



Detoxification of hexavalent chromium using hydrothermally modified agricultural detritus into mesoporous zeolitic materials



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ABSTRACT

The present study reports the removal of hexavalent chromium by bagasse fly ash (BFA) – an agricultural detritus and synthesized modified zeolitic materials. The native BFA was successfully converted into mesoporous zeolitic materials with (ECZBFA) and without electrolyte (CZBFA) media using hydrothermal treatment. The proximate analysis and physicochemical analysis were determined by wet analysis methods. The instrumental techniques like XRF, FTIR and SEM were used to determine the chemical composition of sorbents, functional groups and its surface morphology, respectively. The optimum pH, contact time, sorbent dose, initial concentration of Cr(VI) and effect of temperature on sorption were investigated thoroughly to optimize the uptake condition. Pseudo second order model and diffusion models like film diffusion and pore diffusion models were well characterized for Cr(VI) sorption on sorbent. Langmuir, Freundlich, Dubinin–Redushkwich and Temkin isotherm were used to understand the efficiency of zeolitic materials and its nature of sorption. Out of the three mesoporous sorbents ECZBFA shows better uptake capacity of Cr(VI) than that of CZBFA and BFA. The uptake of Cr(VI) was studied by batch and column method.

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1. Introduction

Many current researchers have worked towards the removal of heavy metals from industrial waste and wastewater as well as domestic waste water. Many industries discharge the wastewater to outlet stream without giving it proper treatment. Hence discharge of untreated industrial effluents containing heavy metals and other hazardous pollutants cause adverse effects to the environment as they are highly toxic and accumulate throughout the food chain also. Environmental pollution and other environmental problems have become important with increase of world's population and development of industrial applications. Out of many hazardous heavy metals, chromium is considered as a priority pollutant. It occurs mainly in two different oxidation states i.e. Cr(III) and Cr(VI). The chromium having oxidation state III is considered as an essential element for living organism. The recommended safe limit of Cr(III) for human body is 50–200 µg per day by the institute of National Research Council [1]. In contrast, the chromium having oxidation state VI is highly carcinogenic and mutagenic substance for humans [2,3]. The tolerance limits for Cr(VI) is 0.05 mg L⁻¹ in drinking water by the US Environmental

Protection Agency (USEPA) [4,5]. Thus, it becomes very essential to remove Cr(VI) from industrial wastewater before discharging it into other water bodies.

The major sources of Cr(VI) pollution are coming from number of industrial processes like chromate preparation, galvanization of steel, leather tanning, electroplating, dye stuff preparation in textile industries, etc. [6,7]. As the heavy metal pollution creates widespread concern over the cumulative toxicity and the big environmental impact, which led to researchers to develop an effective methods and technologies for its removal. There are several conventional methods available to remove the heavy metal pollution from the industrial waste water viz. chemical precipitation, electrochemical treatment, chemical oxidation or reduction, ion exchange, reverse osmosis and membrane technologies [3,8–12]. These processes may be highly expensive when the concentration of heavy metals is higher in the solution or waste water [13]. Also they have other limitations such as typical operating conditions, less efficiency, production of secondary sludge [14]. On the other hand, sorption is the useful and convenient technique because of its simplicity, technical feasibility, economic viability, and social acceptability. It is conveniently used for the eradication of metal ions from wastewater [15,16].

This study aimed to prepare the low cost sorbents (i.e. zeolitic materials) from the bagasse fly ash – an agricultural detritus, to

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investigate their properties and sorption capacities to detoxify the noxious Cr(VI) from the wastewater. Bagasse fly ash (BFA) was used as raw materials for synthesis of zeolitic materials, because BFA contains silica and alumina which is primary building blocks for preparation of zeolitic materials. In present study, BFA was successfully converted into zeolitic materials with electrolyte media (electrolyte treated conventional zeolitic bagasse fly ash – ECZBFA) and without electrolyte media (conventional zeolitic bagasse fly ash – CZBFA) by hydrothermal treatment. The physicochemical properties such as moisture, loss on drying, ash content, etc. are well characterized. Further the sorbents are characterized by instrumental techniques like XRF, FTIR, PXRD, BET and SEM techniques. The operational parameters viz. effect of pH, contact time, dose, concentration of solution, and temperature are optimized by batch equilibrium studies. The equilibrium data of batch sorption study was used to determine the efficiency of Cr(VI) sorption by the sorbents. The sorption kinetics and diffusion models were examined by pseudo first and second order models, external diffusion, intraparticle diffusion models respectively. Different isotherms such as Langmuir, Freundlich, Dubinin Redushkwich and Temkin isotherms are used to evaluate the applicability of sorbents. Desorption capacity of the sorbents was also studied using different desorbing agents. The optimization parameters of batch study were used for practical utility (i.e. column studies) and designing of breakthrough curve. The results of these findings are discussed in the present paper.

