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Low cost synthesis of SiO_2/C nanocomposite from corn cobs and its adsorption of uranium (VI), chromium (VI) and cationic dyes from wastewater

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ABSTRACT

SiO_2/carbon nanocomposite as well as nanoporous carbon has been synthesized using a simple, low cost, industry scalable method from corn cob biowaste. The composition and morphology of the materials have been confirmed via powder XRD, Raman, FTIR, TEM, EDS and XPS studies. The BET specific surface area of both samples has been obtained and the pore volume analyses has been done using BJH method. The prepared nanocomposites have been explored as a novel adsorbent for Methylene blue (MB) dye and U(VI)/Cr(VI) ions from aqueous solution. Different operating conditions of time, pH, initial dye/metal ion concentration and adsorbent amount have been investigated and the results indicate a promising adsorption capacity for all three pollutants. The kinetics data were fitted with pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion and Bangham's kinetic models. The adsorption isotherms were tested with Langmuir, Freundlich, Tempkin and Dubinin & Radushkevich isotherm models. SiO_2/carbon nanocomposite shows a maximum uptake capacity of 255.12 mg/g for U(VI) and 90.01 mg/g for Cr(VI) with adsorption efficiency of 94.2% and 98%, respectively. The uptake of Cr(VI) ions has also been tested in presence of interfering salts like NaCl/Na_2SO_4. The SiO_2/carbon nanocomposite shows adequate reusability making it a cost effective alternative sorbent compared to commercial activated carbon.

1. Introduction

With rapid urbanization, water pollution is becoming a source of increasing concern. The surface water as well as groundwater gets polluted due to agricultural runoffs and untreated industrial and domestic wastes. The major components in polluted waste water are mostly organic chemicals like dyes, pesticides, fertilizers and also heavy metal ions which originate from industries related to textiles, chemicals, mining, tanning, metallurgy, etc. [1]. Most of these pollutants are non-biodegradable in nature which leads to further complications in the clean-up process. Conventional methods like chemical oxidation, membrane processes, coagulation-flocculation, ion exchange, liquid-liquid extraction, electrolytic recovery, etc. are routinely used for treatment of wastewater [2]. However, most of these techniques are either expensive or ineffective when the contaminants are present in low concentration [3,4]. Currently sorption is considered to be a better method for wastewater remediation since it a comparatively cheaper, simpler, and efficient technique in terms of land requirement, infrastructure set up and design [5]. Activated carbon with its porous structure and high specific surface area is considered to be the best sorbent for most of the above-mentioned water pollutants [6]. However, the high cost of commercially produced porous activated carbon via physical or chemical activation process makes its large scale application relatively expensive [7]. To reduce the cost of production, various biowastes have been identified as a good source of activated carbon [8]. Biowastes encompass mostly agricultural waste like nut shells, fruit peels, inedible parts of plants, etc. Consequently, sorption studies on biowaste derived activated carbon has gained prominence in recent years and reported avidly in literature [9]. Corn cob, an agro waste from maize crop cultivation, is a cheap biowaste precursor for activated carbon production. Almost 16% of the maize plant biomass comprises of the waste corn cobs [10]. There are reports on activated carbon synthesis from corn cobs via physical/chemical activation processes which have been used for dye adsorption studies [7,10]. However, reports on use of corn cob derived activated carbon for heavy metal ion adsorption is relatively scarce [11,12].

Nanoporous silica is another sorbent that has been extensively studied due to its high surface area and porous structure which facilitates the sorption process [13]. Its high thermal and hydrothermal stability makes it a robust sorbent material [14]. Efficient sorption of dyes and heavy metal ions by amorphous silica has been reported in literature

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[15,16]. The synthesis of mesoporous silica is generally done using the Stöber process which has been duly modified over the years to yield diverse morphologies like nanocubes, twisted nanorods, etc. [17]. However, in nature, silica is synthesized in various morphologies under ambient conditions [18,19]. The mechanism of bioaccumulation of silica in plants is a well-studied process and many plants sequester silica to the extent of 1–25% on their dry matter basis [20–22]. Corn cob ash has been reported to contain 40–60% of silica by mass and hence can be used as a low cost bio resource [23].

In this work a simple method for low cost synthesis of SiO_2/C nanocomposite from corn cobs has been developed and its sorption affinity for various pollutants like dyes (Methylene blue (MB)) and heavy metal ions (Cr(VI) and U(VI)) has been studied. Generally, carbon nanocomposites have been reported to have better sorption properties compared to their pure carbon counterparts due to the presence of more number of functional groups [24]. In our case, the sorption property of SiO_2/C nanocomposite has been compared to that of pure activated carbon obtained similarly from corn cobs. MB which finds extensive application as colorants in textile and food industry was chosen as the model dye pollutant for sorption studies as it is known to be carcinogenic and neurotoxic [25]. Biological remediation is a time-consuming process for this dye and hence sorption is a better technique for its removal from waste water. Chromium (VI) which is widely used in paint, textiles, anticorrosion coating industries is extremely toxic and carcinogenic and has been listed internationally as one of the prime water contaminants [26]. According to US EPA, the permissible limit for Cr(VI) is 0.1 mg L^{-1} and 0.05 mg L^{-1} in industrial wastewaters and drinking water, respectively [27]. Removal of Cr(VI) from water via adsorption on agro waste based carbon is a cost effective solution and hence the sorption capacity of our SiO_2/C nanocomposite from corn cobs for Cr(VI) uptake has been tested. U (VI) is another toxic and radioactive heavy metal ion which is released into the environment through numerous sources, such as natural deposits, fertilizers, nuclear industries, etc. [28]. When low amount of uranium enters the bloodstream, it tends to bioaccumulate in bone tissues and its affinity for phosphate renders it harmful for the organism. The permissible level of uranium in drinking water is 30 μg L^{-1}. Adsorption of uranium ions is challenging as its exists in various cationic (UO_2^{2+}, UO_2OH^+, $(UO_2)_2(OH)_2^+$) and anionic ($[UO_2(CO_3)_3]^{4-}$) forms in different pH and hence a single sorbent is not quite effective for its complete removal from the system [29]. Uptake of U(VI) has been reported on mesoporous carbon obtained from natural polymers and also on amidoxime functionalized SiO_2 microspheres [30,31]. Hence it was of interest to study the U(VI) adsorption efficiency of our corn cob derived SiO_2/C nanocomposite. The details of this work are reported herein.

