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Nanometal Decorated Carbon Nanomaterials Generated from Agro-Waste as Excellent Adsorbent for Toxic Metal Ions

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Abstract: ***The effluent water contains heavy metals, dyes and other toxic chemicals which are harmful for humans and environments. By using adsorption technique, one can easily remove most of the toxic materials including metal ions. Adsorption depend upon the physical interaction between adsorbate and adsorbent.***
Due to specific structural properties, Carbon nanomaterials are used as the adsorbents for removal of metal ions present in effluents as well as for purification of water.
In the present work, Pb^{2+} and Cr^{6+} ions were removed from aqueous medium using nanomaterials which is a nanocomposite of Carbon nanomaterials decorated with nanometal (Cu). The Carbon nanomaterials were prepared from agro-wastes sugarcane bagasse. It can remove metal ions in the range of 85 to 90 % from solution having low concentrations of 12-14 ppm. Adsorption of metal ions were found to depend on the pH of the aqueous media. It can show maximum adsorption at pH 6 for Pb^{2+} and at pH 1-3 for Cr^{6+}.
Morphological features of nanoparticles were analyzed using SEM, HRTEM, Raman, XRD and Specific surface area was determined using BET.
Keywords: Adsorbents, toxic metal ions, sugar cane bagasse, Pb^{2+} and Cr^{6+}.

I. INTRODUCTION

There are many metals utilized in industries which are toxic and non–biodegradable. For manufacturing of paints and batteries and in many other industries such toxic metals are extensively used. These metals are harmful to animals and human beings. These remain in the environment for a number of years. Such metals are highly toxic and may cause damages to the central nervous system, kidneys, lungs, and other organs.[Reglero M.M et al. 2009; Gybina A.A and Prohaska J.R 2008; Kampa M and. Castanas E 2008; Afroze S and Sen T.K 2018] Many of these metal ions are carcinogenic in nature.[Cocarta D et al. 2016]

Pb^{2+} causes anemia, hypertension, renal impairment, immune-deficiency and toxicity to the reproductive organs. The neurological and behavioral effects of lead are believed to be irreversible.[M Samuel Collin et al. 2022]

Cr^{6+} is responsible for respiratory and pituitary cancer, eye, kidney and liver damage. Respiratory, nose and skin irritation. It also causes upper abdominal pain.[Sinicropi M.S et al. 2010; Vendruscolo F et al. 2017]

These waste waters or effluents containing heavy metal ions are discharged into natural water bodies, many a times in an untreated form. The concentrations of these metal ions may get enriched by precipitation, adsorption and become life threatening to the aquatic organisms. These may then enter the food chain and cause severe health issues. Thus, the removal of such toxic metal ions from wastewater before discharging in water bodies is becoming an outmost necessity.

There are many techniques for removal of such toxic metals viz. reverse osmosis, reduction, ion-exchange, precipitation and membrane filtration. But the main disadvantage of these techniques is operational and maintenance cost.[Jadhav SV et al. 2015; Weng C-H et al. 2008]. Adsorption is one of the easiest techniques for removal of such toxic metals. The use of Nanotechnology is one of the best solutions for removal of such toxic metal by adsorption method. [Kunduru KR et al.-2017; Dasgupta N et al. 2017; Qu X et al. 2013; Zhang Y et al. 2016]

In the present work, preparation of Carbon nanomaterials (CNMs) was carried out by using sugarcane bagasse which is an agro-waste and then the CNMs were decorated with copper nanometals which increases the adsorption capacity of toxic metals, such as Pb^{2+}, Cr^{6+}. The large specific surface area of the material was confirmed by BET, further substantiating it as an excellent candidate for adsorption.

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II. EXPERIMENTAL TECHNIQUES

All the chemicals used were of AR grade.

A. Synthesis of Carbon nanomaterials

For removal of toxic metals, CNMs were used. There are many methods for synthesis of CNMs from agro waste.[Nady A. Fathy et al. 2020]

In the present work, the CNMs were prepared from agro-waste, sugarcane bagasse. Bagasse was collected from local juice center. Bagasse was heated in an inert atmosphere at 730^0C in a furnace and then treated by using alkali solution. This carbon was impregnated with copper and annealed in presence of CO_2 at 730^0C. Metal decorated CNM is highly porous in nature.

B. Removal of toxic metals

1000 ppm stock solutions of $Pb(NO_3)_2$ and of $K_2Cr_2O_7$ were prepared initially. Then, solution in the range of 10-14 ppm of metal ions were prepared from the stock solution.

