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An efficient ultrasound assisted approach for the impregnation of room temperature ionic liquid onto Dowex 1 × 8 resin matrix and its application toward the enhanced adsorption of chromium (VI)

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ABSTRACT

The work discussed in this paper is based on the utilization of ultrasound in conjunction with an ionic liquid (Aliquat 336) impregnated Dowex 1 × 8 resin for the effective adsorption of chromium. Ionic liquids are known for their selectivity toward metal extraction and ultrasonic medium offers efficient energy transfer for impregnating the ionic liquid in the resin matrix. The molecular interaction between the ionic liquid impregnated resin and chromium was studied through various physicochemical and spectroscopic techniques. The influence of various analytical parameters on the adsorption of Cr(VI) such as pH, adsorbent dosage, temperature and interference of foreign ions was studied in detail. Chromium (VI) was quantitatively adsorbed in the pH range of 3.5–4, with a high adsorption capacity of 230.9 mg g^{-1} in conformity with the Langmuir isotherm model. The study of thermodynamic parameters showed that the adsorption process is exothermic and spontaneous. The adsorbent could be regenerated using 1 mol L^{-1} HCl–0.28 mol L^{-1} ascorbic acid mixture. Chromium could be effectively detoxified from an industrial effluent and finally the developed method was validated with the analysis of a certified reference material (BCR-715). The obtained results indicated that the ultrasonic assisted impregnation of the room temperature ionic liquid significantly enhances and improves the removal efficiency of Cr(VI).

1. Introduction

The release of chromium from industries such as chrome tanning and electroplating [1–3], is an important issue that needs to be addressed. The discharged chromium exists in two important oxidation states, +3 and +6 respectively and the toxicity of Cr(VI) is much higher than Cr(III) [4–6]. According to the United States Environmental Protection Agency (USEPA), the permitted concentration of Cr(VI) and total chromium discharged to surface water should be less than 0.05 mg L^{-1} and 0.1 mg L^{-1} respectively [7]. Hence, it is of paramount importance to treat the Cr(VI) containing wastewater before it is discharged into the environment. Several treatment methods have been studied to remove chromium from wastewater. These include reduction [8], chemical precipitation [9], ion exchange [10,11], membrane separations [12,13], electrochemical precipitation [14], nanofiltration [15], flotation [16], electrocoagulation [17], solvent extraction [18], sedimentation [19], reverse osmosis [20] and adsorption [21,22]. Although these methods are quite satisfactory in removing chromium, production of solid residue is a major environmental concern. Moreover, when the concentration of chromium in the wastewater is low, its removal efficiency by chemical reduction is poor [23]. As an alternative, physico-chemical treatments such as ion exchange [24] have also been utilized to treat chromium-laden wastewater. Ion exchange using synthetic resins is an interesting methodology for removing toxic contaminants from aqueous phase at various concentration levels. The main advantages of ion exchange resins include high degree of metal recovery and selectivity. The anion exchange processes can be used for the removal of chromium from wastewater at varying pH in the presence of high concentration of anions such as chloride, sulfate, bicarbonate and nitrate [25,26]. Various anion exchangers have been studied for the removal of heavy metal ions [27]. Similarly, the selectivity of the commercially available strong or weak base anion exchangers for chromate anion has been studied in the pH range 3–8 [28–35]. Modifying the anion exchangers by impregnation, functionalization etc. offers higher affinity toward chromium adsorption [36]. The selectivity of these strongly basic anion exchangers is influenced by the concentration of chromium, the ionic form of the resin and the substituents. These features are well satisfied by Dowex 1 × 8 resin, a styrene-divinyl benzene polymeric resin containing quaternary ammonium functional group with chloride (Cl^-)

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and a total exchange capacity of 1.2 mequiv. mL^{-1}, Dowex M4195 chelating resin [37], functionalized pyridine copolymer with amine groups [38] and hybrid inorganic/organic adsorbents [39]. Wang et al. [40] used Dowex 1 × 8 resin to remove radioisotopes from aqueous solution. Raji and Anirudhan [41] have made a comparative study of polyacrylamide grafted sawdust adsorbent for the removal of chromium with Dowex resin. A relative assessment of the removal efficiency of Dowex 1 × 8 and Amberlite IRA96 resins for heavy metal remediation has been reported [42]. Ionic liquids exhibit good selectivity, sensitivity and reproducibility toward metal extraction [43]. Recently, various ionic liquids have been explored for the removal of metal ions [44]. Aliquat 336 is a room temperature ionic liquid (RTIL), which has been utilized for the extraction of chromium (III) [45] with high degree of metal recovery. Konczyk et al. [12] have reported the competitive transport of Cr(III) and Cr(VI) by polymer inclusion membranes with D2EHPA and Aliquat 336. At pH 1.0 Cr(VI), oxo-anions were removed with a recovery factor of 90%. Herein, Aliquat 336 plays the role of a plasticizer and an ion carrier. Recently, Kalidhasan et al. [46] have reported an effective method for chromium with an adsorption capacity of 38.94 mg g^{-1} using ultrasound assisted impregnation of Aliquat 336 in a cellulose matrix. Solvent impregnation of metal extractants in various matrices is also known for their efficacy [47] toward the removal of heavy metals.