2. Experimental

2.1. Material synthesis

The corn cobs used in this work were gathered from local market in Mumbai, India. The corn cobs were washed thoroughly with water to remove all the dirt and foreign particles which could influence the final composition of the material. The cleaned corn cobs were dried under sun for 24 h till constant weight was achieved before carbonization. The dried cobs were powdered and heated at 500 °C for 2 h in an oxygen starved atmosphere in an alumina boat in muffle furnace. The residue was washed repeatedly with water, filtered out and dried in air. This sample has been named as SiO_2/CCNC. A portion of SiO_2/CCNC powder was stirred in NaOH solution (2N) for 1 h, filtered and then washed with distilled water till the filtrate turns neutral. The residue was air dried and this sample has been named as CCNC.

2.2. Characterization

X-Ray diffraction (XRD) measurements were done using monochromatized CuKα radiation ($\lambda = 1.5406$ Å,) on a Philips Instrument (scan rate 0.02°/s, $10° \leq 2\theta \leq 80°$). The instrumental line broadening was corrected using silicon as an external standard. The Infrared spectra were taken in the JASCO FTIR (V-610) spectrophotometer with KBr pellets. Microstructure of the materials was analyzed using scanning electron microscope (model: AIS 210, Mirero Inc., Seongnam-si, South Korea). Energy-dispersive X-ray spectra (EDS) were taken on an Inca Energy 250 instrument attached to it. Elemental analysis (C,H,N,S,O) was carried out using Eurovector-EA3000 instrument. The basic and acidic groups on the surface of SiO_2/CCNC and CCNC was quantified by applying the Boehms titration method [32]. Conventional TEM micrographs were recorded on Carl Zeiss instrument operating at 120 keV using carbon coated copper grids. The specific surface area was determined using a Bel Japan Inc., Belsorp II surface area analyzer by measuring N_2 adsorption and adopting the well-known BET procedure. The XPS analysis was carried out on SPECS X-Ray Phototelectron Spectroscopy (XPS) setup equipped with a PHOBIOS 100/150 Delay Line Detector (DLD) using Al-K_α (1486.6 eV) dual anode source (385 W) A base pressure of $<10^{-8}$ m bar was maintained in the experimental chamber throughout the measurement period. The UV–vis absorption spectra were recorded using Shimadzu 1650PC instrument.

2.3. Adsorption experiments

2.3.1. Methylene blue adsorption

A stock solution of 100 mg/L of MB was prepared. For finding out the equilibrium contact time (adsorption kinetics), 10 mg of activated carbon was added to 25 ml MB dye solution (10 mg/l) and the supernatants were withdrawn by a syringe (~5 ml) at predetermined time intervals up to 140 min. The process of sorption is affected by the solution pH and to study this, the pH values of the dye solutions were varied from 1 to 9 using 0.1 M HCl or NaOH solution. To study the adsorption isotherms, different concentrations of the dyes solutions (5, 10 and 15 mg/l) were prepared. After equilibration, the amount of dye left behind in solution was measured spectrophotometrically by checking the absorbance at 668 nm. An average data of three identical sets of experiments have been used. During the MB dye sorption experiments, the temperature was kept steady at 25 °C using an isothermal shaker. The effect of temperature on the adsorption capacity of both sorbents was studied by increasing the temperature to 35 °C and 45 °C while keeping all the other operating parameters constant.

2.3.2. Methylene blue desorption

The dye sorbed sorbent was separated from the solution by centrifugation and dried in air. It was then suspended in 25 ml distilled water maintained at pH ranging from 1 to 9 and agitated via ultrasonication for exactly the same time period it was held during the sorption process. The sorbent was separated via centrifugation and the concentration of the dye desorbed was analyzed via UV–visible spectroscopy.

2.3.3. U(VI) adsorption

200 mg/l of uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$ solution was used as the source of U(VI) ions. This stock solution was diluted accordingly for the adsorption experiments. In a typical experiment, 30 mg of adsorbent was added 50 ml of 100 mg/L [$UO_2(NO_3)_2 \cdot 6H_2O$] solution and stirred for 2 h while maintaining the pH at ~5 by adding dilute ammonia solution. The supernatant collected after centrifuging was treated with Arsenazo III (0.05%) and the residual U(VI) concentration was calculated using UV–visible spectroscopy by measuring the absorbance at 656 nm.

2.3.4. Cr(VI) adsorption

The stock solution was 100 mg/l of potassium dichromate ($K_2Cr_2O_7$) solution which was diluted suitably for preparation of calibration curve and for use in the adsorption experiments. 10 mg of adsorbent was added to 50 ml of 50 mg/L dichromate solution and stirred for 4 h at