The experiments were carried out by using 0.1 to 0.2 g of CNMs decorated with copper nanometals. 10 cm^3 of solutions were used for estimation. The solutions were shaken using electronic mechanical shaker for 30 min. pH of the solution ranges from 1-6 pH and the pH was adjusted by using hexamine powder in case of Pb^{2+} and concentrated sulfuric acid for Cr^{6+}. The solution was filtered and the filtrate was analyzed for adsorption using an Inductively Coupled Plasma Atomic Emission Spectrophotometer and UV Visible Double Beam Spectrophotometer.

The adsorption was calculated by initial and final concentration of metal ions.[Jie Ma et al 2019; P. M. Shukla and S.R Shukla-2013]

% Adsorption = $[C_i - C_e] / C_i \times 100$

C_i and C_e is initial and final concentration of metal ions respectively.

III. RESULT AND DISCUSSION

Activation of carbon and then decoration of metals on CNMs increases the active surface area on CNMs,[K.R. Jagdeo et al.2021] which increases % of adsorption of toxic metals.

Depending on the effect of pH and contact time it was found that CNMs decorated with copper nanometals shows very high adsorption for $Pb^{2+}$and Cr^{6+}. Percentage of adsorption for Pb^{2+} and Cr^{6+} were found to be 90% and 85 % respectively.

A. Effect of pH on adsorption

pH of solution plays an important role in adsorption process by affecting active site of CNMs.[Ding C et al. 2016; Palin D et al. 2016].From fig. 1 it was observed that for Pb^{2+}ions the percentage of adsorption increases as pH increases. This is possibly due to presence of low Proton density in the solution, more active site was available on CNMs for metal ions adsorption. Due to higher Proton density in the solution at lower pH, there was competition between Proton and metal ions for active site of CNMs.

In case of Cr^{6+}ions, at a lower pH (1-3) value, Cr^{6+} exists mainly as negatively charged $HCrO_4^-$ ions and CrO_7^{2-} ions. Since, the surface of adsorbent is charged positively, the percentage of adsorption was high at lower pH. At basic pH condition, the suppression of the hydrolysis of Cr^{6+} may be the reason for the decreased adsorption.[L Anah and N Astrini 2017]

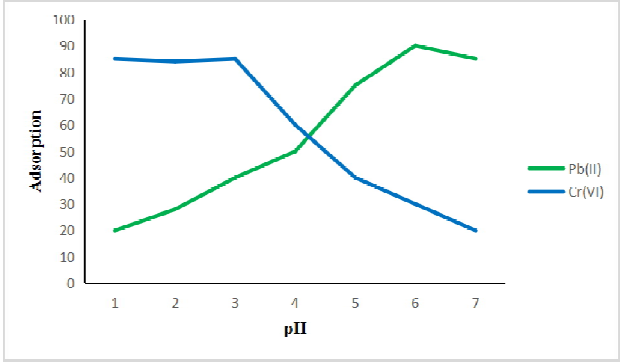


Fig. 1 Effect of pH on adsorption by copper nanometals decorated CNMs
(Initial concentration of Pb^{2+} -12.45 mg L^{-1}, Cr^{6+}- 13.95 mg L^{-1} and adsorbent dosage-10 g L^{-1})

B. Characterization of carbon nano materials

1) Scanning Electron Microscopy (SEM) By using SEM surface morphology was studied. [G. Thomas 1986]. SEM of the CNMs (Fig.2[a] and 2[b]) show their surface morphological features. The CNM particles shows highly porous ridge like structures, decorated copper nanometals.

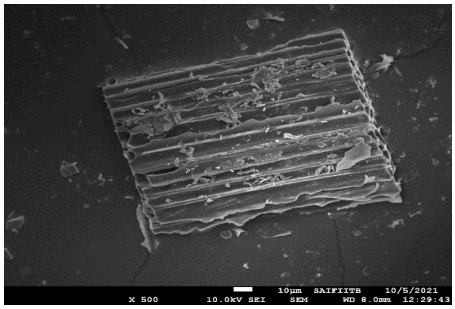


Fig. 2[a]

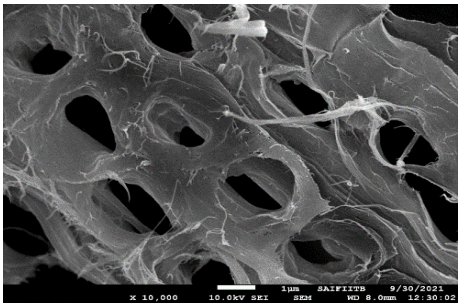


Fig. 2[b]

Fig. 2[a] and [b] SEM images of copper nanometals decorated on CNMs

2) High-resolution transmission electron microscopy (HRTEM) shows structural features of CNMs decorated with copper nanometal (Fig.3[a] and 3[b]). These show copper nanometal having diameters in between 20 to 40 nm and also shows the thickness of CNMs.

