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Biomass-Derived Metal Oxide Nanocomposite Adsorbents for the Purpose of Sequestering Heavy Metals from Wastewater Effluent

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Abstract—*In this study, advanced biomass-derived adsorbents, particularly bio-nanocomposites sourced from corncobs, were investigated for their effectiveness in eliminating heavy metals from wastewater. Modification of these adsorbents with metal oxides resulted in a remarkable increase in their capacity for heavy metal removal, surpassing existing literature-reported capacities. Characterization via FE-SEM, BET and FTIR techniques provided insights into the structural and surface properties of these adsorbents. The unmodified corncob adsorbents exhibited notable adsorption capacities for chromium (VI), further significantly improved after metal modification, reaching outstanding levels of adsorption capacities. These findings highlight the potential of these modified adsorbents as highly efficient solutions for addressing heavy metal pollution in wastewater treatment applications.*

Keywords: *Metal oxide nanocomposites; Biobased nanocomposites, Adsorption capacity.*

"1. INTRODUCTION"

Heavy-metal contamination is a major environmental issue due to non-biodegradable pollutants [1]. Industrial effluent with significant heavy metal concentrations pollutes water and soil [2]. Lead (Pb), cadmium (Cd), Chromium (Cr) and nickel (Ni) are the most toxic heavy metals, causing environmental and health issues even at low quantities.Adsorption method for heavy metals removal from wastewater has gained popularity in recent years due to its low cost and high efficiency [3-5]. A by-product of biomass pyrolysis, biochar possesses a number of physicochemical features that make it an effective adsorbent for removing and fixing heavy metals in water. The adsorption of heavy metals by metal oxide nanocomposites-treated biochar is highly promising due to its enhanced micro- and nanopores, aromatic structures, surface adsorption sites [6].

Biochar's physicochemical qualities, and therefore its heavy metal adsorption capability, can be affected by the type of biomass raw materials used, pyrolysis temperature and metal nanoparticle modifications [7-9]. The characteristics of biochar are remark-ably modified by the pyrolysis temperature, heating rate, and residence time and metal oxide incorporated [10,11]. The adsorption performance is heavily influenced by factors other than the physi-cochemical characteristics of the wood metal nanocomposites, such as coexisting chemicals, the biochar dose, the adsorption period, the adsorption temperature, and the starting concentration. In addition, understanding the adsorption mechanism will allow for the modification of nanocomposites to enhance their adsorption ability. Indeed, bio-chars' use in heavy metal adsorption and the processes behind it have been the subject of much research [12–14]. A survey of the relevant literature, however, reveals that much research has been devoted to comparing the before and after adsorption states morphologically and qualitatively.

In order to fill this knowledge gap, the purpose of this research was to explore methodically the physical, chemical, and morphological properties of metal oxide nanocomposite adsorbents produced from corncob and formed by pyrolysis at a variety of temperatures. In addition to this, the adsorption capabilities of corncob-based metal oxide nanocomposites and unmodified corncob adsorbents were investigated for chromium (VI) in wastewater. This study offers valuable insight into the thorough recycling and use of biomass waste as well as treatment of wastewater.

"2. MATERIALS AND METHODS"

2.1 Materials

Ripe corncob were collected from the Kanpur district of Uttar Pradesh, India. Individual heavy metal stock solutions of Cr(VI) of concentration 100 mg/L each were made using $K_2Cr_2O_7$ and analytical grade ingredients obtained from Merck (Mumbai, India). For both the individual and multi-component investigations, the following volume of heavy metals solutions was created in deionized water with adequate dilution.

2.2 Preparation of adsorbents

The synthesis of different adsorbents has been schematically shown in Fig. 1. The corncobs were used as a starting material for the preparation of adsorbents. The ripened corncobs were washed thoroughly to remove dust particles and chopped into small pieces. The raw materials were dried for 24 hours in an oven at 100°C and pulverized to obtain particles of around 10.0 mm size. For the bio-nanocomposite, Fe_2O_3 nanoparticles (1% by weight) were added and mixed well. The powdered biomass was pyrolyzed in a tubular pyrolizer under N_2 atmosphere. The pyrolysis temperature was raised to 400°C, 500°C, and 600°C at a rate of 10°C·min^{-1} and held for 1 h. The biochar was transferred to desiccators after cooling below 100°C inside the reactor. Biomass-metal oxide nanocomposite was stored in airtight containers for future experiments.

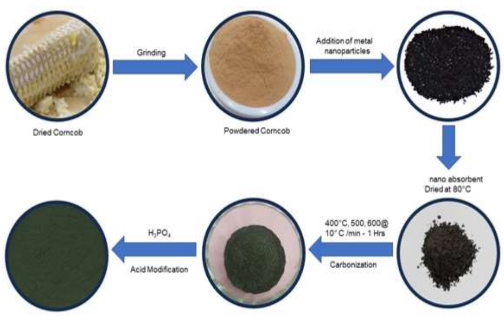

Figure 1: The procedure for making metal-nano adsorbents.

2.3 Preparation Adsorbent characterization

The morphological properties of the adsorbents were examined using a field emission scanning electron microscope (FESEM). The surface area and pore size analysis was performed using Brunauer–Emmett–Teller (BET). With the use of Fourier transform infrared spectroscopy (FTIR) the functional groups included in the samples were verified.

