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Scavenge of Hazardous Metal Ions Using Decorated Nanometal on Carbon Nanomaterial Synthesized from Cotton

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Abstract: ***Eradicating hazardous materials using carbon nanomaterials (CNMs) is a cutting-edge approach in environmental remediation. The study involves procurement of plant material cotton as a feasible precursor for the synthesis of carbon materials which is further activated by using alkali solution. Activated carbon was decorated with copper nanoparticles to create a copper decorated CNMs. The effective adsorption of Cd^{+2} and As^{+3} is 85% to 90% at pH 6 and 7 respectively. Thus, this recently developed cost-effective novel adsorbent CNMs can be used to mitigate the Cd^{+2} and As^{+3} even at a very low concentration level. The prepared adsorbent was characterized by various analytical techniques such as SEM, TEM, Raman and XRD. The specific surface area and pore volume was confirmed by BET.***

Keywords: Cotton, carbon nanomaterials, adsorption, Cd^{+2}, As^{+3} and hazardous ions.

I. INTRODUCTION

In many countries, due to urbanization and industrialization various organic and inorganic pollutants are discharged into the environment from different sources like metal plating, glass production industries, mining operations, pulp industries, petrochemical fertilizers, refining ores, manufacturing of paints, leather tanning, etc. (Argun *et.al.*, 2007, Atieh *et.al.*, 2011 and Varma *et.al.*, 2010). These pollutants are hazardous as well as carcinogenic in nature which will affect not only human-life but also other living species existing in the ecosystem.

The pollutants include many heavy metal ions which are resistant to biodegradation. Various technologies are available in the present scenario which are either expensive or non-effective for solving all types of pollutants present in waterbodies. (Anirudhan and Sreekumar, 2011)

Arsenic poisoning can cause severe health effects in humans, even when exposure occurs at low concentrations. (Carneiro *et.al.*, 2015). The toxicity of arsenic ranges from vomiting to skin cancer to death. (Gupta *et.al.*, 2010).

Cadmium leads to cancer and organ toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous; in addition, it decreases bone density and causes respiratory disorder. (Rahimzadeh *et.al.*, 2017). It is imperative to prevent such toxic metals from entering the water bodies.

There are numerous methods and technologies available for the removal of heavy metal ions viz. ion exchange, chemical precipitation, chemical oxidation, reduction, reverse osmosis, co-agulation-flocculation, ultrafiltration, flotation, membrane filtration, electrodialysis, electrochemical methods and adsorption. Among the following methods, adsorption is an effective treatment method. (Roy *et.al.*, 2013). It is fascinating to account that most of the work carried out so far has used activated carbon nanomaterials (CNMs) with or without metal nano particle decoration for removal of hazardous ions. The CNMs derived from petroleum-based products are extortionate and, in most cases, the CNMs are prepared from petroleum products, which are on the verge of extinction. The innovation, forthcoming development and challenges of cost-effective are taken into consideration for the synthesis of CNMs and adsorption of toxic metal ions. In recent years, many researchers have developed CNMs from durian shell (Chandra *et.al.*, 2009), marigold straw (Qin *et.al.*, 2014), rice husk (Ratan *et.al.*, 2018), cocoa pods (Tiegam *et.al.*, 2021), pineapple leaf (Latif *et.al.*, 2021), etc. However, the precursor cotton contains excess of cellulose is good enough for adsorption capacity (Sharon *et.al.*, 2011, Mukherjee *et.al.*, 2013, Tamilselvi and Asaithambi., 2015). The privilege of the precursor is its renewability, marvelous yield with short span of time and easily available on earth.

The aim of the present work is to synthesize CNMs using plant-based precursor (cotton) impregnated with copper nanometal leading to enhancement of adsorption capacity of hazardous metals Cd^{+2} and As^{+3}. BET analysis confirmed material's extensive specific surface area, further supporting its suitability as a strong adsorbate for adsorption.

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II. EXPERIMENTAL TECHNIQUES

Double distilled water is employed both as a solvent and for all dilution purposes, along with this all the chemicals used for the study are of analytical grade reagent.