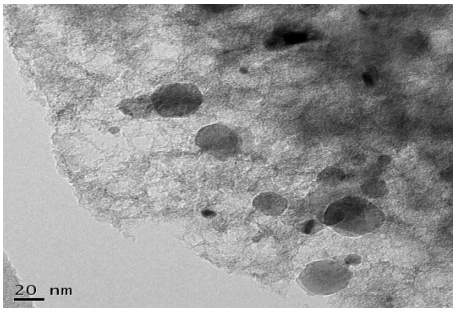


Fig. 3[a]

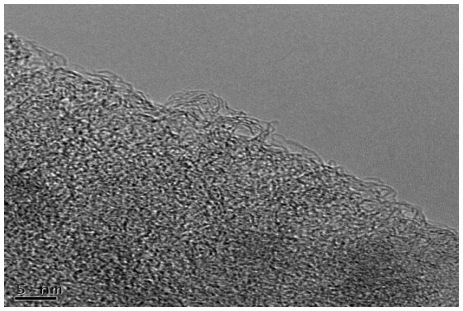


Fig.3[b]

Fig. 3[a] and [b] HRTEM images of copper nanometal decorated on CNMs

3) X-Ray Diffraction (XRD) of the CNMs decorated with copper nanometals were graphitic (graphene oxide) in nature. It shows one broad peak at 2θ of 23º and small sharp peaks at 43.4º, 50.5º and 74.4º correspond to the planes (111), (200) and (220) respectively indicate copper metal. (JCPDS, copper file no.04-0836).[Z.-Z. Zhu et al. 2008; Z. Yong et al. 2007; T.Theivasanthi and M.Alaga 2010]

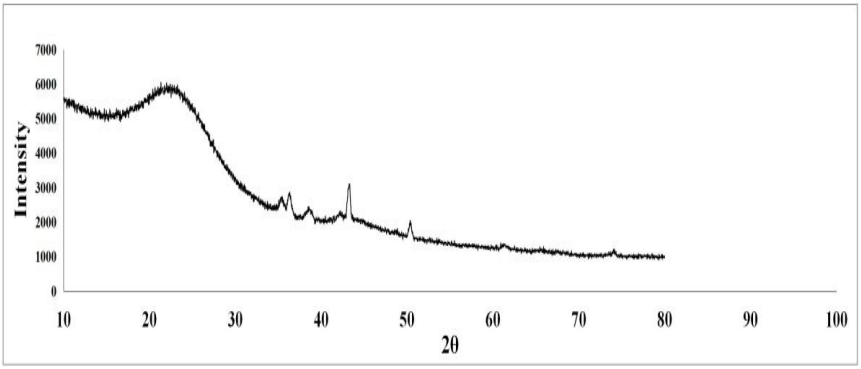


Fig. 4 XRD graph of copper nanometal decorated on CNMs

4) Raman Spectroscopy Fig. 5 shows two peaks in Raman spectra at 2451 and at 3151 which corresponds to G and D band. This signifies the graphitic nature of CNMs along with amorphous particles.[J.-M.Herrera-Ramirez et al. 2004; Gwenael Gouadec and Philippe Colomban 2007]

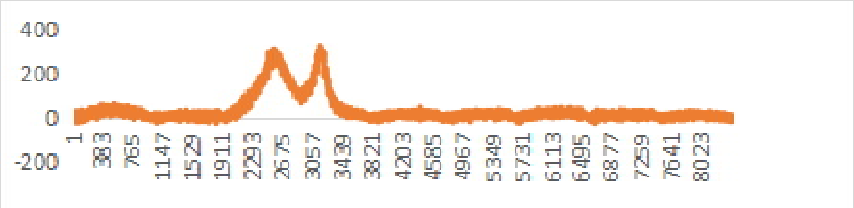


Fig.5 Raman spectra of copper nanometal decorated on CNMs

5) BET analysis of the CNMs indicates specific surface area to be 443.21m^2/g having pore volume 0.200 cc/g making it a good adsorbent.[Eleni A. Deliyanni et. al. 2015]

IV. CONCLUSION

In present work, sugarcane bagasse (an agro-waste) was used as precursor for synthesis of CNMs, a very cost-effective material. The CNMs decorated with copper nanometal was found to be a good adsorbent for toxic metal ions. Due to the high specific surface area and severely porous surface, it was able to remove the toxic ions in the range of 85 to 90% but is pH dependent. Percentage of adsorption for Pb^{2+} and Cr^{6+} were found to be 90% and 85 % respectively.

