sugarcane bagasse pith and modified with citric acid and sodium hydroxide, can be successfully used to treat industrial wastewater.

- The surfaces of the adsorbents were complex due to the presence of several functional groups. Some functional groups such as –OH, -CH and –CO which are responsible for cation binding were found on the surfaces of all the adsorbents. In SG and BSG carboxyl group (-COOH) and in ASG carboxylate group (-COOR) was found. This showed that carboxylate groups were developed when acid treatment of sugarcane bagasse was given, so that removal efficiency of Cu(II) was increase by using ASG as adsorbent. It also seen that after treatment with sodium hydroxide or citric acid, adsorbent had more irregular and porous structure than that of without treatment, and therefore more specific surface area developed which was responsible for high Cu(II) ion intake.

- Batch studies on removal of Cu(II) from synthetic wastewater showed significant effects of the parameters i.e. adsorbent dose, contact time, initial Cu(II) concentration and pH. The results provide a good indication of the different operating conditions that would be required for efficient removal of heavy metal. The optimum conditions found from this batch study at constant 150-160 rpm were contact time 60min, adsorbent dose 5g/L, initial Cu(II) ion concentration 10mg/L and pH 5. The maximum removal efficiency for Cu(II) using AC, SG, ASG and BSG were 98.5%, 88.9%, 96.9% and 94.8% respectively at optimum condition. This indicated that ASG can be act like AC and can be used in industries instead of AC to treat wastewater.

- Langmuir, Freundlich and Temkin isotherms were observed to fit the equilibrium data and model parameters were calculated using linearized equations. Langmuir isotherm model is in good agreement with the experimental data for AC, SG and ASG as compared to Freundlich and Temkin models and Freundlich model is good for BSG. This represent that monolayer of Cu(II) ion formed at the AC, SG and ASG and heterogeneous adsorption occurred in BSG.

- In the textilel industry wastewater, the percentage removal of Cu(II) is decreased by the presence of other co-ions (Na+, Mg+, Ca+2, Fe+2). The removal efficiency of Cu(II) ion was 83.45%, 62.53%, 81.40% and 71.77% using AC, SG, ASG and BSG respectively in real wastewater

VI. REFERENCES

1. Annadurai G., Juang R.S. and Lee D.J., 2002, Adsorption of heavy metals from water using banana and orange peels, Water Science and Technology, 47 (1), 185–190

2. Aman T., Kazi A. A., Sabri M. U. and Bano Q., 2008, Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent, Colloids and Surfaces B: Biointerfaes 63, 116-121.

3. Ashkenazy R., Gottlieb L. and Yannai S., 1996, Characterization of Acetone-Washed Yeast Biomass Functional Groups Involved in Lead Biosorption, Biotecnology and Bioengineering, 55 (1), 1-10.

4. Banerjee K., Ramesh S.T., Gandhimathi R., Nidheesh P.V. and Bharathi K.S., 2012, A Novel Agricultural Waste Adsorbent, Watermelon Shell for the Removal of Copper from Aqueous Solutions, Iranica Journal of Energy & Environment, 3 (2),143-156.

5. Barakat M.A., 2010, New trends in removing heavy metals from industrial wastewater, Arabian Journal of Chemistry, 4, 361–377.

6. Bernard E., Jimoh A. and Odigure J.O., 2013, Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell, Research Journal of Chemical Sciences, 3(8), 3-9.

7. Boota R., Bhatti H. N. and Hanif M. A., 2009 Removal of Cu(II) and Zn(II) Using Lignocellulosic Fiber Derived from Citrus reticulate (Kinnow) Waste Biomass, Separation Science and Technology, 44:16, 4000-4022.

8. Castro R. S. D., Caetano L., Ferreira G., Padilha P. M., Saeki M. J., Zara L. F., Martines M.

9. A.U. and Castro G. R., 2011, Banana Peel Applied to the Solid Phase Extraction of Copper and Lead from River Water: Preconcentration of Metal Ions with a Fruit Waste, Industrial and Engineering Chemistry Research, 50, 3446–3451.