A. Synthesis of Cu-doped CNMs

The work involves pyrolysis of cotton fiber at 700°C in the presence of inert atmosphere to synthesize carbon material. Activation of carbon material using various alkali solution followed by doping of copper metal is done. Further, annealing of prepared material is carried out at 750°C in an atmosphere of CO_2. The synthesized CNMs is highly porous and has substantially high surface area due to doping of metal which will be an excellent candidate for adsorption of hazardous metal ions.

B. Removal of Hazardous Metal Ions

Initially 1000ppm stock solution of Cd^{+2} and As^{+3} was prepared by using reagent $CdSO_4.H_2O$ and As_2O_3 respectively. Cd^{+2} solution was prepared by dissolving in 2N HNO_3 whereas As^{+3} was dissolved in 10% NaOH solution and PH was adjusted using 1N H_2SO_4. Further in the range of 10-15ppm both the solution was prepared from stock solution.

The experiment of the adsorption was carried out at room temperature. The dosage of 0.1g Cu-doped CNM is added to 10ml of solution in the conical flask. The analyte was kept in a digitally controlled shaker machine for half an hour and the rate of agitation was maintained at 120 shake per minute. The other parameter like pH was adjusted by using hexamine powder and 1N H_2SO_4 for Cd^{+2} and As^{+3} respectively. The analyte was filtered and the concentration of the filtrate was determined by using ICP-AES. (ARCOS, Simultaneous ICP Spectrometer of SPECTRO Analytical Instrument GmbH Germany, was used for analysis. The RF Generator: Maximum of 1.6 KW, 27.12 MHz and the spectrometer wavelength range 130-770nm with the resolution of 9 picometer).

The amount of metal ions adsorbed was calculated by the difference in the initial (*Ci*) and the final (*Cf*) concentration of analyte. (Hawari, 2006) The percentage of adsorption was calculated by using following relationship.

$$\% \text{ Adsorption} = \frac{Ci - Cf}{Ci} \times 100$$

III. RESULT AND DISCUSSION

A. pH-Dependent Metal Ion Adsorption by CNMs

Figure 1 reveals dynamic trends in the adsorption behaviour of metal ions in response to changes in pH. As the pH increases both As^{+3} and Cd^{+2} generally experience an upward trend in adsorption but the adsorption rate decreases towards the higher pH range.

The highest adsorption values are observed at pH 6 for Cd^{+2} around 88% because at low pH the adsorbent is saturated with hydrogen ions which discourages the removal of Cd^{+2} ions. (Osasona *et.al.*, 2017). There is negligible change from pH 6 to 8 afterwards it decreases. (Gour *et.al.*, 2018). The pH range 6 to 9, As^{+3} is mostly present as neutral arsenious acid ($H_3As_3O_3$), and its adsorption is favorable when the surface is close to neutral. (Carneiro *et.al.*, 2015).

