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Novel Carbon Nanomaterial Synthesized from Banana Leaf Decorated with Metal Nanoparticles for Remediation of Toxic Metal Ions

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Abstract: In the present work, a novel carbon nanomaterial decorated with metal nanoparticles was prepared from banana leaf. An eco-friendly, carbon neutral with a high-cost efficiency quotient substance. The precursor, banana leaf was pyrolyzed in an inert atmosphere and activated by using alkali solution. It was then decorated with copper nanoparticles to obtain the final product. BET analysis revealed its significant specific surface area. The synergic effect of high surface area and nanometal decoration makes this carbon nanomaterial suitable for removal of Pb, Co and Cr toxic metal ions. It is very effective even when the concentration of metal ions is very low. Characterization of nanomaterials was carried out by SEM, HRTEM and XRD. The effect of pH on removal of toxic metal ions was also studied.
Keywords: Banana leaf, carbon nanomaterials, carbon neutral, Pb, Co and Cr metal ions.

I. INTRODUCTION

There are many methods for preparations of carbon nanomaterials (CNMs) [Szabó *et al.,*2010] such as, chemical vapour deposition (CVD), catalyst chemical vapour deposition (CCVD), laser ablation, arc discharge, sol gel method and by a simple pyrolysis method or carbonization.

The carbon nanotubes and most other CNMs are prepared using petroleum products. It is a well-known fact that these materials are non-renewable and likely to get exhausted in the near future. Today, there is a growing need to utilize agro-waste for production of CNMs to make the process carbon neutral.

Saw dust,corn leaf, rice husk, wood fiber and coconut shell are some of the agro-wastes used for the preparation of CNMs [Fathy *et al*.,2020; Thangadurai *et al*.,2021]. In the current study, Banana leaves were employed in the synthesis of CNMs.

Carbon has many allotropic forms because of its electronic configuration [Delhaes,2001]. CNMs represent some of carbon's exceptional allotropes. These allotropic forms have various chemical and physical properties. One of the optimal properties of CNMs is their high specific surface area (SSA).

Various methods, including chemical activation and decoration of nanometals contribute to the increase in SSA of CNMs [Yoon *et al.,*2004]. The high surface area proves beneficial for removal of toxic metal ions [Liu *et al*.,2018].

Various industrial wastewater releases contribute numerous toxic metal ions, leading to water pollution when discharged into water bodies without proper treatment. These non-biodegradable metal ions persist in the environment, exacerbating water pollution concerns.

Pb, Cr and Co are some of the toxic metal ions harmful to human and the environment [Mahurpawar, 2015]. The current imperative is the removal of toxic metal ions from wastewater to address environmental concerns. There are many methods for the removal of such metal ions [Fenglian and Wang,2011], like chemical precipitation [Motsi *et al*.,2009] ion exchange [Gode and Pehlivan,2006], adsorption [Taffare and Rubio,2009], reverse osmosis, coagulation and flocculation, flotation and extraction, irradiation, electrochemical treatment, advanced oxidation processes and biosorption processes. But among these, adsorption by using CNMs synthesized by agro-waste, stand out as a fundamental, efficient and cost-effective approach for removal of toxic metals. [Burakov *et al*.,2018]

In the present work, CNM decorated with nanometals was prepared from banana leaf (agro-waste). By analysis, it was found that the CNM removed Pb^{2+}, Co^{2+} and Cr^{6+} ions to a good extent. The efficacy of these depends on pH of metal ions solution.

II. EXPERIMENTAL TECHNIQUES

All the chemicals used in the entire work were of AR grade.

1) Preparation of CNMs decorated with nano metals from banana leaf

Banana leaf derived CNMs were crafted in the current study. Banana leaves were collected from near-by farms. The leaves were pyrolyzed in an inert atmosphere. The carbon obtained was activated by using NaOH solution and was decorated with copper nanometals in presence of CO_2. By analysis it was found that the CNM was highly porous in nature and had a high SSA.

2) Removal of toxic metal ions

For the preparation of Pb, Cr and Co metals ions solution, 1000 ppm of $Pb(NO_3)_2$, $K_2Cr_2O_7$ and $Co(NO_3)_2$ was prepared respectively. The required range of 10-15 ppm metal ion solutions were prepared by dilution. 0.1 g of synthesized CNMs and 10 cm^3 metal ion solution was used for analysis. pH of metal ions solution ranges from 1-6 pH were adjusted by using hexamine powder and conc.sulfuric acid. The analyte was agitated on an agitator for half an hour. The final concentration of metal ion was determined by using ICPAES.

