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SEM, FTIR and XRD Studies for the Removal Of Cu(II) from Aqueous Solution Using Marine Green Algae

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ABSTRACT

In this present investigation, activated carbons prepared from marine green algae Ulva fasciata (CCUC, SCUC and SSUC) were utilized as the adsorbents for the removal of Cu(II) ions from aqueous solution. Batch adsorption method was employed to optimize the process parameter. The surface morphology, chemical functional groups and crystalline nature of the carbon absorbents were studied by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD) respectively. The FTIR results show that the different functional groups such as hydroxyl, carbonyl, ether, alcohol, phosphate anion, cyanide and sulphate etc. were responsible for the adsorption process. And the XRD analysis indicates crystalline nature of adsorbents.

KEYWORDS : FTIR, Morphology, Ulva fasciata, Absorbents, Hydroxyl

INTRODUCTION

Water pollution by heavy metals remains as an important environmental issue in water. The import of heavy metals associated negatively with health and ecosystem [1]. Several industrial processes generate metal containing wastes. Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment. Copper, Nickel, Mercury, lead, Zinc, Arsenic etc. are such toxic metals which are being widely used. They are generated by dental operation, electroplating, tanning, textile, paper and pulp industry and are potentially toxic to humans [2]. Copper at high concentrations is toxic to living organisms from humans to bacteria, and is especially toxic to fish [3].

Traditional technologies for heavy metal removal, including ionic exchange and precipitation, are frequently inefficient and or expensive when applied for removal of metal ions in low concentrations. New technologies with acceptable costs are necessary to reduce the concentration of heavy metals in the environment to acceptable levels [4, 5]. Adsorption is a well-established technique for heavy metal removal and activated carbon is the most widely used adsorbent. However, the use of activated carbon can be expensive and there has been considerable interest in the use of other adsorbent materials, particularly biosorbents [6, 7]. A factor that has stimulated research of new biosorbent materials from seaweed alga biomass is their great availability.

Although thousands of seaweed species have been identified during the last 200 years, few have been investigated to determine their relative ability to take up toxic metal ions [8].The main purpose of present research work is the removal of copper ions by adsorption method from aqueous media using green marine algae *Ulva fasciata* activated carbons. Also to investigate surface morphology, chemical functional groups and nature of the carbon absorbents by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD) respectively.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbent

The green marine algae *Ulva fasciata* in the present study were collected from the coastal area of Kanyakumari district, Tamil Nadu, India. The collected algae were washed with tap water and deionized water several times to remove impurities. The washed algae were then completely dried in sun light for seven days. Then the dried algae *Ulva fasciata* were pretreated with Calcium Chloride, Sodium Sulphate and Sodium Carbonate salts respectively. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400°C powdered well and finally thermally activated at 800°C for 10 minutes [9]. The carbons are further known as Calcium Chloride treated *Ulva fasciata* Carbon (CCUC), Sodium Sulphate Treated *Ulva fasciata* Carbon (SSUC) and Sodium Carbonate treated *Ulva fasciata*Carbon (SCUC).

2.2. Preparation of metal ion solution

Stock solution of copper concentration 1000 mg/L was prepared by dissolving 3.93g of 100% $CuSO4.5H2O$ (Merck) in 1000 ml of DD water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 10 to 80 mg/L and they were prepared by diluting the copper stock solutions, which were obtained by dissolving in deionized water.

2.3. Batch Adsorption Studies

Batch adsorption equilibrium experiments were conducted for the adsorption of copper on activated carbons of *Ulva fasciata* as a function of initial pH, contact time and adsorbent dose by adding 0.2 g of carbon to 100 mL of copper solution with different concentrations in 250 mL stoppered reagent bottles at a constant shaking speed (250 rpm). All the experiments were carried out at room temperature. The concentrations of copper metal ions in solution before and after adsorption were determined using atomic adsorption spectrophotometer by monitoring the absorbance for the metal ion used.