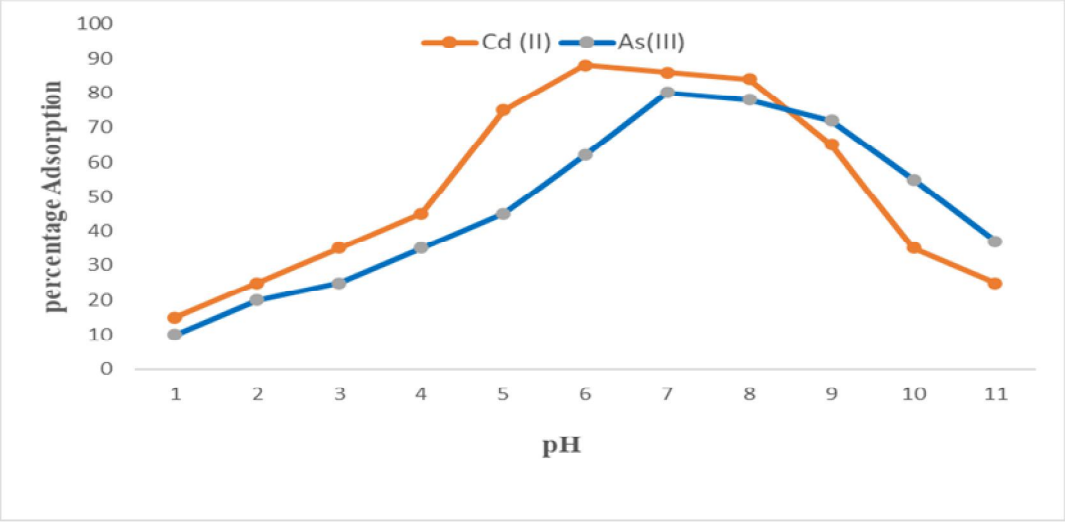


Figure: 1 pH-Dependent Metal Ion Adsorption by CNMs

B. Characterization of Carbon nano Materials

1) *Scanning Electron Microscopy (SEM) [Make: FEI and Model: Quanta 200]:* Analysis of CNMs was done using SEM, where the surface morphology was studied. Figures 2 and 3 shows the particular morphology of hollow carbon nanofiber (CNF) decorated with copper nanometal. The thickness of the CNF was found to be in the range of 50-70nm.

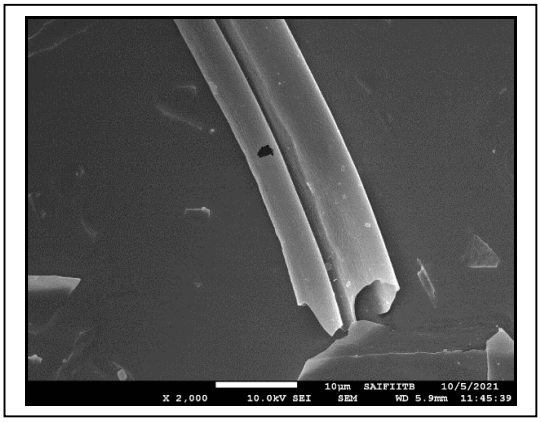


Figure: 2 SEM

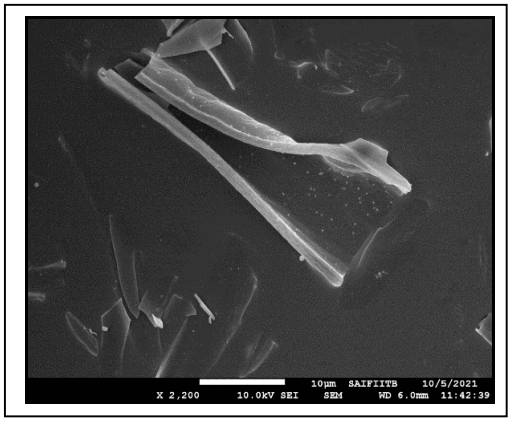


Figure: 3 SEM

2) *High-resolution Transmission Electron Microscopy (HRTEM) [Make: FEI and Model: Tecnai]:* Figures 4 and 5 depicts morphology of CNMs embedded with Cu nano metal having diameter 5nm to 50nm whereas CNMs having sheet like edges whose thickness lies between 20 to70nm.

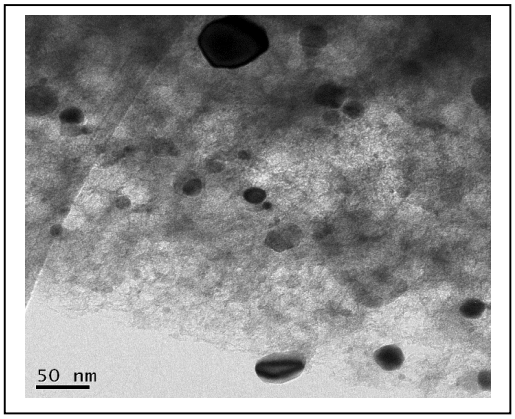


Figure: 4 HRTEM

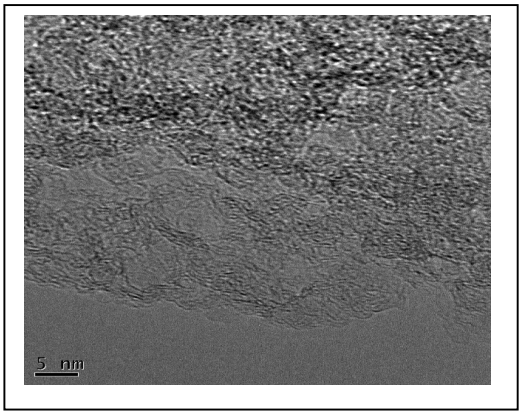


Figure: 5 HRETM

3) *X-Ray Diffraction (XRD) [Make: PANalytical, The Netherlands and Model: EMPYREAN]:* Figure 6 reveals one broad peaks at 2θ values of 23ºand three intense peak at 43.44º, 50.54º and 74.42º corresponding the planes (111), (200) and (220) which confirms the presence of copper metal. (JCPDS, copper file no. 04-0836). (Theivasanthi, 2010). This indicates the synthesized CNMs doped with copper nanometals has graphitic carbon along with graphene oxide.