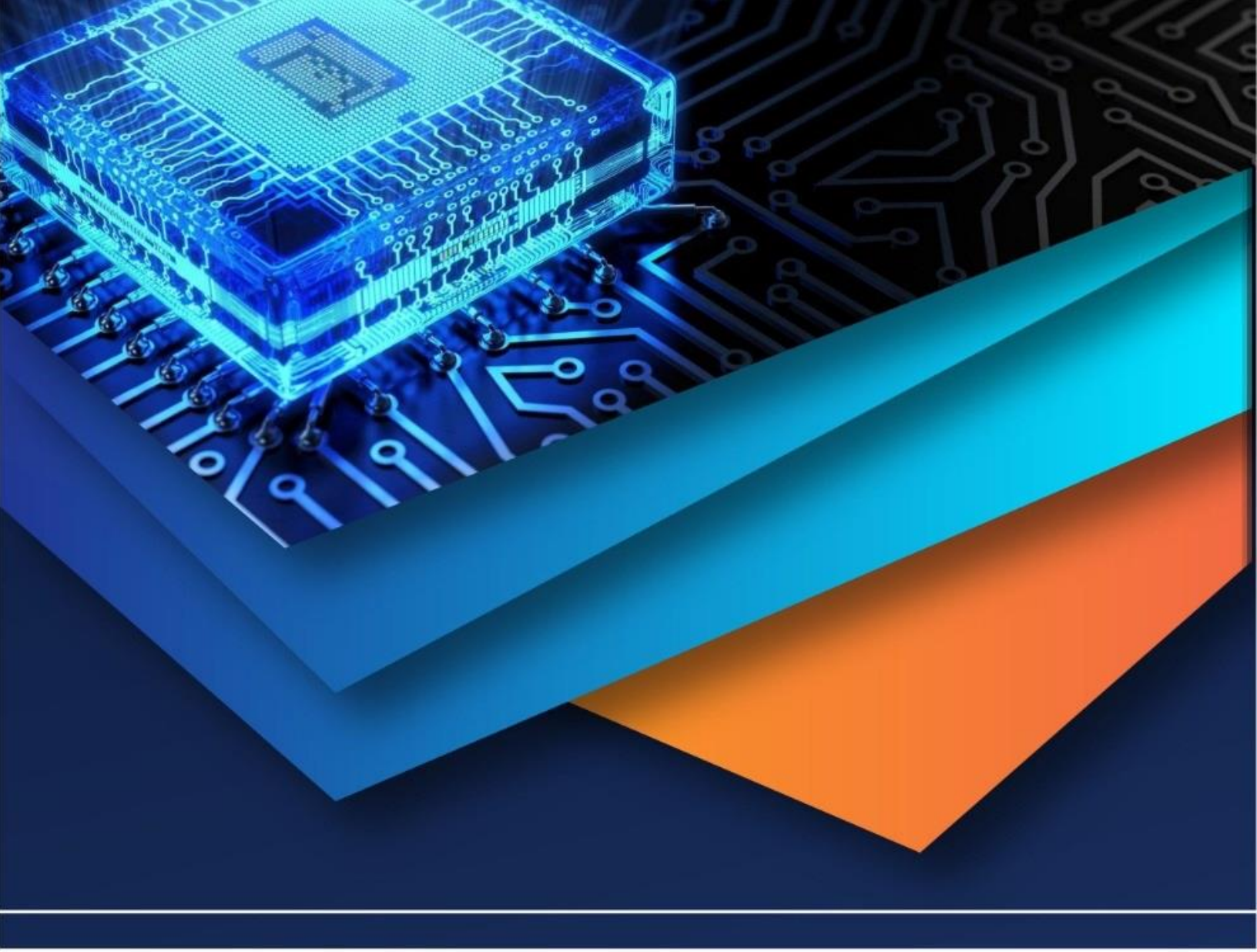
V. ACKNOWLEDGEMENT

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