During the adsorption, a rapid equilibrium was established between adsorbed metal ions on the active cites of adsorbent (q_e) and unadsorbed metal ion in the solution. The amount of adsorption at equilibrium (q_e) (mg/g) and the percentage adsorption (%) were computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{X}$$

$$\%\ \text{of adsorption} = \frac{(C_0 - C_e)}{C_0}\text{X}100$$

Where C0 and C_e are represented the initial and equilibrium concentrations (mg/L), V is the volume of solution and X the weight of adsorbent (g).

3. RESULTS AND DISCUSSION

In order to find out optimum pH, contact time and adsorbent dose the batch adsorption experiments were carried out as follows:

3.1 Effect of pH

The effect of hydrogen ion concentration was examined from solutions at different pH levels covering a range of 1.0–10.0 with 100 mL of Cu (II) concentration 20 mg/L containing 0.2g activated carbon. The optimum pH values are shown in Table-1.

3.2. Effect of contact time

The optimum contact time on the adsorption efficiency of Cu (II) the on activated carbons of *Ulva fasciata* is shown in Table- 1. The experiments were carried out using 100 mL of Cu(II) concentration 20 mg/L containing 0.2g activated carbon at pH 5. A set of solutions containing these carbons were equilibrated for varying periods ranging from 30 to 300 minutes at an agitation speed 250 rpm.

3.3. Effect of adsorbent dose

The dependence of Copper adsorption on the amount of carbon adsorbent was studied by varying the adsorbent amount from 0.05g to 0.4 g at optimum pH for CCUC, SCUC and SSUC. The experiments were carried out using 100 mL of Cu(II) concentration 20 mg/L, contact time (2h) and agitation speed (250rpm).

Table-1. Different parameters and the optimum values of Cu (II) ions removal

Adsorbent	pH	Time	Dose	% Removal
CCUC	5	1h	0.15g	88.47
SSUC	5	1h	0.15g	97.53
SCUC	5	1h	0.15g	95.78

3.4. Scanning Electron Micrograph Analysis for the adsorption of Cu(II)

SEM analysis also studied for the adsorption of Cu(II) ions on the surfaces of the adsorbent carbons. The SEM images of CCUC, SSUC and SCUC after adsorption of Cu(II) are shown in Figs.1,2 and 3 respectively. The micrographs of all these carbon adsorbents show that formation of white layers on the surface, which may be due to adsorption of Cu(II) ions. From the SEM micrograph analysis of carbon adsorbents (CCUC, SSUC, SCUC and CAC) after the adsorption of Cu(II) it is observed that most of the pores in the adsorbents were covered by carbon adsorbents. It could be also seen that more uneven and rough surface morphology exist in Cu(II) loaded adsorbents. Difference in the adsorption capacity of these adsorbents was mainly due to difference in their surface porosity.

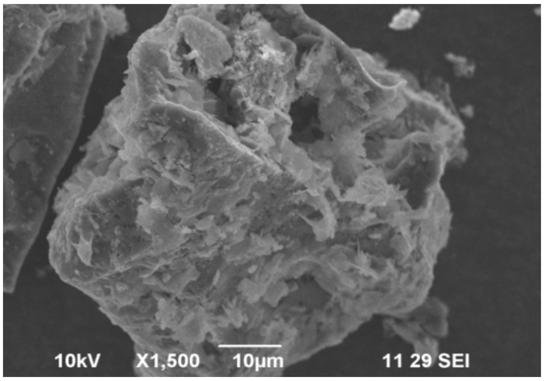

Fig.1. Scanning micrograph of CCUC after Copper(II) adsorption.

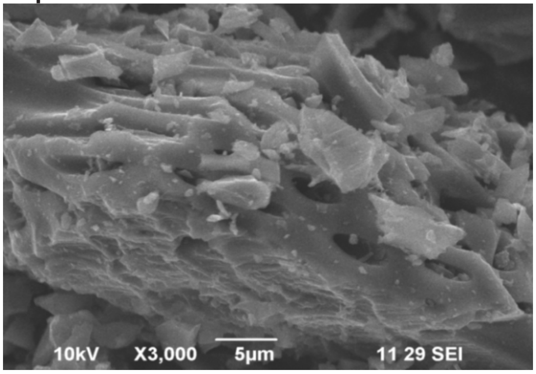

Fig.2. Scanning micrograph of SSUC after Copper(II) adsorption.

