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Adsorptive Removal Of Cu(II) From Aqueous Solution By Using Newly Prepared Adsorbent from Agricultural Waste Material

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Abstract:
The main causes of different types of metal contamination in natural water are massive amounts of industrial waste. Many metals are indestructible and cannot be broken down. Cu(II) and several other toxic metals are significant. Various physiochemical approaches have been created for the elimination of metals from wastewater, as well as multiple ways have been implemented to recover and remove the metals from our environment. Adsorption is one of the option in these situations which is a very successful purification as well as separation method widely implemented in industry, particularly for treating water moreover wastewater. Raw form of graphite, which is utilized in lead pencils, is called activated carbon, often called as activated charcoal. Elimination of heavy metals along with dyes, among other contaminants, is a typical implementation of activated carbon. Adsorption rates of activated carbon from gas alongside liquid phases are high, as is its surface area moreover adsorptive capacity. From agricultural waste, activated charcoal has been created. The chitosan coating has altered the activated carbon's surface area. The results indicate that, in comparison to activated carbon, surface-modified activated carbon is the most effective in eliminating Cu(II). The investigation outcomes showed that, under ideal conditions, chitosan-coated activated carbon made from agricultural waste can remove up to 94% of copper. XRD ("X-ray diffraction"), thermogravimetric analysis, SEM ("scanning electron microscopy"), along with Fourier transform infrared (FTIR), had been employed for analyzing produced chitosan-coated activated carbon (CCACGM).

Keywords: Heavy Metals, Activated Carbon, Chitosan, Agricultural Waste, Adsorption.

1. INTRODUCTION:

Environment is defined as surroundings in which microbes, plants, animals, and humans exist or operate. It is made up of atmosphere, sea, and land. Four spheres that comprise Earth's system that encompass lithosphere (land), hydrosphere (water), atmosphere (air), and biosphere (living things), all these four work together harmoniously. Compounds that are more prevalent in the atmosphere than anywhere else are known as pollutants or contaminants of the environment [1,2]. The environment sustains life. Man must understand the value of the environment and do his part to maintain its health and productivity. To restore a sustainable ecosystem, environmentalists worldwide continually seek sustainable solutions [3].

In the last few decades, the rapid rise in industrial activity, urbanization, along with the widespread application of chemical compounds in numerous sectors has made the spread of heavy metal ions that have harmful characteristics, in water bodies a major worldwide issue. [4]. These chemicals carry a major danger to environmental preservation since they may have harmful and far-reaching impacts on species and

the natural environment [5,6]. Numerous dangerous heavy metal pollutants may be observed in wastewater effluents from manufacturing procedures, and the primary variables contributing to the rise in environmental toxicity are human and human-induced processes [7]. Numerous natural events, which might involve wind-driven soil erosion, forest fires, volcanic eruptions, biogenic processes, as well as discharge of sea salt, may naturally introduce heavy metals into the atmosphere [8]. Mining activities, the spraying of pesticides, fertilizers, alongside herbicides moreover irrigation of agricultural land along water that has not been treated and waste from factories, are all instances of anthropogenic pollution of the ecosystem by heavy metals [8,9]. Multiple human activities, which comprises the production of medications, the preservation of paper as well as pulp, the production of caustic soda alongside chlorine, and agricultural operations, can introduce mercury into the environment. Rocks, coal, soils, and mineral fertilizers are just a few of the geological components which contain cadmium, a distinct heavy metal. Additionally, it is widely employed in electroplating procedures for various applications, including the production of metal coatings, batteries, textiles, and pigments. The environment becomes more contaminated with heavy metals as a result of these activities [8,10].

Due to their cancer-causing effects, biological buildup, toxic effects, and non biodegradability, heavy metals carry an alarming risk to aquatic environments and health of humans [11]. In contrast to organic contaminants, heavy metals typically accumulate in living organisms rather than decompose when introduced into the atmosphere. The overall wellness of every living thing, encompassing humans, animals, as well as plants, could potentially be affected by this [7, 12, 13]. Hence, reducing detrimental impacts of heavy metals on ecosystem requires removing them from water.