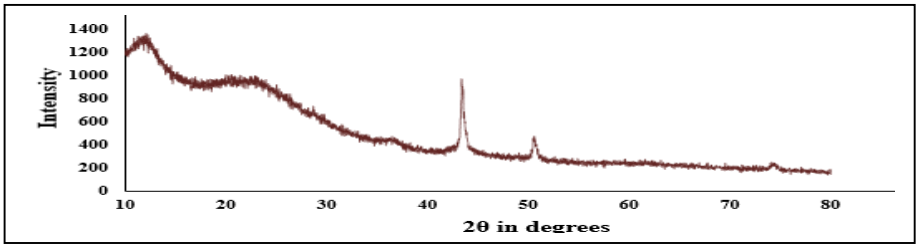


Figure: 6 XRD

4) *Raman Spectroscopy [Make: Renishaw, UK and Model: Invia Reflex]:* Figure 7 of Raman spectroscopy reflects two different peaks indicating the presence of D band at 1226 cm^{-1} and G band at 1518$cm^{-1.}$ This corresponds the presence of disorder in sp^2 hybridized carbon system as well as presence of crystalline graphitic structure. (Andrews and Young, 1993). Henceforth the synthesize CNMs is a mixture of graphitic and amorphous carbon nanomaterial**.**

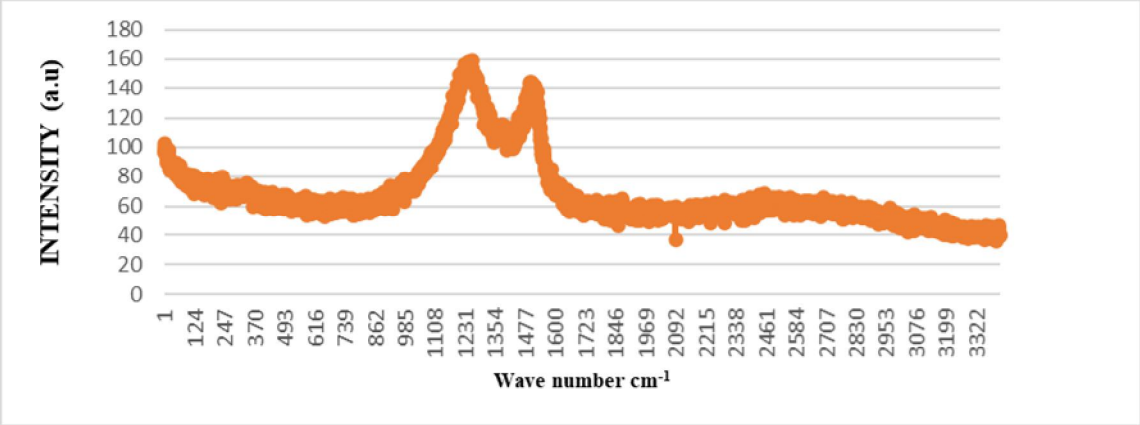


Figure: 7 Raman Spectroscopy

5) *BET [Make: SMART INSTRUMENTS and Model: SMART SORB 93]:* The specific surface area of the as obtained CNMs was found to be 1130 m^2g^{-1} by BET (Brunauer-Emmett-Teller) along with pore volume of 0.240 cc/g. This signifies an excellent candidate for the adsorption of hazardous metal ions by increasing the porosity of carbon nanomaterial (Kumar and Jen, 2016).

IV. CONCLUSION

In this investigation, the CNMs with excellent surface characteristic were conveniently and economically synthesized using precursor cotton. Impregnation of copper nano particles enhance the adsorbing capacity of hazardous metal ions. Finally, the characterization of synthesized CNMs was done using SEM, HR-TEM, XRD, RAMAN confirms the presence of crystalline and amorphous carbons whereas BET shows an excellent adsorbent material. The result also confirms 88 % to 92 % adsorption of Cd^{+2} and As^{+3} metal ions by using low dosage of synthesized CNMs within a short span of time. Hence it can be concluded that the CNMs obtained from cotton is a marvelous candidate for removal of arsenic and cadmium metal ions from the effluents.

