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Efficient adsorption of chlorpheniramine and hexavalent chromium (Cr(VI)) from water system using agronomic waste material

Arush Sharma[a], Kamal Kishor Thakur[a], Pankaj Mehta[b], Deepak Pathania[b,*]

[a] Shoolini Institute of Life Sciences and Business Management, Solan 173212, Himachal Pradesh, India
[b] Department of Environmental Sciences, Central University of Jammu, Rahya-Suchani, Bagla Distt., Samba 181143, Jammu and Kashmir, India

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ABSTRACT

In present study, we report *Cornulaca-monacantha* stem (CS) and its activated carbon (CS-AC) for the removal of Cr(VI) and chlorpheniramine (CP) from aqueous system. The chemical composition and surface characteristics of samples were investigated using instrumental techniques such as Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX). The surface area was determined by Brunauer-Emmett-Teller(BET) method. The BET surface area of CS-AC (288.67 m^2/g) was found higher as compared to CS adsorbent (47.58 m^2/g). The adsorption behavior of adsorbates was extremely dependent on the solutions pH. The maximum uptake for Cr(VI) and CP were observed at pH of 2.0 and 8.0, respectively. The equilibrium data adequately follow the Langmuir isotherm (R^2 = 0.98–0.99), suggesting the monolayer sorption of adsorbate molecules. Kinetic investigations indicated that sorption behavior of Cr(VI) follow the pseudo-second-order model. While in case of CP, both pseudo-second-order and Elovich model provides the higher value of regression coefficient (R^2). This revealed the chemical adsorption of adsorbate molecules. Thermodynamic study indicated the feasible, spontaneous and endothermic sorption of adsorbate molecules. The regeneration study implies that adsorbent was efficiently recovered from Cr(VI) and CP under different desorbing agents.The CS-AC adsorbent was possess 89.19% and 88.45% uptake for Cr(VI) and CP after 5th cycles of desorption-adsorption, respectively. Finally, we summarize that prepared adsorbent (CS-AC) is highly proficient, versatile and cost-effectively explored for Cr(VI) and CP decontamination from water system.

1. Introduction

The increasing demand for energy,reckless utilization of various resources and industrial world have been chieflyresponsible for the serious environmental disaster (Pan et al., 2018; Ahmad and Majid, 2018; Zhang et al., 2017a, b; Song et al., 2017). These environmental crisis imposed threats to the entire bionetwork. A variety of noxious organic and inorganic pollutants are released into the aquatic system, which pollutes the aquatic system. The most hazardous pollutants, that affects the environment includes heavy metals and emerging contaminants (ECs) (Vu et al., 2017; Lv et al., 2014; Dashairya et al., 2018; Ma et al., 2017; Huang et al., 2017; Hu et al., 2017). These contaminants are globally-circulated and frequently detected in the groundwater. During last decades, exploitation of various heavy metals definitely increased the concentrations of metal ions in the aquatic and terrestrial system (Saber-Samandari et al., 2014; Wu et al., 2018). The continual liberation of huge amount of metal ions into water system poses adverse effects on entire ecosystem (Gupta et al., 2013a, b, c, d). Therefore, heavy metals are of great concern due to non-biodegradable and persistent nature (Li et al., 2012).

Chromium and its compounds are broadly used in various technological sectors and textileindustries.Chromium exists in a number of oxidation states ranged from +2 to +6. The trivalent and hexavalent forms of chromiumare only the oxidation states, which found environmentally (Gupta et al., 2013a, b, c, d). Cr(III) is less toxic than Cr (VI) because of very low tendency to bioaccumulate in human body. Recent investigation indicates that 99% of Cr(III) ingested orally must be recovered in faeces (Choi et al., 2009). Hence, the trivalent form of chromium is weakly absorbed and easily excreted.However, hexavalent chromium has beenconsidered as extremely noxious pollutant by US Environmental Protection Agency (EPA). The consumption of Cr(VI) contaminated water causesvarious illnesses such as chromium poisoning, lung cancer,liver necrosis, brain damage,premature death and kidney problems etc. (Yan et al., 2016; Bhaumik et al., 2011; Lingamdinne et al., 2017). EPA recommended thattolerance limits for Cr(VI) is 0.1 and 0.05 mg/L for inland surface and portable water, respectively. However, effluents emission from various industries frequently contain higher amount than approved by EPA. Hence, it is