For elimination of heavy metals from wastewater, different approaches have been established and employed, encompassing biological, chemical, and physical methods. After the initial treatment, additional methods are still needed to eliminate content of heavy metals to levels that are satisfactory. Physical methods, which encompass adsorption, membrane technology, and ion exchange [14-16]. Heavy metal ions have been eliminated using biological techniques like phytoremediation and biochar [19,20] as well as chemical techniques including electrokinetic technology, chemical precipitation, along with precipitation [17,18]. A semipermeable membrane has been employed in the membrane filtering process to extract impurities from water. Reverse osmosis and nanofiltration are two membrane filtration methods that have been employed in several investigations to eliminate heavy metals [21,22,23]. Electrochemical treatment, which employs an electrical current to initiate chemical processes, has been employed to flush out heavy metals from wastewater. Elimination of heavy metals has been accomplished by the use of electrochemical treatment techniques encompasses electrocoagulation, electrooxidation, and electroflotation [24,25]. It is crucial to remember that these approaches have some disadvantages. As an instance, membrane technology may be high-priced, specific chemical procedures yield huge volumes of sludge, as well as phytoremediation may require lot of time as well as close observation. Nonetheless, advantages of the natural ion-exchanger and adsorption technology are cheap cost, high efficiency, and the absence of sludge creation.

Conventional techniques that encompass electro-chemical treatment, chemical precipitation, filtration, oxidation/reduction, ion exchange, evaporative recovery, extraction, coagulation flocculation, phyto-extraction, ultra, as well as membrane technologies can remove excessive amounts of heavy metals from waste water, but they may inefficient or costly, particularly when metal ion concentrations in solution are between 1 and 100 mg/l [26,27]. Effectiveness, operating costs, and the creation of hazardous byproducts are key aspects that need to be considered when selecting best

approach.

Adsorption has been the most commonly employed and successful method for reducing heavy metals from wastewater past few decades [28-33]. Canes from some easy-growing wood species, nutshells, fruit shells, bagasse, coconut shell, coir pith, agricultural residues from sugarcane, rice, oil palm waste, peanuts, sawdust, as well as orange peel are among farming wastes that have become a better option. A significant amount of research has been done on their preparation [34-38]. The high concentration of pectin (galacturonic acid), hemicelluloses, cellulose, as well as lignins in biosorbent material makes it a promising material. Biosorbents are pretty inexpensive. Numerous research suggest that biosorption might be employed to eliminate heavy metals from wastewater [38].

2. MATERIALS & METHODS

2.1 Chemicals

Substances that are of analytical-grade were employed in this research work. Chitosan, copper sulphate CuSO4 (95%), NaOH pellets (98%), along with KOH pellets (90%), as well as methanol (99.5%) and hydrochloric acid (HCl) (36%) all these chemicals are purchased from Global Marketing, Nagpur. Every reagent was utilized just as it was acquired, without any further processing. At some point throughout the experiment, deionized water is employed.

2.2 Preparation of Activated Carbon from agricultural waste of Glycine max (ACGM)

Glycine max agricultural waste (Fig. A) was collected from the local farm. Before dealing with formaldehyde to prevent its coloring from exploding into an aqueous solution, the trash was divided into little pieces and rinsed with tap water for eliminating any remaining sand debris. After that, it had been repeatedly cleaned along deionized water and let to dry in sun for three to four days. Pyrolysis process, which entailed utilizing a muffle furnace set at a temperature between 300 and 500 degrees Celsius for 15 to 20 minutes, was applied to the waste after it had been dried. This was done to ensure that any volatile elements were removed and that any residual was converted straight into a char. After that, char had been activated for forty minutes in a microwave oven. The resultant activated carbon particles were sieved and ground to a size of 120–200 µm. After being cleaned by double-distilled water, activated carbon had been dried for 24 hours at 70 ^{0}C moreover kept in a closed container.

2.3 Preparation of Chitosan Gel

With frequent stirring, in 900 mL of 10% oxalic acid, 50 g of chitosan is added. To ensure uniform mixing, the mixture is heated between 45 and 55 ^{0}C. The combination of chitosan and oxalic acid turns into a white, thick gel.

2.4 Surface coating of ACGM along Chitosan Gel

After being double diluted with distilled water, 500 ml of chitosan gel were heated to 45 to 50 ^{0}C. Employing a rotary shaker, 200 g of ACGM was gradually added to a diluted chitosan gel along with agitated for 24 hours. After that, deionized water was employed to wash and dry the chitosan-covered ACGM (CCACGM) (Fig. B). To create a thick layer of chitosan on the ACGM surface, the procedure was carried out three or four times. By weight, the coated chitosan increased to 30–35%. An oxalic acid solution containing 0.5 % sodium hydroxide was employed to quantitatively neutralize it. After being filtered and cleaned with deionized water, the solid form of CCACGM was dried and stored in an airtight container.