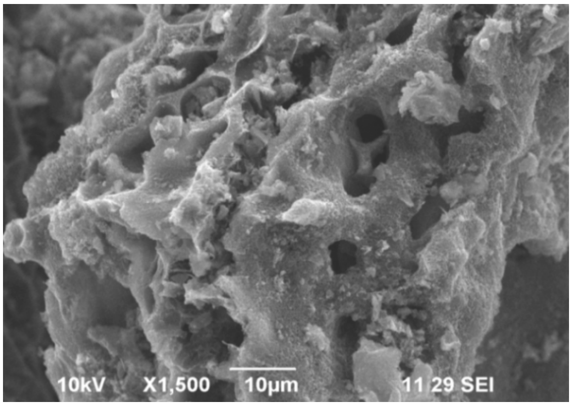

Fig.3. Scanning micrograph of SCUC after Copper(II) adsorption.

3.5. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) study was carried out to identify the functional groups present in the adsorbents in the 4000-400 cm^{-1} range. The adsorption capacity of adsorbent depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface [10]. Table-2 represented the shift in the wavenumber of dominant peak associated with the plots by comparing between the carbon adsorbents and Cu(II) loaded adsorbents (Figs. 4 - 9). These shifts in the wavelength showed that there was metal binding process taking place at the surface of the adsorbents [11,12]. There were clear shifts from wavenumber 3456 cm^{-1} (CCUC) to 3483 cm^{-1} (copper loaded CCUC), 3464 cm^{-1} (SSUC) to 3426 cm^{-1} (copper loaded SSUC) and 3426cm^{-1} (SCUC) to 3426.4cm^{-1} (copper loaded SCUC) which indicated surface -OH group was one of the functional group responsible for adsorption [14]. The FTIR spectrum also showed intense bands around 2355 cm^{-1} (CCUC) which shifted to 2369 cm^{-1} (Cu(II) loaded CCUC), 2357 cm^{-1} (SSUC) which has shifted to 2345 cm^{-1} (Cu(II) loaded SSUC) and 2359 cm^{-1} (SCUC) which shifted to 2359 cm^{-1} (Cu(II) loaded SCUC). This was attributed that the cyanide ions were responsible for the adsorption of Cu(II) on the carbon adsorbents. The shifting and broadening of the bands located at 620-720 cm^{-1} was due to the loading effect of metal. These broadenings can be explained by the involvement of sulphate ion [13].

Also the bands at 1618 cm^{-1}, 1460 cm^{-1} and 1482 cm^{-1} (CCUC, SSUC and SCUC) became broadening and stretching indicates an interaction between Cu(II) and C=O groups on the surface of the carbon adsorbents [14].The broadening and stretching of the bands at CCUC (883 cm^{-1}), SSUC (862 cm^{-1}) and SCUC (830 cm^{-1}) were totally disappeared after adsorption of Cu(II) which showed that phosphate group was strongly involved in the adsorption process. Table-2 also indicated that the minor shift for the other band (C-O stretching of ether and alcohol, OH of alcohols and phenols) which showed that these groups were not involved in the adsorption process. The Cu(II) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups.

3.6. X-ray diffraction analysis for the adsorption of Cu(II)

X-ray Diffraction (XRD) analysis was carried out by using Siefert Model SF 60 XRD system with Cu-Kα radiation. The XRD patterns for CCUC, SSUC and SCUC before and after adsorption of Cu(II) ions are shown in Figs.10, 11 and 12 respectively. Sharp intensity XRD peaks have been observed at typical scanning angles of 2θ = 20 - 600 for Ulva fasciata carbons before Cu(II) adsorption. The Sharp peaks present in the figures indicated the crystalline nature of the material. In addition, several other low intensity peaks corresponding to other crystalline phases of carbons have also been observed. After adsorption of Cu(II) ions, the porous structures of the carbon adsorbents decreased. These causes low intensity XRD peaks. Hence crystalline phases should have been reduced.