The percentage removal of toxic metal ions was calculated by initial and final concentration of metal ions. [Jie Ma *et al.,*2019; Shukla and Shukla,2013]

$$\% \text{ removal of toxic metal ions} = [C_i - C_e] / C_i \times 100$$

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

III. RESULT AND DISCUSSION

By studying the effect of pH, CNMs decorated with nanometals prepared from banana leaf shows 94%, 92% and 80 % removal of Pb^{2+}, Co^{2+} and Cr^{6+} ions, respectively.

1) Effect of pH on removal of toxic metals ions

pH of metal ions solution plays a crucial role in the removal of the metal ions by using CNMs decorated with nanometals [Maslova,2021]. In this case, the maximum percentage removal of Pb^{2+} and Co^{2+} ions were observed at pH 6, and in the case of Cr^{6+} metal ions maximum percentage was removed at pH 1. [Khan *et al.,*2001; Padmavathy *et al.,*2016]

In the case of Pb^{2+} and Co^{2+} ions, at higher pH low proton density in solution, so a more active site was available on CNMs decorated with nanometals for adsorption of metal ions that is removal of metal ions. But in the case of low pH more proton density in the solution so a less active site was available on CNMs decorated with nanometals for removal of metal ions.

But in the case of Cr^{6+} ions, it existed as $HCrO_4^-$ ions and CrO_7^{2-} ion at pH 1-3, so it can be adsorbed on CNMs decorated with nanometals easily and at higher pH such negative ions did not form due to suppression of hydrolysis Cr^{6+} ions which was responsible for less percentage removal of Cr^{6+} metal ions. [Anah and Astrini,2017]
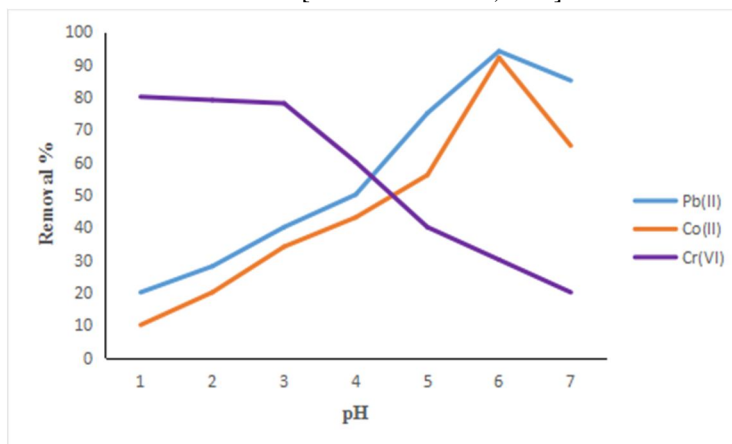

Fig. 1 Effect of pH on % removal of Pb^{2+}, Co^{2+} and Cr^{6+} ions by CNMs decorated with nanometals
(Initial concentration of Pb^{2+}-12.45 mg L^{-1}, Cr^{6+}- 13.95 mg L^{-1} and Co^{2+}- 14.286 mg L^{-1})

2) Characterization Of Carbon Nano Materials

a) Scanning Electron Microscopy (SEM)

By using SEM surface morphology and topography was studied. [Thomas,1986]. It shows fibers like structure of CNMs decorated with nanometals. Nanometal distributed all over the CNMs, having size 35-75 nm.
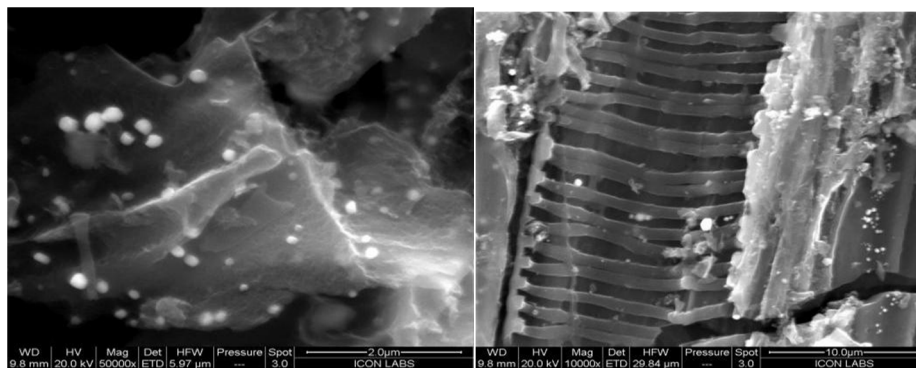
Fig. 2(a)   Fig.2(b)