2.5 Characterization of CCACGM

The prepared composite's structure was determined by XRD. With the application of SEM, the

composite's morphology was examined. For evaluating functional groups, FTIR is employed. TGA tests were conducted in order to check for CCACGM's thermal stability.

FIG A: Agricultural waste of Glycine max FIG B: Chitosan Coated Activated Carbon (CCACGM)

3. RESULT AND DISCUSSION

3.1 Characteristics of CCACGM

3.1.1 XRD Pattern of CCACGM: Fig.1 recommends X-ray diffractographs of CCACGM, showing 2 diffraction peaks at 110-240, indicative of the material's crystalline form. A peak at 2θ = 380 to 390 further confirms crystalline structure of material. Pure chitosan shows a distinctive peak at 2θ = 290-300, which defines its functioning properties and crystallinity. Peak area for the peak at 2θ=290 -300 in each diffractogram is noticeably minimal.

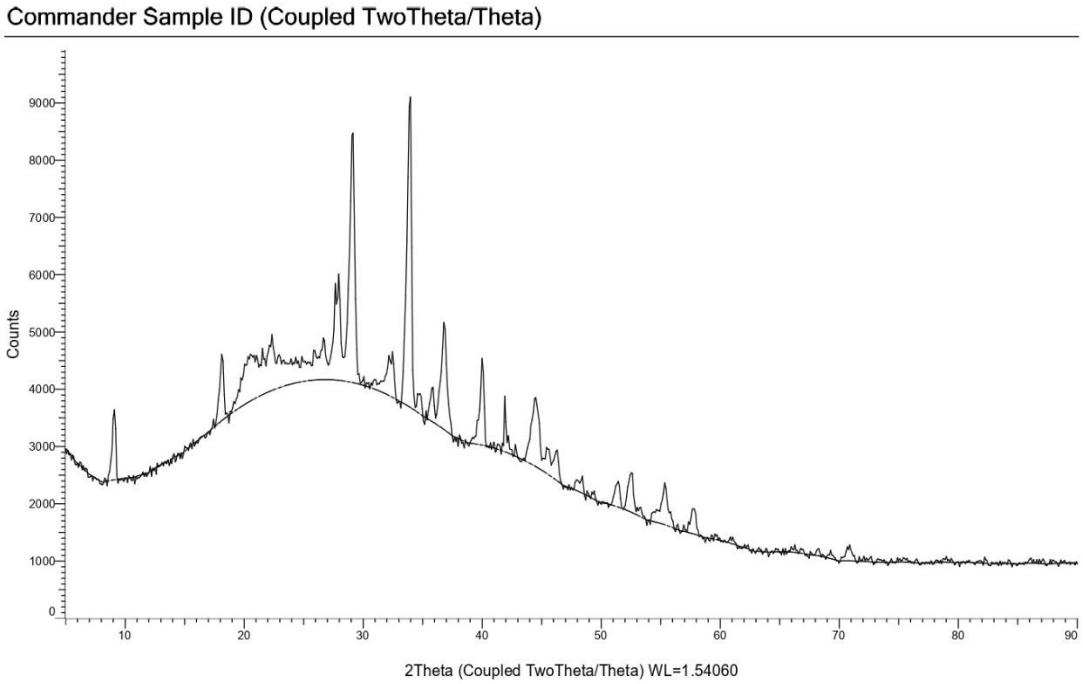

Fig.1 X-Ray Diffraction Pattern of Chitosan Coated Activated carbon of Glycine max (CCACGM)

3.1.2 FTIR Studies: The FTIR spectrum of CCACGM has illustrated in Fig. 2. Band at 3442.21 cm^{-1} has been associated with –OH stretching. Since bands for hydroxyl groups that are not involved in hydrogen bonding can often be observed as a sharp band positioned above 3500 cm^{-1}, OH groups appear to be related

through hydrogen bonding. The range below 3700 cm^{-1} is where the band for –OH stretching occurs. C=O stretching in aldehydes or ketones (carbonyl groups) is represented by a band at 1633.75 cm^{-1}. Significant decrease in band location, suggesting C=O group could also be associated with hydrogen bonding. The stability of intramolecular hydrogen-linked structure is due to the phenomenon of resonance. Signal at 1084.14 cm-1 signifies ortho-substitution. The low band at 565.20 cm^{-1} corresponds to the C-I stretching vibration.

