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Column mode removal of copper through physically entrapped algal bioadsorbents

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A polyurethane column with physically entrapped algal materials has been designed and tested for copper removal from aqueous medium. The performance of the column is assessed on the basis of the parameters viz. bio-removal efficiency, metal sequestered in the column and bio-sorption capacity. The findings show that the combination of calcium alginate and *S. platensis* exhibit highest bio-removal efficiency (38.42%) for Cu(II) in the concentration range 5-20 mg L^{-1}. The maximum bio-sorption capacity (80.30 mg/g) is recorded for a mixture of calcium alginate and *S. platensis* after 60 min treatment time. FTIR analysis of algal adsorbents show that the adsorption efficiency depended on the availability of negatively charged groups such as carboxylic and hydroxyl groups. The study concluded that the algal compounds and dried biomass of *S. platensis* are effective bio-adsorbents for the removal of Cu(II) from water.

Keywords: Algal adsorbent, Copper bio-sorption, Physical entrapment, Polyurethane column

Column bed sorption of heavy metal ions is a novel approach for removal of heavy metals from water[1,2]. The conventional methods like oxidation, filtration, electrochemical precipitation and coagulation-flocculation do not provide an efficient and cost effective solution for heavy metal removal. Therefore, column mode adsorption processes are considered as a preferred method for removal of heavy metals. In contrast to batch mode processes, where the adsorbent is added to the metal solution for the sequestration of heavy metal ions, the column mode removal mainly depends upon the creation of a larger surface/volume ratio of adsorbents by forming a uniformly thin layer in the interstitial space in the matrix. This curtails the quantity of bioadsorbents required to a considerable extent, and makes desorption of heavy metals and regeneration of column material less cumbersome. In view of the above, there is a growing interest among scientists to explore the novel technologies for low cost column bed based treatment processes for heavy metal remediation[3,4].

Copper contamination in water is of great environmental concern due to its toxic effects on important aquatic species. Enormous quantity of copper enters aquatic ecosystems through the discharge of copper containing effluents[5,6] and unregulated use of copper sulphate as a weedicide.

Biosorption by dead biomass is a passive process, mainly based on the affinity between the sorbent and sorbate[7]. Algae as biosorbent are gaining importance because of the presence of various types of metal binding groups (hydroxyl, carboxyl, sulphhydril, thioletc.) in the algal biomass. These groups enable the biomass of these organisms to sequester the heavy metals and metalloids effectively[8]. Earlier reports have confirmed that biomass of algae entrapped in a suitable matrix has a greater efficiency for heavy metal removal than suspended biosorbents. Entrapment of biomass in a matrix such as polyurethane, polyvinyl or polyacrylamide gel(PAG) has following advantages over suspended biosorbents (i) the particle size of the bio-sorbents can be effectively controlled (ii) biomass can be easily separated from the effluent after the treatment cycles (iii) the possibility of clogging under continuous flow conditions is minimized. In addition to above, the easy method of biosorption-desorption makes the column based bio-sorption process more cost-effective than batch mode treatments.

In the present investigation, the selection of algal compounds was based upon the earlier reports[9]. However, in contrast to calcium alginate which is the most commonly used algal compound for immobilization of algae, the reports on the use of alginic acid and agar-agar are very few. Therefore, an attempt was made to assess the bio-sorption capacity of Alginic acid along with dehydrated biomass of *S. platensis.*

In the light of the above, present study aimed to provide base-line information about the potentialities of the entrapped algal compounds viz. alginic acid – a mixed polymer of mannuronic acid and glucuronic acid; calcium alginate - a calcium salt of alginic acid;

agar-agar- a complex algal polysaccharide and dried *S. platensis* powder for bio-sorption of Cu(II) in column mode using polyurethane as an entrapment matrix. The finding of this investigation will be useful in developing cost-effective technology for heavy metal removal.

Experimental Section

Biomass production of *Spirulina(Arthrospira) platensis*

Mother culture of the cyanobacterium *S. platensis* was obtained from Algal laboratory of Central Institute of Fisheries Education (CIFE), Mumbai. The organism was sub-cultured and maintained in Zarouk's medium[10] under photoautotrophic conditions. Upscaling of biomass production was carried out in an outdoor aerated FRP tank of 1000 L. The medium used for outdoor cultivation was NRC (Nallayam Research Centre) medium modified by replacing urea and phosphoric acid with KNO_3 and K_2HPO_4. Purity of the biomass was checked by inoculating 0.1 mL of algal slurry on nutrient agar bacterial medium (Hi-media, India). The biomass not showing any bacterial colonies on nutrient agar was used for entrapment in the column matrix.