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[*] Corresponding author.
E-mail addresses: deepakpathania@cujammu.ac.in, dpathania74@gmail.com (D. Pathania).

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necessary to decrease the concentration of Cr(VI) to the acceptable level before discharging into aqueous system.

Among emerging contaminants (ECs), CP is a first-generation antihistamine drug usually commercialized in salt formwith maleate. It is used for reveling the symptoms of various allergic reactions. The major concern for the removal of CP is mainly due to its higher solubility, rapid dissolution rate and greater permeabilityaccording to biopharmaceutics classification system (Xia et al., 2014). Additionally, CP is converted into another more toxic byproduct such as nitrosaminesand it is proved to be highly carcinogenic chemical (C.M. Li et al., 2017; Y. Li et al., 2017). However, emerging contaminants frequently detected in the waste of various pharmaceutical products.

Adsorption is an economical viable method for the removal of pollutantsfrom aquatic system (Pathania et al., 2016; Ali et al., 2016; Jiang et al., 2017). It involves the shifting of pollutant molecules from aqueous phase to a solid phase. Therefore, adsorptional treatment meets the economic aspects with higher effluent standards and water reuse requirements (Kadu and Chikate, 2013). Hence, it has beenpreferred overconventional techniques in terms of cost, ease of operation, flexibility, negligible disturbance with diurnal variations, technical feasibility and reusability (Baccar et al., 2010; Liao et al., 2012). Activated carbon (AC) is mostly explored adsorbent due to higher surface area, chemical reactivity and greater degree of porosity (Tovar-Gómez et al., 2015). But, due to its high-cost, long duration heating and difficult to regenerate, attempts are needed to findcost-effective substitute. Natural or agronomic materials, which are present in bulk quantities offers low-cost and discarded without any expensive regeneration (Cheng et al., 2018). Thus, abundance and availability of lignocellulosicmaterials obtained from variousagronomic products make them excellent precursors for the preparation of activated carbon (Sayğılı et al., 2015; Sayğılı and Güzel, 2016). Activated carbon (AC) prepared from the agronomical materials possess higher surface area, chemical reactivity and greater degree of micro-porosity and hence, efficiently explored as adsorbent for toxic pollutants from water system.

Alternatively, new biomaterial namely *Cornula camonacantha* is a cost-effective, renewable and eco-friendly lignocellulosic material and employed as precursor material for the preparation of activated carbon. It is a species of flowering plant and woody shrub grows upto 60 cm height. To the best of our knowledge, no study has been described on the use of CS and its AC as an adsorbent for the remediation of Cr(VI) and CP from water system.

Herein, we describes the adsorption of Cr(VI) and CP from aqueous system using CS and its activated carbon (CS-AC). The microstructure and chemical compositions were investigated by FTIR, FESEM, EDX and BET instrumentations. The adsorption isotherms (Langmuir, Freundlich and Tempkin model) and kinetic models (pseudo-first-order, pseudo-second-order, Elovich and diffusion model) have beeninvestigated. Furthermore, various thermodynamic parameterhave been studied to explain the physisorption and chemisorption mechanism.