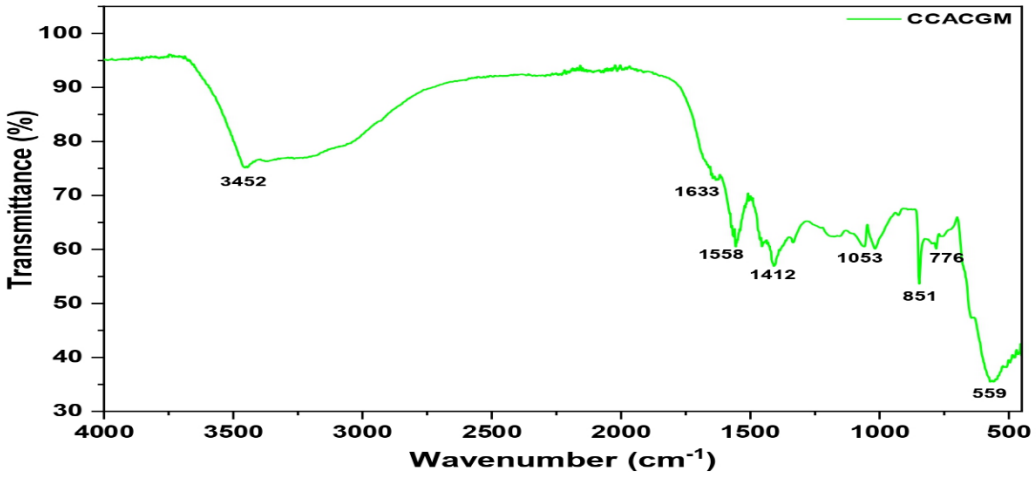

Fig.2. FTIR Spectrum of Chitosan Coated Activated Carbon of Glycine max (CCACGM)

3.1.3 SEM images of CCACGM has shown in Figure 3. These images were taken at an accelerating voltage of 20 kV with magnifications of X 500, X 1500, and X 3500. High-magnification SEM micrographs clearly illustrate existence of diverse pores on surface of Chitosan-coated activated carbon produced by Glycine max (CCACGM), along with a fibrous structure. The amount of surface area available for adsorption is increased when adsorbent's surface has holes and cave-like openings.

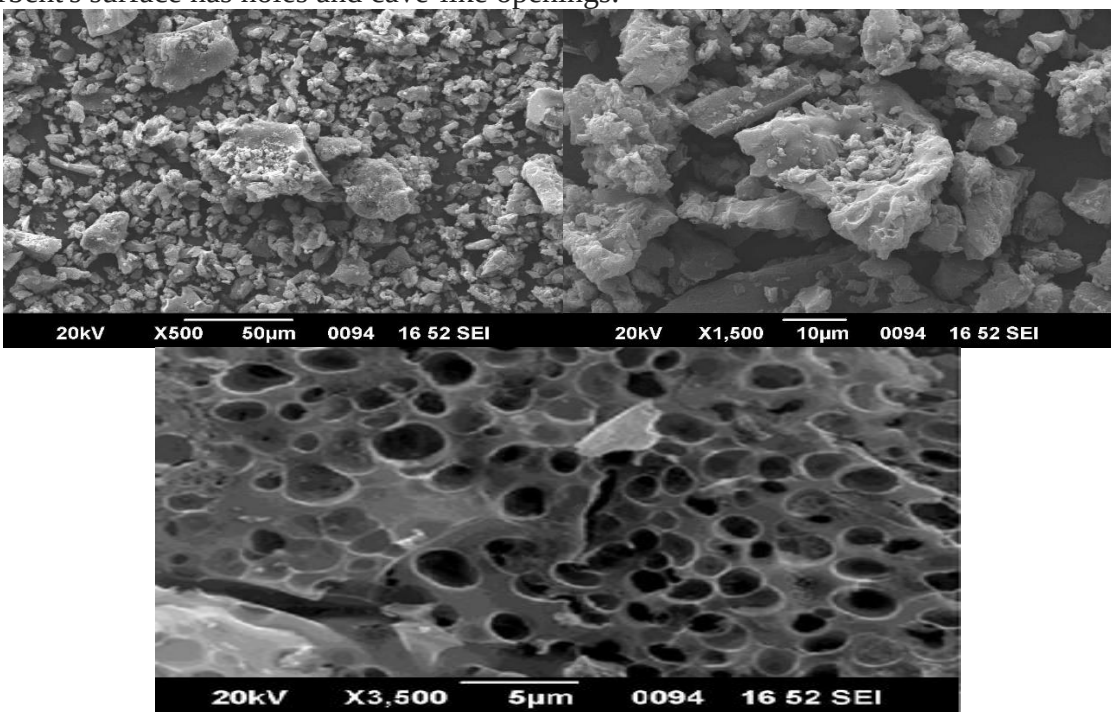

Fig. 3 SEM image of Chitosan Coated Activated Carbon of Glycine max (CCACGM)