Designing and preparation of fixed-bed column filtration unit

Locally available low density PU foam was purchased for the preparation of polyurethane foam discs. The discs used for the experiment were prepared by pre-washing the PU foam in sterilized distilled water followed by drying. The detailed schematic design of the unit (Fig. 1) and the process of entrapment of algal adsorbents are described elsewhere by Ranjith *et al.* (2011)[9].

Column bed adsorption experiment

The adsorption study was carried out for initial concentrations of Cu(II) viz. 5, 10, 15 and 20 mg L^{-1}. Duration of the experiment was 1 h and water samples were collected in triplicates in polypropylene bottles at every 15 min after passing through the column. The fixed flow rate was 65 ± 2 mL per min.

Digestion and analysis

Water samples were digested using microwave based closed vessel (Anton Parr, USA). Cu(II) was analyzed by atomic absorption spectrophotometer (AAnalyst 800, Perkin-Elmer, USA) using flame atomization. The results are expressed in terms of mg $L^{-1}$and the variation within the values of triplicate samples was less than 5%.

Bioremoval efficiency

The bioremoval efficiency, *R* (%) at 30 min and 60 min interval was calculated by the formula given below;

$$R=\frac{(C_0-C_e)}{C_0}\times 100$$

where, C_0 and C_e were the concentrations (mg L^{-1}) of the metal before and after treatment.

Metal adsorbed in the column

The metal adsorbed in the column (m_b) was calculated by the following formula given by Zhang and Banks (2006)[11].

$$m_b=\sum[(C_0-C_i)\times V_i]$$

where, C_0 is the initial metal concentration (mg L^{-1}), C_i is the metal concentration (mg L^{-1}) of the i^{th} fraction and V_i is the volume (L) of i^{th} fraction.

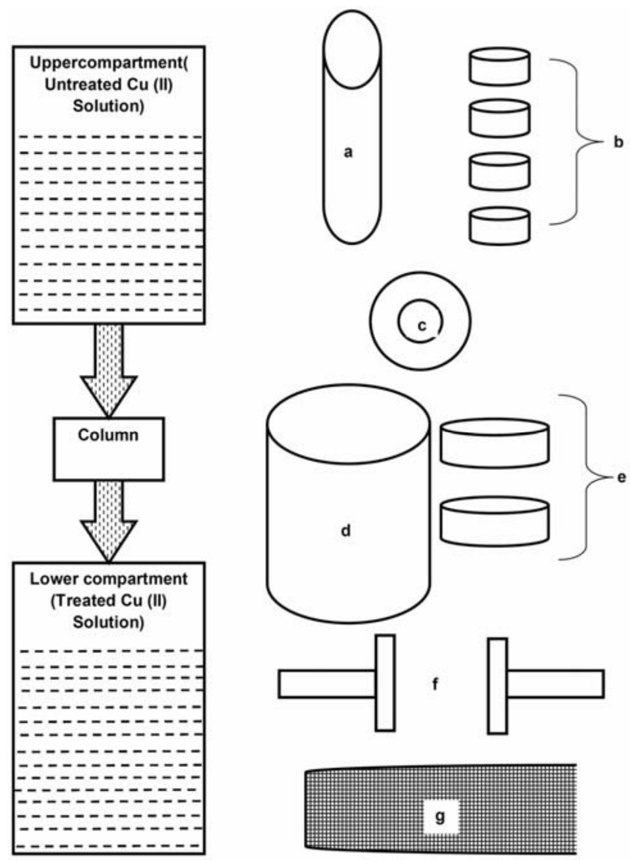

Fig. 1 — Schematic and Blown-up view of filtration unit: (a) Column I, (b) Column I discs, (c) Column I holder, (d) Column II, (e) Column II discs, (f) Column II holder, (g) Nylon mesh(10 µ) (A-Alginic acid, AA-Agar agar, CA-Calcium alginate, SP-*Spirulina* powder)

Biosorption capacity

The biosorption capacity (mg/g) was calculated by the following formula (Zhang and Banks, 2006)[11]

$$\text{Biosorption capacity} = \frac{m_b}{M}$$

where, m_b is the quantity of metal adsorbed in the column (mg), and M is the mass of bioadsorbent in the column (g).