V. ACKNOWLEDGEMENT

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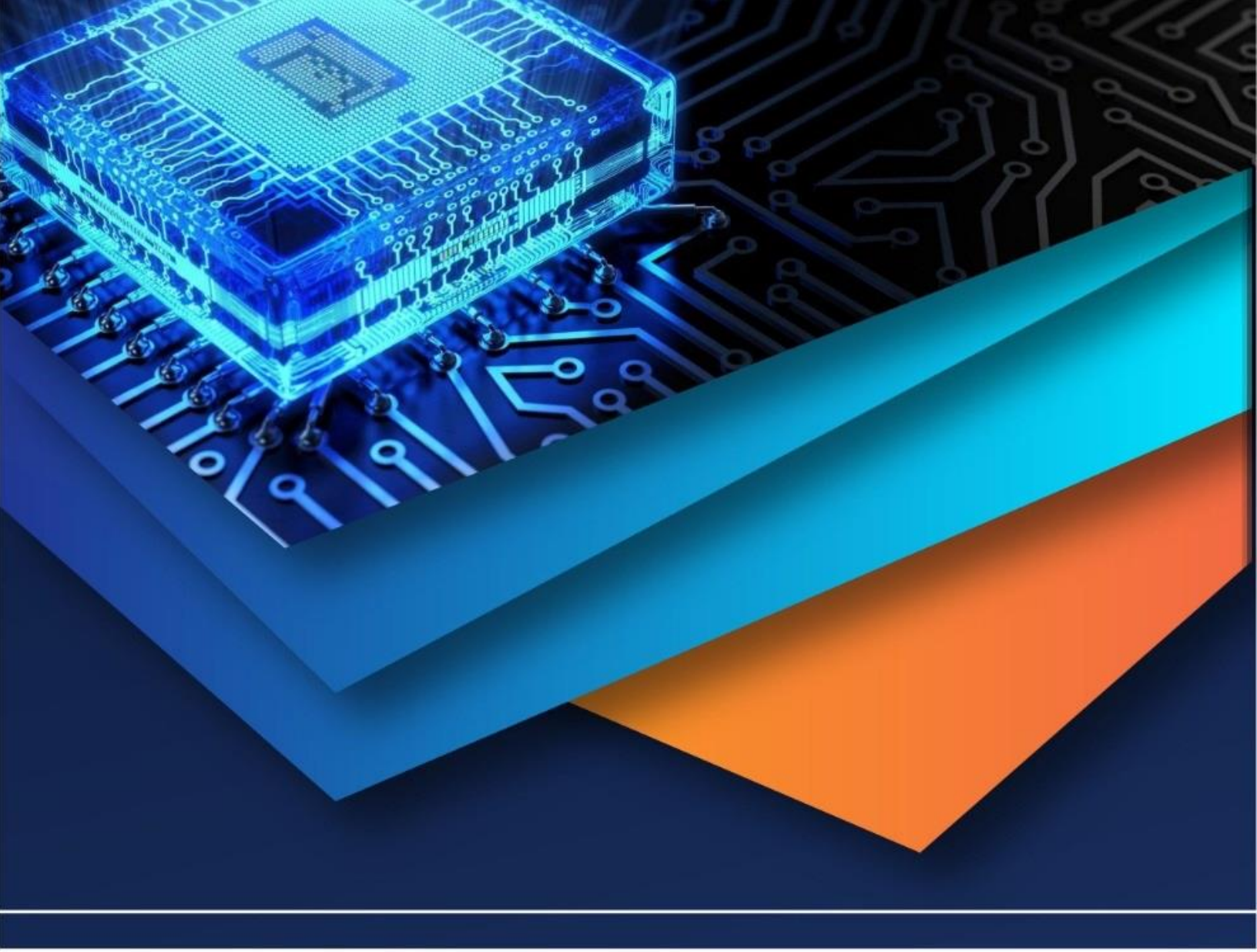
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