3.1.4 T. G curve of CCACGM has shown in Figure 4 initial derivative peak occurs at a lower heat of 620°C, corresponding to a weight loss of 5.90% of material. The loss of water molecules that are weakly connected

to the CCACGM surface could be the cause of this. At 1000°C, a 7.0% weight loss revealed that moisture had evaporated from the adsorbent's surface. The adsorbing material is thermally stable if there is no weight loss at temperatures of 100°C - 650°C. At a temperature of 683.68°C, the greatest weight loss observed was 25%, suggesting the decomposition of the chitosan composite as well as different organic components.

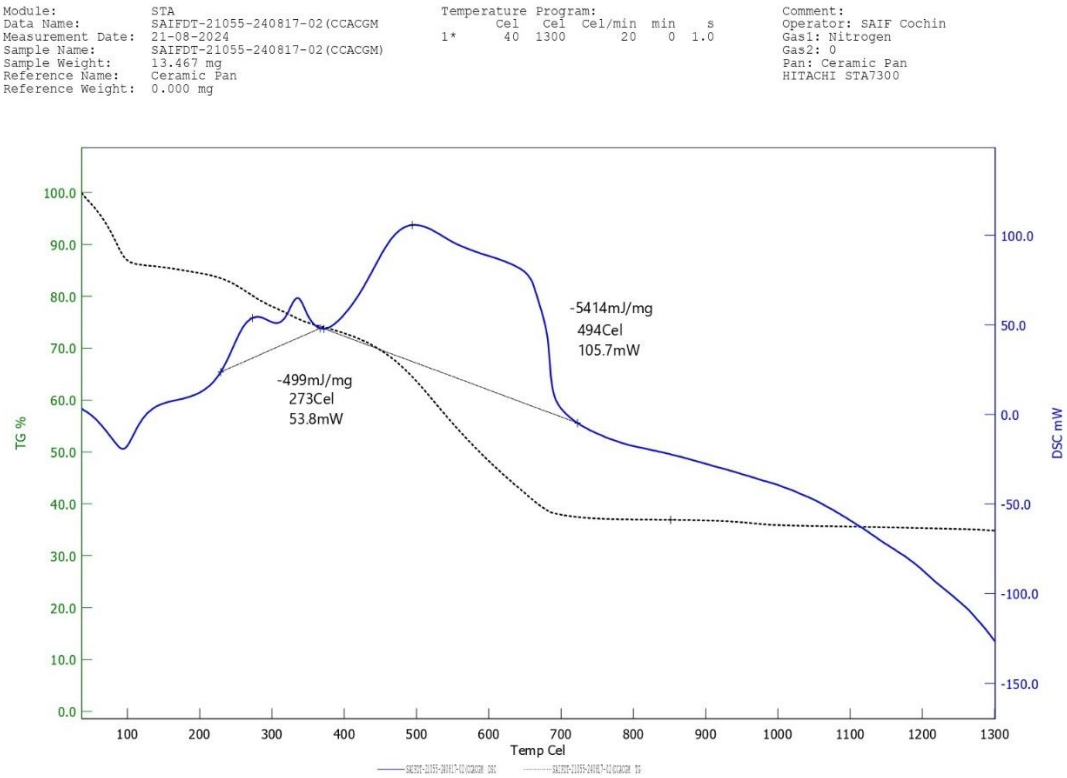

Fig. 4: "TG Curve of Chitosan Coated Activated Carbon of Glycine max (CCACGM)"

3.2 Adsorbent Dosage Figure 5 illustrates the influence of adsorbent dosage on surface adsorption of CCACGM for th**e** elimination of Cu^{2+}. The efficacy of Cu(II) removal by CCACGM increases significantly with the dosage of CCACGM ranging from 0.5-10g/L, with maximum elimination efficiency of Cu(II) ions, namely 95.7%, obtained at an adsorbent dose of 6 g/L. Increasing CCACGM dosage enhances the available active sites for Cu(II) biosorption, therefore facilitating a greater removal of Cu(II). An additional dose increase above 6 g/L failed to produce a significant enhancement in removal efficiency. This result could have been explained to overlap or aggregation of active sites at higher doses, along with a shrink in total surface area of sorbent. Maximal dose of CCACGM was 6 g/L.