Fourier Transform Infrared Spectroscopy (FTIR) of algal adsorbents

In order to identify the functional groups present in the algal materials, FT-IR analysis was performed. 50 mg of algal adsorbent sample of the algal material was mixed with KBr to form a pellet (Diameter: 5 mm). The pellet was kept on a sample holder and scanned in the range 500 cm^{-1} to 4000 cm^{-1} wave numbers using FT-IR spectrometer (Perkin-Elmer- Spectrum BX).

Results and Discussion

Bioremoval efficiency

The observations recorded on percent removal of Cu(II) at different initial concentrations (5-20 mg L^{-1}) suggest that the magnitude of removal of Cu(II) varied with initial concentration of Cu(II) . Agar-agar showed best removal (23.75%) at the lowest concentration 95 mg L^{-1}). However, this compound showed less than 5% removal at higher concentrations (10-20 mg L^{-1}) after 30 min of treatment. The combination of calcium alginate and *S. platensis* was best among all the bio-sorbents tested, which exhibited 32.7% bio-removal efficiency at 15 mg L^{-1} concentration of Cu (II) after 30 min treatment time (Fig. 2). The combination of calcium alginate and *S. platensis* exhibited 38.4% removal after 60 min of treatment at 15 mg L^{-1} concentration of Cu(II) which was the highest value recorded during the study. In general, the bio-removal efficiency of the above biomaterials ranged between 8 to 38% after 60 min exposure (Fig. 2). The variation in removal efficiencies of different combinations of algal materials can be attributed to the differences in the constituent functional groups (discussed in detail in later part) of the algal compounds and their ability to bind with each other, and also upon the firmness of the binding with the polyurethane matrix.

Quantity of Cu(II) adsorbed in the column bed reactor at different initial concentrations

A time course study on the amount of Cu(II) adsorbed in the column during different time periods i.e. 0-15, 15-30, 30-45 and 45-60 min indicated that the quantity of Cu(II) adsorbed in the column varied