Fig 2 (a) and (b)SEM images of CNMs decorated with nanometals

b)   High-resolution transmission electron microscopy (HRTEM)

Fig 3 (a) and (b)show structural features of CNMs decorated with nanometal. Fig 3(a) show fiber like structures having 40-50 nm diameter, fig 3(b) shows decorated copper nanometals having sizes 35 to 75 nm.
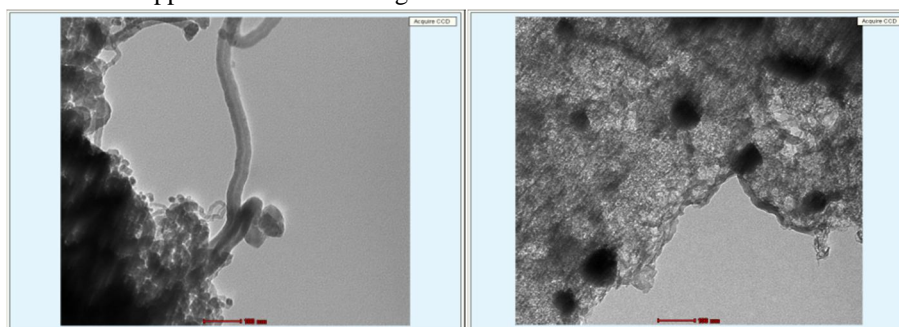

Fig.3(a)   Fig.3(b)

Fig 3(a) and (b) HRTEM of CNMs decorated with nanometals

c)   X-Ray Diffraction (XRD)

XRD shows one broad peak at $2\theta = 23.5^0$ shows amorphous carbon, which was graphene oxide. It also shows three sharp peaks at 43.118^0, 50.26^0 and 73.92^0 corresponding to planes (111), (200) and (200) indicated copper nanometals. (JCPDS, copper file no.9013014). [Zhu *et al.,*2008; Yong *et al.,* 2007; Theivasanthi and Alaga, 2010]
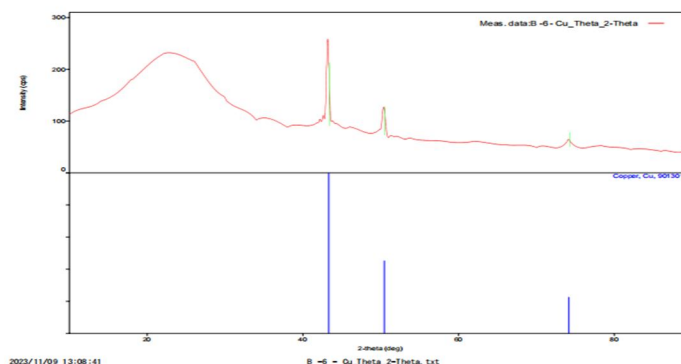

Fig.4 XRD of CNMs decorated copper nanometals

d)   BET

From BET analysis the SSA of CNMs decorated with nanometals prepared from banana leaf was found to be 534.259 m^2gm^{-1} and total pore volume 0.2919 ccg^{-1}. Such a large surface area was helpful for the removal of toxic metal ions. It was found that the decoration of copper metal on CNMs, increases the SSA of nanomaterials.

IV. CONCLUSION

In the present work, a novel CNMs decorated with nanometals was prepared from agro-waste banana leaf. Due to their porous nature and high SSA, by using low dose of CNMs decorated with nanometals were able to remove toxic metal ions such as Pb^{2+}, Co^{2+} and Cr^{6+}. Efficiency of removal of Pb^{2+}, Co^{2+} and Cr^{6+} ions were found to be 94%, 92% and 80% respectively at pH 6 for Pb^{2+} and Co^{2+}, and for Cr^{6+} pH was 1.

V. ACKNOWLEDGEMENT

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