3.3 pH effect: pH of solution has a notable influence on adsorption of important heavy metals as it impacts adsorbent's characteristics, including surface charge, as well as the adsorbate's manufacturing and ionization level in aqueous solutions. Along with pH values ranging from 1-10, illustrated in Figure 6, influence of pH on Cu(II) elimination has been examined. Adsorption of Cu(II) from aqueous solutions is greatly impacted through pH level. It has been demonstrated that when pH reached from 1.0-7.0, percentage of elimination efficiency gradually enhanced and thereafter declined substantially at pH levels above 6.5. At pH 6.0, CCACGM's highest removal efficiency of 94.6% has been observed. According to research, concentration of H+ ions in solution significantly increases at lower pH, which helps to generate functional groups on adsorbent surface. Cu (II) ion adsorption was being hindered by competition amongst H+ and Cu2+ for adsorption sites on adsorbent surface. Concentration of H+ in solution falls due to elimination of functional groups on adsorbent surface at greater pH levels (>pH 6.5), which reduces adsorption capability. As a result of less competition between H+ and Cu2+, more Cu (II) ions were absorbed. The adsorption capacity was

thereby reduced. This is mainly because when Cu (II) precipitates, hydroxyl radical metal complexes are formed.

3.4 Effect of contact time on Cu (II) elimination: Figure 7 illustrates impact of contact length on reduction of Cu(II).Cu(II) elimination efficiencies of CCACGM significantly enhnaced along extended contact time, achieving maximum equilibrium at 110 minutes. The biosorption of Cu (II) by CCACGM occurs quickly, with 75 % of Cu (II) ions adsorbed in 80min. Equilibrium sorption had been achieved after 110 minutes, with Cu(II) removal efficiencies at 93.20% for CCACGM. No substantial enhancement in removal efficacy has been observed with an extended contact duration (>120 min). The existence of open binding sites on surface of adsorbent, that improve interaction along Cu(II) ions, explains high initial absorption of Cu(II) ions. Likelihood of Cu (II) ions interacting along functional groups on adsorbent decreased as duration of contact grew because the sorption sites were extensively occupied. Since the maximum number of binding sites have no effect on Cu (II) adsorption, equilibrium has been reached, resulting to an almost constant adsorption capacity.

3.5 Effect of initial concentration: Driving force that overcomes mass transfer barrier among solution as well as adsorbent is greatly impacted by initial concentration of Cu (II) metal ions in solution. Fig. 8 illustrates that % elimination of Cu (II) decreased from 91.79%-50.70% for CCACGM when concentration of Cu (II) ions rise from 10-100 mg/L. At reduced Cu (II) concentrations, noticeable no. of Cu (II) ions will be attached to adsorbent surface because of a substantial difference in availability of surface adsorption sites contrast to Cu (II) in solution. As initial Cu (II) concentration rose, percentage of empty binding sites decreased. The decreased removal of Cu (II) at higher concentrations can be identified to a shortage of available active sites on surface of CCACGM.