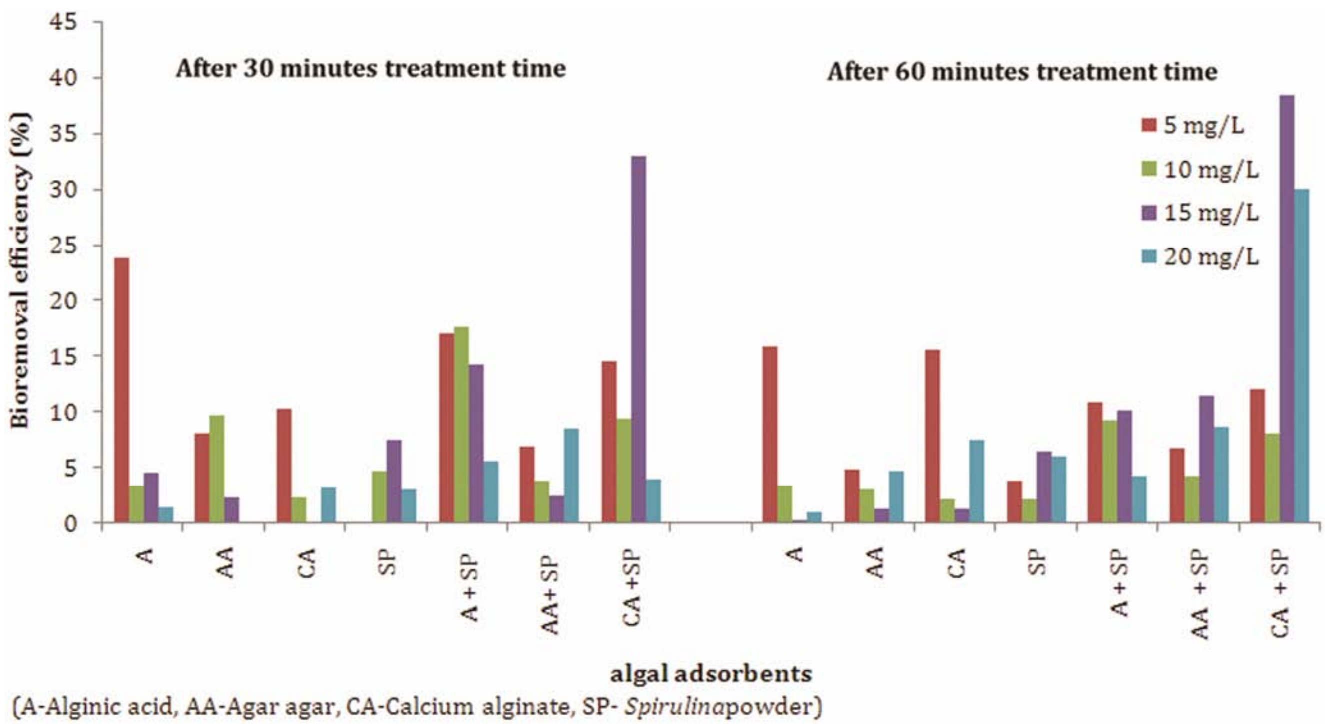

Fig. 2 — Effect of initial concentrations (5 to 20 mg/L) of Cu (II) on bioremoval efficiency (after 30 and 60 min treatment time) (A-Alginic acid, AA-Agar agar, CA-Calcium alginate, SP- *Spirulina* powder).

with the change in initial concentration of Cu(II) and the type of bio-sorbent used for the column preparation. Highest adsorption (1.03 mg Cu II) was observed in case of agar-agar during 15-30 min (Fig. 3).

Among all the bio-sorbents, highest adsorption was observed in agar-agar and *Spirulina* combination after15 min treatment time 2.14 mg Cu(II)/gram biomass which was followed by calcium alginate (15-30 min), and calcium alginate and *S. platensis* combination during 45-60 min (Fig. 3).

The observations reveal that calcium alginate and *S. platensis* combination had highest adsorption capacity (5.28 mg Cu II) which is followed by alginic acid and *S. platensis* combination during all the time courses except in 0 to 15 min (Fig. 3).

During 45 to 60 min, calcium alginate and *S. platensis* biomass combination showed highest adsorption capacity (4.86 mg Cu II), similar trend was observed during 45 to 60 min for calcium alginate and *S. platensis* biomass (Fig. 3).

The overall observation on adsorption of Cu(II) ions by different adsorbents at various time intervals suggest that for 5 and 10 mg L^{-1}initial concentrations, agar-agar, and a combination of agar-agar and *S. platensis* were better than other adsorbents. At 15 mg L^{-1}initial concentration, calcium alginate and *S. platensis* combination, and alginic acid and *S. platensis* combinations were most effective in metal removal. A combination of Calcium alginate and *S. platensis* showed best removal at 20 mg L^{-1} initial concentration.

Biosorption capacity

It was evident from the results presented in Fig. 4 that the bio-sorption capacity of the biomaterials used in present study varied from 1.3 to 143.4 mg/g at 5 to 20 mg L^{-1} Cu(II) for initial concentrations 5 to 20 mg L^{-1}. The highest value (143.4 mg/g) was recorded for agar-agar and *S. platensis* biomass combination. The combination of calcium alginate and *S. platensis* biomass showed a lower bio-sorption