"3. EXPERIMENTAL STUDIES"

The goal of the analysis was to determine how different process parameters affected the adsorption phenomena for both unmodified corn cob and corncob metal nanocomposites. Many parameters were examined: pH (A: 3–7), initial metal concentration (B: 10–50 mg/L), adsorbent dose (C: 0.05–0.5 g/L), temperature (D: 20–50 °C), and contact time (E: 5–90 min) but initial metal concentration was studied in detail and presented in this study. Additionally, the samples were filtered and subjected to atomic absorption spectroscopy to determine residual heavy metal concentrations.

"4. RESULTS AND DISCUSSIONS"

The percentage of chromium (VI) removal 'R' and q_e (mg/g) that is amount of metals adsorbed per unit of the mass of the adsorbent were determined using the formula (1) & (2). [15-17]

Removal of Cr (VI) (%)

$$R = (C_i - C_e/C_i)100 \quad (1)$$

Cr (VI) adsorbed

$$(q_e) = (Ci - C_e/M)\,V \quad (2)$$

Where Ci and C_e (mg/L) are initial and equilibrium concentrations, V is volume of solution (L) and M is the weight of adsorbents (g).

4.1 FTIR Analysis

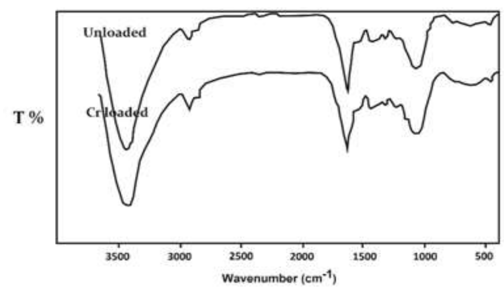

Figure 2: FTIR spectra of corncob-metal oxide nanocomposite & corncob-metal oxide nanocomposite loaded with Cr(VI).

The functional groups contained in the corncob biomass are shown by the peaks of different wavelengths in Figure 2: 3543 cm -1 (hydroxyl (–OH) or amine (–NH)), 2962 cm -1 (–CH), 1642 cm -1 (C=O), and 1068 cm -1 (C-O or C-N). Reduced peaks appeared on the biomass surface following the adsorption of Cr(VI), suggesting that the Cr (VI) ion may have bound to amines, carboxyl, carbonyl, and aliphatic interactions[18-21].

4.2 SEM Analysis

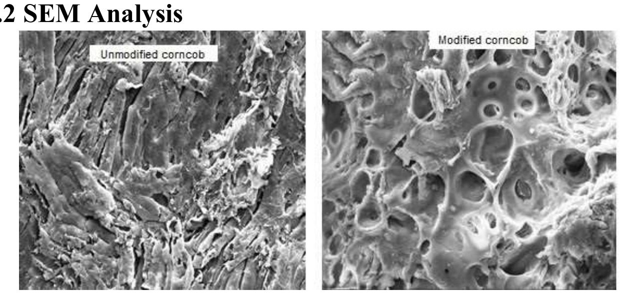

Figure 3: Scanning electron images of (a) unmodified corncob (b) modified nanocomposites corncob.

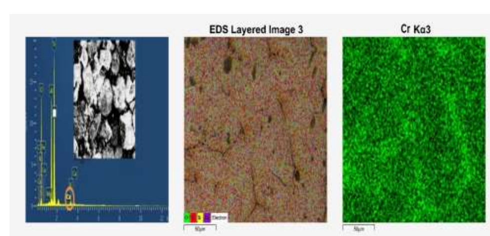

Figure 4: SEM micrographs and SEM-EDX of modified nanocomposites corncob loaded with Cr(VI) along with metal mapping.

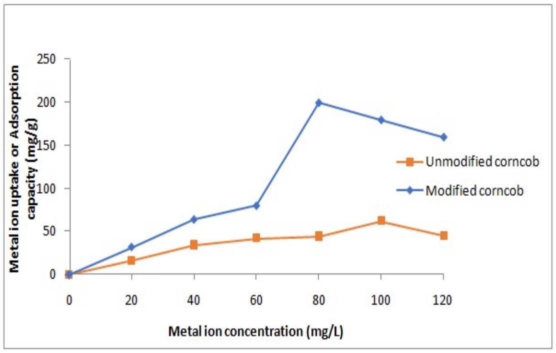

Figure 5: Effect of initial metal concentration on adsorption Cr (VI) on to unmodified and modified corncob biomass.

The adsorption capability rises with increasing chromium metal ion concentrations. Adsorption capacity improves as a result of a decrease in the mass transfer barrier between metal ions and biosorbents, as seen in figure 5. It is evident that the adsorption capacity nearly tripled at a concentration of 80 mg/L. This shown that biobased metal oxide nanocomposites are a good material with a high yield for adsorbing heavy metals.

"5. CONCLUSION"

In this research, advanced adsorbents derived from biomass, specifically bio-nanocomposites derived from corncobs, were systematically studied for their efficacy in the removal of heavy metals from wastewater. The augmentation of these adsorbents with metal oxides resulted in a noteworthy augmentation of their heavy metal removal capacity, surpassing the capacities reported in existing literature. The unaltered corncob adsorbents demonstrated significant chromium (VI) adsorption capacities, which were further enhanced approximately threefold post-metal modification, achieving exceptional levels of adsorption capacity. These outcomes underscore the potential of these modified adsorbents as highly effective remedies for addressing heavy metal pollution in the realm of wastewater treatment applications.

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