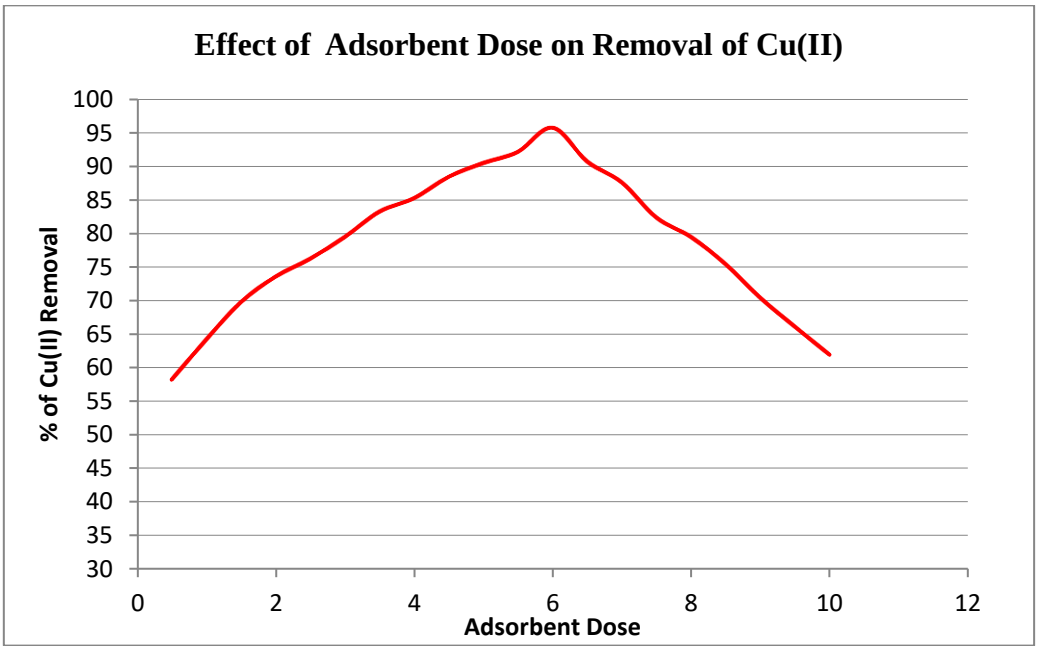

Fig 5 Effect of Adsorbent Dose

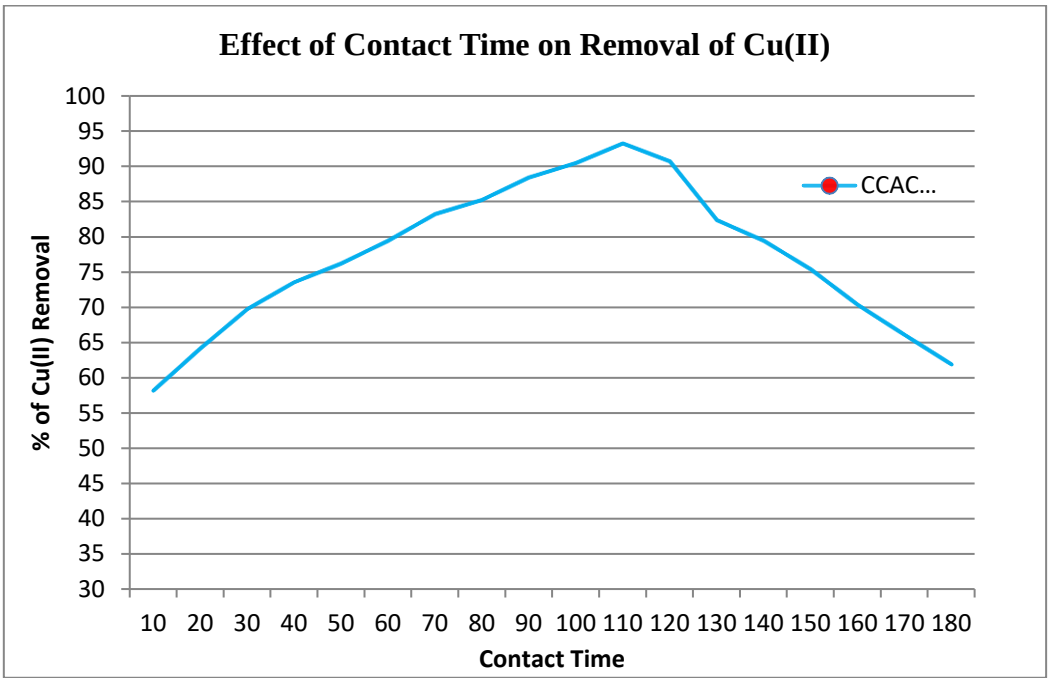

Fig 6 Effect of Contact Time

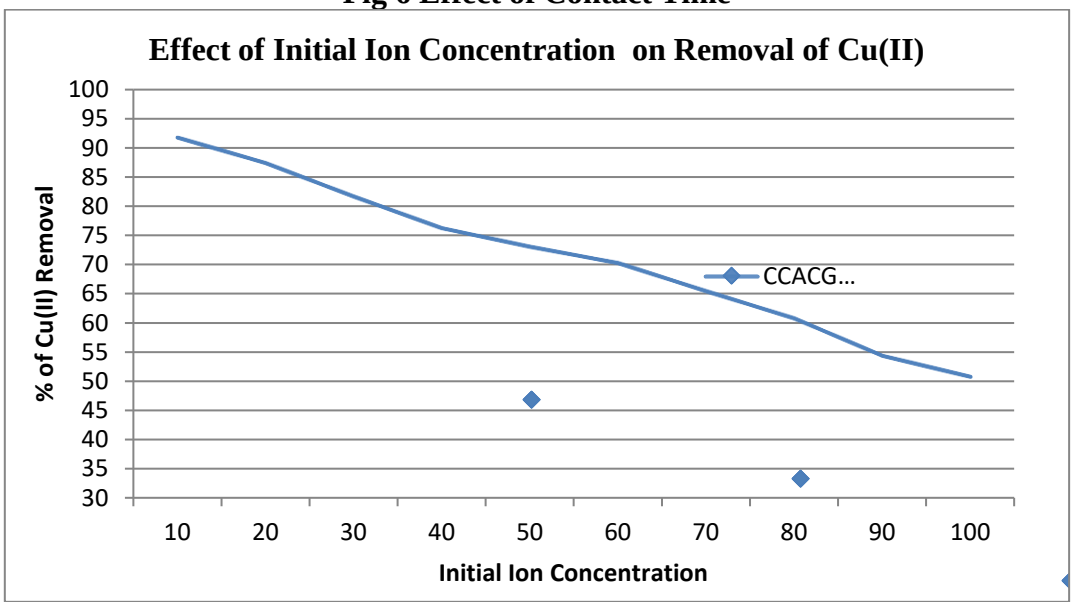

Fig 7 Effect of Initial Metal Ion concentration

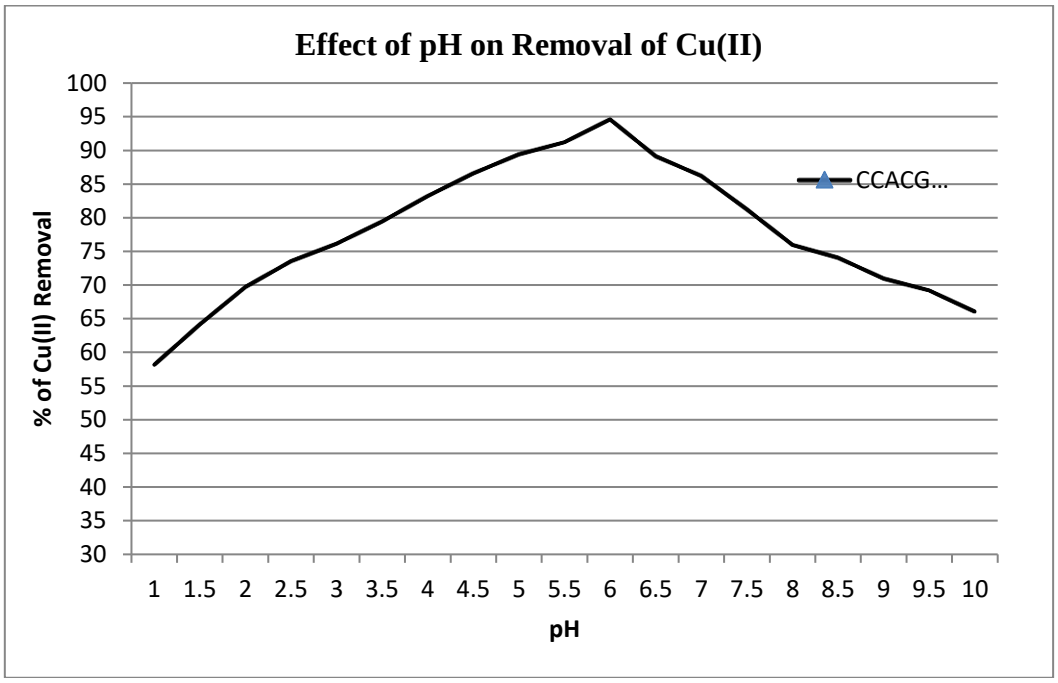

Fig.8 Effect of pH

4. CONCLUSION

Research highlights efficacy of CCACGM, derived from agricultural waste, as a sustainable and effective adsorbent for extracting harmful heavy metals, including Cu(II), from wastewater. Among many treatment strategies, adsorption with surface-modified activated carbon has proven to be a superior strategy because of its elevated surface area, enhanced functional groups, as well as increased adsorption capacity. A maximum removal efficiency of copper of 94% was achieved under optimized conditions, demonstrating the effectiveness of chitosan modification. The prepared adsorbent was successfully characterized using SEM, FTIR, XRD, and TGA techniques, confirming the structural and functional enhancement. This work supports the use of sustainable, low-cost materials for environmental remediation and contributes to the development of advanced adsorbents for water purification.

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