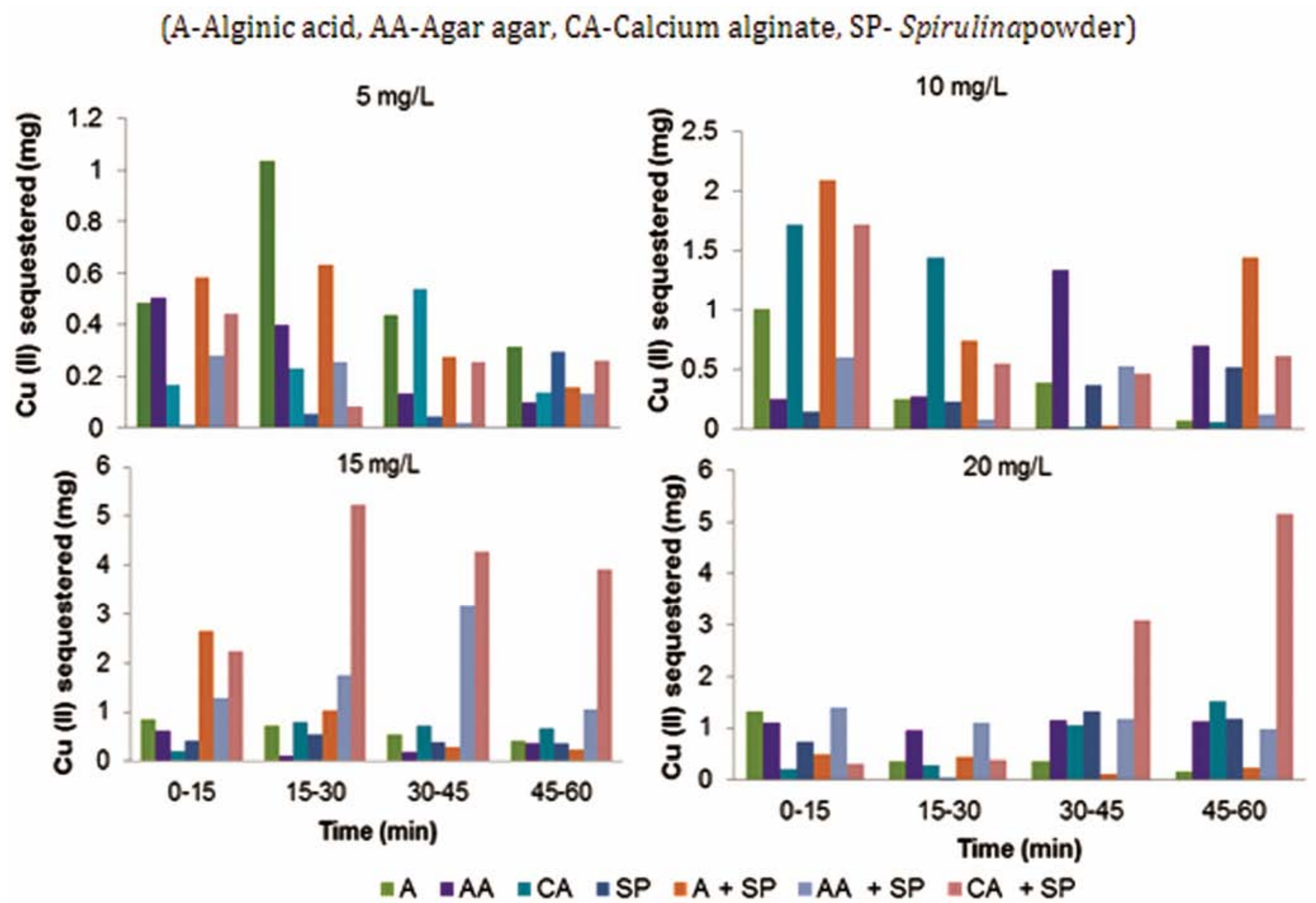

Fig. 3 — Quantity of Cu (II) sequestered by various algal adsorbents in the column bed reactor for 60 min treatment time at different concentration of Cu (II). (A-Alginic acid, AA-Agar agar, CA-Calcium alginate, SP- *Spirulina* powder).

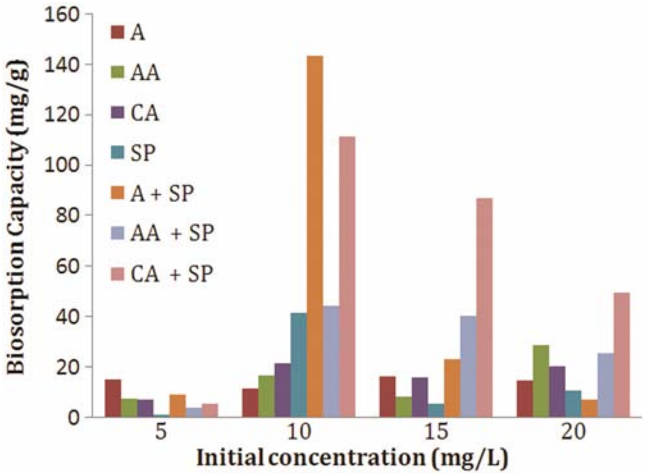

Fig. 4 — Biosorption capacity of various adsorbents at different initial concentrations of Cu (II) after 60 min treatment time.

capacity (112 mg/g) at 10 mg L^{-1}concentration. Among all the bio-sorbents, *S. platensis* biomass showed minimum bio-sorption capacity (1.3 mg/g) recorded at 5 mg L^{-1}initial concentration.

The combination of agar-agar and *S. platensis* biomass showed 15-fold increase in the bio-sorption capacity at 15 mg L^{-1}concentration. The observations indicate that the combination of calcium alginate and *S. platensis* biomas exhibited highest bio-sorption capacity at all the concentrations of Cu(II) except 5 mg L^{-1} (Fig. 4).