2. Materials and methods

2.1. Synthesis of zeolitic materials

The starting raw material i.e. sugarcane's bagasse fly ash (BFA – an agricultural waste) was acquired from a local Sugar mill named as Shree Khedut Sahkari Khand Udhyog Mandali Ltd., Bardoli, Gujarat, India. BFA was thoroughly washed with deionised water to remove unknown impurities and dried in hot air oven (373 ± 1 K). After drying, it is crushed in mortar grinder and sieved ($75\text{--}90 \mu\text{m}$). In a typical preparation of zeolitic material, a stoichiometric proportion of 1:10 (solid:liquid) were added in a refluxing flask for 72 h with temperature of 373 ± 1 K. In liquid portion, the first experiment was carried out using 3 M NaOH_(aq) solution mixed with BFA and reflux it as above condition, obtained product is called as conventional zeolitic bagasse fly ash (CZBFA). In the second experiment of zeolitic materials, BFA was mixed well with 3 M NaOH and 1.5 M NaCl solution in a reflux flask for 72 h at 373 ± 1 K. The final product was electrolyte treated conventional zeolitic bagasse fly ash (ECZBFA). Hydrothermally synthesized CZBFA and ECZBFA were further washed with deionized water to eliminate excess sodium hydroxide. The BFA, CZBFA and ECZBFA adsorbents were dried in hot air oven and sieved up to $75\text{--}90 \mu\text{m}$ mesh size. Finally, the sieved BFA, CZBFA, and ECZBFA materials were stored in airtight desiccators to prevent from atmospheric moisture. The same sorbents were used for all the further experiments. The stock solution (1000 mg L^{-1}) of Cr(VI) was prepared in deionized water (conductivity = $1.5 \pm 0.01 \mu\text{S}$). All the chemicals used were analytical reagent grade (Rankem, India).

2.2. Characterization of sorbents

The native BFA and zeolitic materials were well characterized by proximate analysis and instrumental analysis [17]. Wet analysis or proximate analysis contains measurements of moisture, loss on drying (LOD), ash content, and specific density. The moisture contents of the sorbents were carried out by Karl-Fischer instrument

(1204R VMHI, Metrohm Ltd., USA). Sorbents were chemically characterized by X-ray Fluorescence technique (XRF, X-ray XDL-B, Fischer scope, Japan). Thermo-Nicolet iS-10 instrument was used to obtain FTIR spectra using KBr pallet method. The powder X-ray diffraction patterns (PXRD; Panalyticals X'-Pert Pro, Netherlands) of the sorbents were obtained using nickel filtered CuK α ($\lambda = 1.5406 \text{ \AA}$) radiations. Mass titration method [18] was used to determine the point of zero charge (pH_{pzc}) values of sorbents. The specific surface area and pore volume of the sorbents were determined using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods using Micromeritics Gemini 2360, Shimadzu instrument. The surface morphologies of sorbents were analyzed by scanning electron microscopy (SEM; Hitachi S-3400N, Germany).

2.3. Sorption

2.3.1. Batch system

The sorption of Cr(VI) on BFA and hydrothermally treated sorbents were investigated in batch mode sorption equilibrium experiments. All batch experiments were carried out in 100 mL glass stoppered flasks containing 50 mL volume of sorbate solution at a known initial concentration. The flasks were agitated in an incubator shaker at a constant speed of 150 rpm at 303 K temperature until the equilibrium was attained. At predefined time intervals the sorbate solution was filtered through $0.45 \mu\text{m}$ Millipore membrane filter. The sorbate solution was directly analyzed or it should be further diluted for desired calibration concentration range with deionised water. The atomic absorption spectrophotometer (AAS, GBC Avanta version 1.32, Australia) was used to determine unadsorbed metal solution concentration with air acetylene flame. Initially always check the desired metal concentration and blank experiments were carried out for each and every study to check the deviation in the solute concentration and leaching/sorption either by glassware and Millipore membrane filter and hence minimize the errors, respectively using AAS. The results of above experiments found no significant values of metal concentration. Operational conditions of AAS were adjusted according to manufacturer's guidelines to yield optimal determination. Absorbance was recorded in triplicate to evaluate the reproducibility and the mean values were used for the concentration calculation. Furthermore, each experiment was repeated thrice and the mean values were reported. The required pH of the sorbate solutions was bringing with 0.1 M NaOH or 0.1 M HCl using pH meter (Equip-Tronics, micro controller pH meter, EQ-621 model, India). The uptake of Cr(VI), q_e (mg g^{-1}) was calculated using below Eq. (1);

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

Here, where, C_0 is the initial concentration (mg L^{-1}), C_e is the equilibrium concentration (mg L^{-1}), m is the mass of the sorbate (g) and V is the volume of the metal solution (L).

Experimental parameters for each sorption studies are presented below. The effect of pH on sorption process was studied in the pH range of 1.0–7.0. The experiment condition was set up with 100 mg L^{-1} of initial Cr(VI) concentration with 2 g L^{-1} of each sorbent dose at 303 ± 1 K temperature, 24 h equilibrium time and 150 rpm agitation speed. In order to study the effect of sorbent dose on removal of Cr(VI) from the metal ion solution of 100 ppm, experiments were conducted by varying the amount of sorbent dose (i.e. $0.25\text{--}10 \text{ g L}^{-1}$). The effect of initial metal concentration on Cr(VI) sorption was carried out at 300 ± 2 °C using different initial concentration of Cr(VI) (i.e. 100, 200, 300, 400 and 500 mg L^{-1}) at optimum pH 3.0 and 150 rpm for 360 min time period. The temperature study is carried out in the range of $303\text{--}333$ K at optimum pH, contact time, dose and concentration of Cr(VI).

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