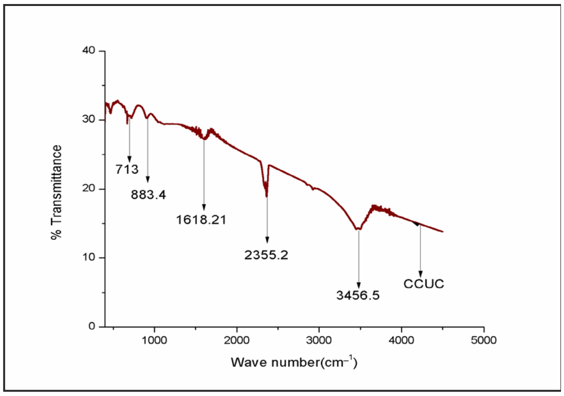

Fig.4. FTIR spectrum of CCUC

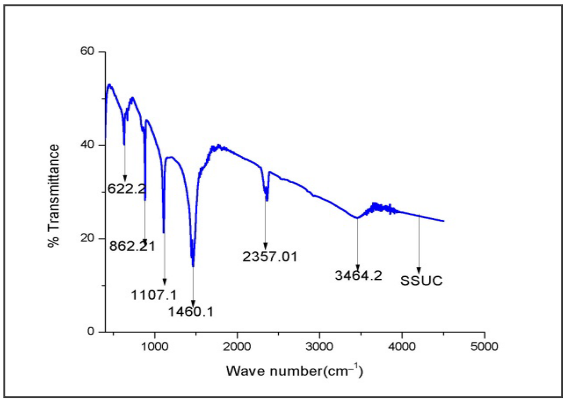

Fig.5. FTIR spectrum of SSUC

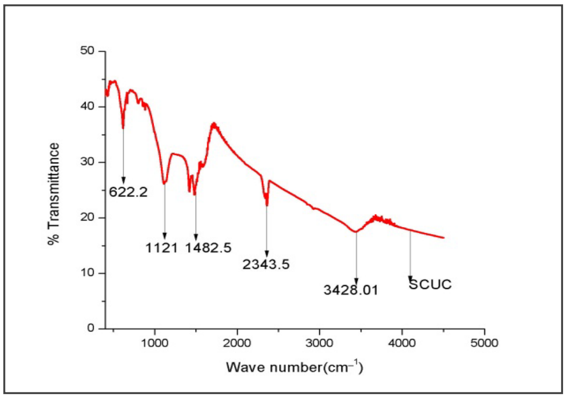

Fig.6. FTIR spectrum of SCUC

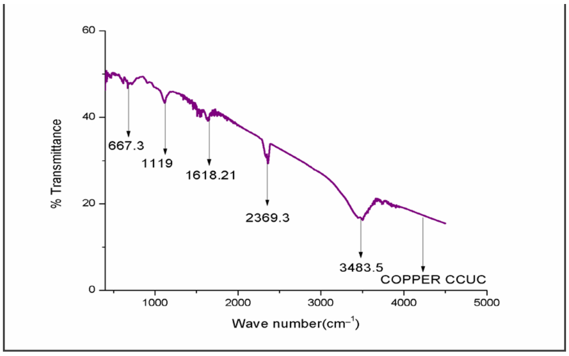

Fig.7. FTIR spectrum of CCUC after Cu (II) adsorption.

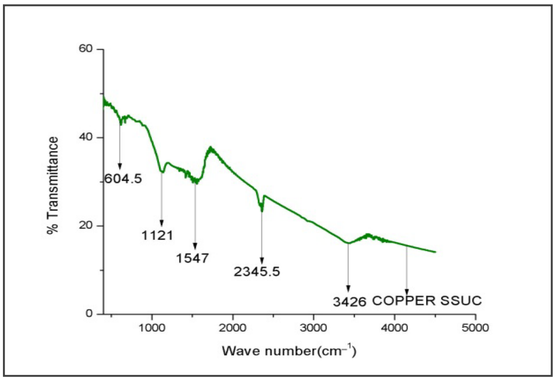

Fig.8. FTIR spectrum of SSUC after Cu(II) adsorption.