The column bed reactor designed in the present investigation was constructed with low cost materials such as polyurethane, PVC pipes, nylon cloth and the average cost of the unit for a flow rate of (4 liter/hour) was Rs 500-600 Indian Rupees (US $ 10-12). Thus, it is suggested that PU loaded with appropriate quantity of algal compounds and *S. platensis* biomass can be produced in a separate unit and supplied in the market at reasonable price. The dried *S. platensis* powder, available at a price of 400-600 Indian Rupees (US $ 9-11) per kg can be used for the column preparation as the cultivation of *S. platensis* involves heavy investment cost . Though, this will enhance the cost of construction of the filtration unit, but considering the small quantity of the algal compounds and *S. platensis* biomass required for column bed preparation, there will not be a considerable enhancement in the overall cost.

In the present study, only 38.42% bio-removal efficiency was obtained in the matrix made of calcium alginate and *S. platensis* biomass at initial concentration of 15 mg L^{-1} but Lau *et al*. (1998)[12] showed over 97% copper removal from wastewater at 30 mg L^{-1} initial concentration using *Chlorella vulgaris* entrapped in alginate beads. At 10 mg L^{-1} initial concentration, the bio-sorption capacity for *S. platensis* biomass alone was 41.9 mg/g, which is comparable to the value (45.4 ± 3.4 mg/g) as reported by Vannela and Verma (2006)[6] for the column prepared by *S. platensis* immobilized in polyacrylamide gel (PAG) cubes.

The data available from the literature pertains to higher initial concentrations of copper. In the present study, the column bed reactor showed an appreciable level of efficiency for the removal of Cu(II) at lower concentrations also. As the above concentration ranges are frequently found in many wastewater sources, the present study would help to develop cost-effective treatment of metal containing water to obtain good quality water for drinking and domestic purposes. There is also an immense potential for the up-scaling of the technology for wastewater treatment.

FTIR analysis of algal adsorbents

The FTIR spectrum confirms the presence of various functional groups capable of binding with heavy metal ions. Alginic acid showed absorption peaks at 2352.06, 2634.07 and 2927.37 cm^{-1}, they may be attributed to the presence of carboxylic groups in the compound. A band at 1740.20 cm^{-1} indicates the presence of aldehyde group (C=O). The absorption band at 3445.87 cm^{-1} wave number was also noticed in the FTIR spectrum of alginic acid which confirms the presence of alcohol/Phenol groups (0-H). Presence of aromatic functional groups was also evident from absorption bands at 714.20, 788.71 and 806.70 cm^{-1}. Calcium alginate also showed the presence of carboxylic group indicated by strong absorption at 2922.65 cm^{-1}. Other noteworthy functional groups detected in FTIR spectrum were alkynyl (C=C) and aromatic groups at 2136.10 and 1615.33 cm^{-1}, respectively. Secondary alcohol groups were noticed at 1031.81 cm^{-1}. *Spirulina* powder showed absorption at 3309.79 cm^{-1} which corresponds to presence of alcohol and phenol groups whereas the bands observed at 2960.08 and 2927.78 cm^{-1} in the FTIR spectrum confirm the presence of Carboxylic group in the biomass. Agar-agar showed the presence of amide and amine groups which was indicated by absorption at 1653.97 and 3447.90 cm^{-1}. Absorption bands at 2926.99 and 2152.48 cm^{-1} were also observed in the spectrum which correspond to

Table 1 — Major binding groups in algal adsorbents (A-Alginicacid, CA-Calcium alginate, AA-Agar agar, SP- *Spirulina* powder)

Binding group	Structural formula	Present (+)/Absent (-)			
		A	CA	AA	SP
Hydroxyl	-OH	+	+	-	-
Carbonyl	>C=O	+	+	+	+
Alkyl	C-H	+	+	+	-
Amide	-C=O	+	+	-	-
Amine	N-H	-	-	+	+
Ester	C=O	+	-	-	-
Aromatic	C=C, C-H, Variable	+	+	-	-

carboxylic and alkenyl groups. Presence of aromatic groups in agar-agar was indicated by the bands at 694.29, 715.69, 741.16 and 771.95 cm^{-1}. Major functional groups of their algal adsorbents are presented in Table 1.

The overall observations reveal that presence of carboxylic and alcohol groups in the compounds confer an ability to bind with copper ions, however, the efficiency to bind with copper ions mainly depends upon the abundance of negatively charged functional groups e.g. carboxylic and hydroxyl groups and other negatively charged groups in the algal adsorbents.

Conclusion

The results show that physical entrapment of algal compounds in polyurethane matrix is a novel and effective technology for the removal of copper ion from water. The distribution of algal compounds in the polyurethane matrix is an effective and low cost treatment method due to the reusability of the polyurethane material.

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