2. Experimental

2.1. Chemicals

The Potassium dichromate ($K_2Cr_2O_7$) and chlorpheniramine maleate (CP) salt were purchased from SigmaAldrich, India (purity > 99%). Sodium hydroxide (NaOH), sodium hypochlorite (NaClO) and nitric acid (HNO_3) were supplied by CDH Pvt. Ltd. India. The stock solutions of Cr(VI) and CP (1000 mg/L) have been prepared by dissolving required amount of salt in double distilled water. All glassware were well-cleaned, rinsed with deionized water and oven dried at 50 °C.The working solutions were prepared from stock solution using double distilled water.

2.2. Preparation of adsorbent

C. monacantha stem was obtained from the plant situated in the desert of Saudi Arabia. The stem was thoroughly washed with deionized water to remove the contaminant particles and dried in oven at 65 °C for 24 h. Then, it was slashed into small pieces and sieved to uniform particles size. It was then divided into two parts: the first part was used for the sorption experiment and designated as “CS”. While, second part undergoes carbonization process under nitrogen atmosphere by taking 20 g of dried CS into the muffle furnace. It was heated at 600 °C for 10 min. The carbonized product was then chemically activated. It was dipped into the mixtures of NaOH (6%) and NaClO (5.6%) at 1:1 ratio and placed under microwave irradiation (550 W) for 6 min. The resulting product was withdrawn, filtered and continually washed with distilled water until the pH of final product reached to neutral point. Subsequently, it was dried, leveled as “CS-AC” and stored in airtight vessel for subsequent experiments.

2.3. Instrumentation

TheShimadzu UV-1601 double beam UV-visible (UV-vis) spectrophotometerwas used to determine the concentrations of Cr(VI) and CP in aqueous phase. pH measurements were conducted on ELICO model LI-127, India. Fourier transform infrared (FTIR) spectra of biomaterials before and after sorption of CP were recorded by KBr pallet using Perkin Elmer-Spectrum RX-IFTIR spectrophotometer in the range between 4000 cm^{-1} and 350 cm^{-1}. The surface area analyzer Brunauer-Emmett-Teller (BET) method was employed for the measurement of surface area, pore diameter by ASAP 2020. The instrument was equipped with two independent vacuum systems, where sample preparation and sample analysis occur simultaneously having relative pressure ranged from 0.0 to 1.0. Samples were usually degassed at 250 °C for 5 h in prior to BET investigations. The morphology of samples were studied over field-emission scanning electron microscope (FESEM) using JEOL-JSM-7001F instrument. The adsorption of Cr(VI) onto samples were tested by energy dispersive X-ray (EDX) equipped with FESEM instrument.

2.4. Equilibrium experiment

The adsorption of Cr(VI) and CP were investigated using batch experiments. Typically, a known amount of adsorbent was taken into the 100 mL aqueous solutions of Cr(VI) and CP having initial concentrations ranged from 20 to 140 mg/L. These solutions were prepared in 250 mL of Erlenmeyer flasks and mixtures were agitated on PT-622 incubator shaker at 185 rpm for definite contact time. The pH of adsorbate phase was adjusted by adding few drops of 0.1 N HNO_3 or 0.1 N NaOH. At predetermined time, flasks were withdrawn from the shaker andcentrifuged at 5500 rpm for 10 min to remove the adsorbent particles from aqueous phase. The residual concentrations of supernatant Cr (VI) and CP solutions were determined by UV-vis spectrophotometer at their respective λ_{max}. The remaining concentrations of Cr(VI) in supernatant liquor was measured bycolorimetric method using 1,5-diphenylcarbazide as a complexing agent under acidic medium at $\lambda_{max} = 540$ nm. While, equilibrium concentrations of CP were analyzed spectrophotometrically at 265 nm.The adsorption experiments have been performed in triplicate and average values were reported. The equilibrium study was conducted using different initial concentrations (20–160 mg/L), contact time (15–135 min) and different temperature (30–65 °C). The adsorption capacity q_e (mg/g) and % adsorption of Cr (VI)and CP were calculated using following Eqs:

$$q_e = \frac{(C_0 - C_e) \quad V}{m} \tag{1}$$