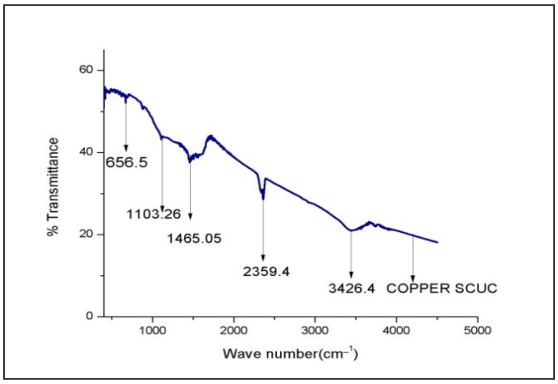

Fig.9. FTIR spectrum of SCUC after Cu (II)

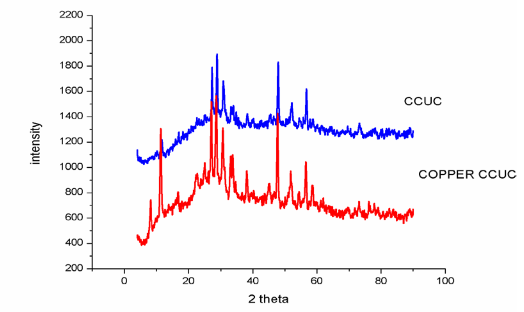

Fig.10. XRD image for CCUC and CCUC after Copper (II) adsorption

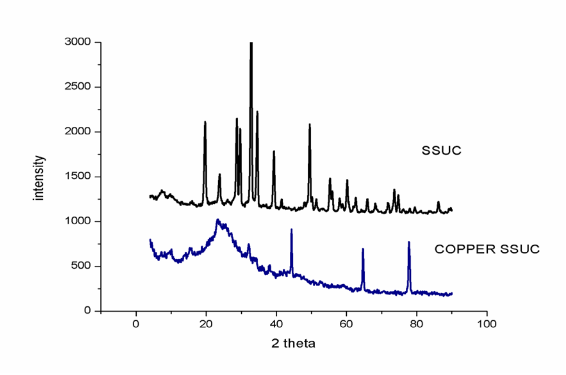

Fig.11. XRD image for SSUC and SSUC after Copper(II) adsorption

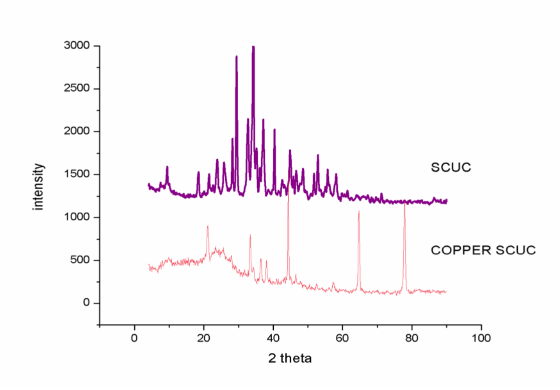

Fig.12. XRD image for SCUC and SCUC after Copper (II) adsorption.

4. CONCLUSION

The activated carbons made from marine green algae *Ulva fasciata* were used as adsorbents for the removal of Cu(II) ions from the water solution. Batch adsorption method was employed to optimize the process parameters of pH, contact time and adsorbent dosage. The SEM analysis shows that the Cu(II) ions adsorbed in the pores of carbon adsorbents, FTIR results show that the different functional groups such as surface hydroxyl, carbonyl, ether, alcohol, phosphate anion and sulphonate etc were responsible for the adsorption process.The XRD analysis of adsorbents and loaded with Cu(II) ions shows that crystalline nature of activated carbons

Table -2. FTIR study for Cu(II) adsorption FTIR peaks and group assignment

Functional groups assigned	Wave number of precursor carbon adsorbents			Wave number of carbons after loaded with Cu(II)		
	CCUC	SSUC	SCUC	CCUC	SSUC	SCUC
OH of alcohols and phenols	3650	3654	3651	3652	3655	3652
O-H and NH groups	3456	3464	3428	3483	3426	3426
Cyanide ion (CN)	2355	2357	2343	2369	2345	2359
C-O groups of carbonyls, carboxylic acids	1618	1460	1482	1618	1547	1465
C-O stretching of ether and alcohol	1121	1122	1121	1119	1121	1103
Aromatic phosphate (P-O-C stretch)	883	862	830	-	-	-
Sulphate group	713	622	622	667	604	656

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