The conventional methods followed in the preparation of solvent impregnated resins are quite time consuming and hence an alternative green and economic process involving ultrasonication is proposed for the impregnation of the metal extractant. In this work, we report an enhanced method for the adsorption of chromium by impregnation of Aliquat 336 in Dowex 1 × 8 resin matrix using ultrasonication. The resin before and after the adsorption was thoroughly characterized using various analytical techniques followed by the optimization of vital experimental parameters. The feasibility of the method has been successfully demonstrated in the detoxification of chromium from industrial wastewater samples and validated with the analysis of chromium in a certified industrial wastewater effluent sample (BCR-715).

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Milli-Q water (MQW) was used in the preparation of solutions. An appropriate amount of potassium dichromate (S. d. Fine Chemicals, Mumbai, India) was diluted to 100 mL with MQW to give 1000 mg L^{-1} chromium (VI) solution. Working solutions were prepared by appropriate dilution. 1 mol L^{-1} sulfuric acid (S. d. Fine chemicals, Mumbai, India) was prepared by appropriate dilution with MQW. Dowex 1 × 8 resin was procured from Merck, India. Sodium hydroxide, ascorbic acid, sodium nitrite, sodium sulfite, methylisobutylketone (MIBK), hydrochloric acid, thiourea, and Aliquat 336 were procured from S. d. Fine Chemicals, Mumbai (India). MIBK was used as the diluent for the ionic liquid, Aliquat-336. BCR-715 (certified industrial wastewater effluent) was used for the validation of the method.

2.2. Instrumentation

A Branson (model 1510) ultrasonic bath with frequency 40 kHz was utilized in the adsorbent preparation. The morphological changes in the adsorbent were obtained from JSM-840 scanning electron microscope (SEM). The surface area of the adsorbent was determined using Micromeritics porosimeter model ASAP2020 analyzer in a nitrogen atmosphere, and this was out gassed at 150 °C for 12 hr. The solid state ^{13}C NMR spectra were recorded in Bruker DSX-300 NMR spectrometer at ambient temperature. The characteristic changes in the vibrational frequency of the adsorbent before and after the adsorption of chromium were recorded using Jasco-4200 FT-IR spectrometer. X-ray diffraction pattern was recorded in XPERT-PRO X-ray diffractometer using Cu Kα radiation. The Energy Dispersive X-ray spectrum (EDX) was recorded with Hitachi S-3000H spectrometer and the removal efficiency of chromium was estimated quantitatively using a Jasco V-650 UV-visible spectrophotometer. The pH of the reaction medium was adjusted using an Elico LI-127 (India) model pH meter.

2.3. Adsorbent preparation

A known amount of Dowex 1 × 8 resin was washed with a mixture of ethanol, hydrochloric acid and water in the ratio 2:1:1. It was dried in hot air oven for 5 h at 60 °C and kept in desiccator for further use. 5 g of the resin was sonicated for 3 h with 30 mL of 1.01 mol L^{-1} Aliquat 336 in MIBK medium for effective impregnation. The resin adsorbent was dried at 60 °C and used for further study. The prepared adsorbent was well characterized using various analytical techniques.

2.4. Adsorption studies

Adsorption experiments were performed by equilibrating 0.25 g of adsorbent containing 10 mg L^{-1} Cr(VI) solution for 30 min in rotatory orbital incubator shaker (Biotechnics, India) at room temperature (27 ± 1 °C). The pH was adjusted to 3.5 using sodium hydroxide and sulfuric acid. After 30 min, the reaction mixture was filtered and the percentage of chromium adsorbed was estimated by measuring its concentration in the supernatant by the standard diphenylcarbazide method at λ_{max} 540 nm [22]. The uptake of chromium by the adsorbent was calculated from the following equation,

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

where q_e is the chromium uptake (mg g^{-1}), C_0 and C_e are the initial and equilibrium Cr(VI) concentrations in the aqueous phase (mg L^{-1}), W is adsorbent dosage (g) and V is the solution volume (L). The desorption could be done using 5 mL of 0.1 mol L^{-1} HCl–0.28 mol L^{-1} ascorbic acid mixture in 1:1 ratio wherein the adsorbed chromium (VI) is reduced to Cr(III) and this brings out the greener aspect in the rejuvenation of the adsorbent.

3. Results and discussion

3.1. Characterization of adsorbent

Increasing the effective adsorption sites along with the existing active adsorption center without any functionalization was achieved by simple impregnation through ultra-sonication. The ultrasound assisted impregnation results in an effective mass transfer with enhanced sorption and desorption kinetics [48]. The generation of pressure waves in liquids leads to the creation and breakdown of tiny bubbles and the energy released during this process ensures homogenous dispersion and impregnation of the ionic liquid in the Dowex resin matrix. In this method, isobutylmethylketone (MIBK) was used as a diluent for the ionic liquid [46,49]. MIBK is known to be a good diluent for Aliquat 336 [50] in the extraction of aliphatic acids from aqueous solutions. The extractant is impregnated into the polymeric backbone by van der Waals force of attraction and π interaction with the phenyl ring of the resin. The impregnation of ionic liquid in the Dowex resin matrix and its application toward the adsorption of chromium is shown schematically in Fig. 1. The molecular interaction before and after