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Removal of hexavalent chromium ions using polyaniline/silica gel composite

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ABSTRACT

In this study, a composite composed of polyaniline and silica gel was successfully prepared via in situ polymerization. The prepared polyaniline/silica gel (PANI/SiO_2) composite was used as an adsorbent for the removal of Cr(VI) ions from the aqueous solutions. Structure and morphology of the composite were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX). A batch adsorption system was applied to study the ability of the adsorbent to remove Cr(VI) ions from aqueous solution. Results revealed that the PANI/SiO_2 composite requires minimum contact time as 60 min, pH 4.2, a dosage of 0.1 g and 50 mg/L as an initial concentration of Cr(VI) ions for the maximum removal capacity at 303 K. Langmuir and Freundlich adsorption isotherm models were studied to describe isotherm constants. The Cr(VI) ion uptake by the composite follows Freundlich isotherm. The maximum Cr(VI) ion adsorption capacity of PANI/SiO_2 composite was found to be 63.41 mg/g at 303 K. Thermodynamic parameter studies concluded that the nature of Cr(VI) ion adsorption was spontaneous and endothermic. The kinetic study revealed that the adsorption of Cr(VI) ions by the composite follows the pseudo-second-order and pore diffusion models. The mechanism was mainly driven by both ion exchange and adsorption coupled reduction.

1. Introduction

Heavy metal pollution is one of the most concerned environmental problems today. Among the heavy metals, Cr(VI) is being one of the important heavy metal pollutants present in the environment. Besides, Cr(VI) is released to the environment from various industries like mining, electroplating, leather tanneries, paints, pigments and chrome manufacturing industries [1,2]. As such Cr(III) and Cr(VI) are the most stable oxidation forms of chromium. However, Cr(VI) is found to be 500 times highly toxic than Cr(III) [2]. Owing to high toxicity and potential carcinogenicity, removal of Cr(VI) is of more concern than Cr(III) [3]. The permissible limit of Cr(VI) for industrial effluents to be discharged to the surface water is 0.1 mg/L and for potable water it is 0.05 mg/L by World Health Organization [4].

Several conventional methods include adsorption, chemical precipitation, solvent extraction, filtration, ion exchange, oxidation/reduction, membrane separation, electrochemical coagulation that are in practice for the removal of Cr(VI) from aqueous solution [5–10]. Among them, adsorption technique is the most widely used feasible technique than other techniques due to its low cost, high efficiency, regeneration ability, etc. Adsorbents like polyaniline, polypyrrole, silica based materials, chitosan, zeolite, activated carbon, clay, metal oxides, etc. have been studied for the removal of Cr(VI) ions from water/wastewater [5–7].

Recently, syntheses of organic–inorganic polymeric materials have gained much attention for the removal of heavy metals from the wastewater. Synthesis of polymer based organic–inorganic materials via sol–gel process is a very promising route for direct preparation of porous sorbent with available functional groups [11–13].

In recent years, organic polymer PANI has been evaluated as a potential adsorbent for the removal of heavy metal ions from aqueous solution. This is due to the presence of the lone pair of electrons on nitrogen atoms which can make a co-ordinate bond with positive metal ions [5,14–18]. It is worth mentioning that the spontaneous reduction of highly toxic Cr(VI) ions into less toxic Cr(III) ions is also possible by surface chemical reaction with PANI [14,15]. Although, PANI has shown excellent potential for the removal of heavy metals, extensive researches have been carried out by amending PANI with various materials, as a result of which the resultant materials get improved thermal stability, mechanical

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resistance and higher sorption capacity for the removal of heavy metals [19–27]. On the other hand, among various inorganic materials, silica materials have gained more attention due to its defined pore geometry, large surface area, high porosity, good mechanical strength, high thermal resistance, stability in a wide range of pH, etc. [28,29]. The hydroxyl groups present in the silica gel make it an excellent candidate for suitable modification [30–32]. In view of this, many studies have been reported on the preparation of composites of silica with PANI [33–37].

It is worth mentioning that the composites of PANI with silica have been evaluated as a potential adsorbent for the removal of various contaminates from the water. For instance, Belaib et al. [38] reported that the significant uptake of Cu(II) was observed when silica is coated with PANI. Pan et al. [39] carried out the removal of 2,6-dichlorophenol from aqueous solution using PANI/SiO_2 composite as an adsorbent. Recently, Sowa et al. [40] have demonstrated the separation of inorganic anions such as, nitrate (NO_3^{2-}), bromide (Br^-) and iodide (I^-) by non-suppressed ion-chromatography technique using silica gel coated with polyaniline composite as a stationary phase. Zhou et al. [41] studied the removal of heavy metal ions from wastewater using functionalized silica fumes as an adsorbent. Ayad et al. [42] have demonstrated the adsorption of methylene blue onto polyaniline nanotube base/silica composite. Though, PANI/SiO_2 composite has been used as an effective adsorbent for the removal of various pollutants from aqueous solution, this composite have not yet been used as an adsorbent for the removal of Cr(VI) ions. Therefore, the main objective of the present work is, to study the removal of Cr(VI) ions from aqueous solution using PANI/SiO_2 composite by the batch equilibrium method. The effect of various parameters on the removal of Cr(VI) ions including, pH, dosage, contact time and initial concentration of Cr(VI) were studied in batch mode. The synthesized PANI/SiO_2 composite was characterized by FT-IR, XRD, SEM and EDX. The experimental data were fitted to isotherm and kinetic models.

2. Experimental

2.1. Materials

Aniline was purchased from Sigma–Aldrich, India. Silica gel GLR TLC grade was purchased from S.D. Fine-Chem limited, India. Ammonium peroxydisulfate (APS), potassium dichromate, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Chemical Drug House (CDH) Ltd., India. The double distilled water (DD) was used to prepare all the aqueous solutions. The stock solution (1000 mg/L) of Cr(VI) ions was prepared by dissolving potassium dichromate in 1000 mL of DD water.

2.2. Preparation of PANI/SiO_2 composite

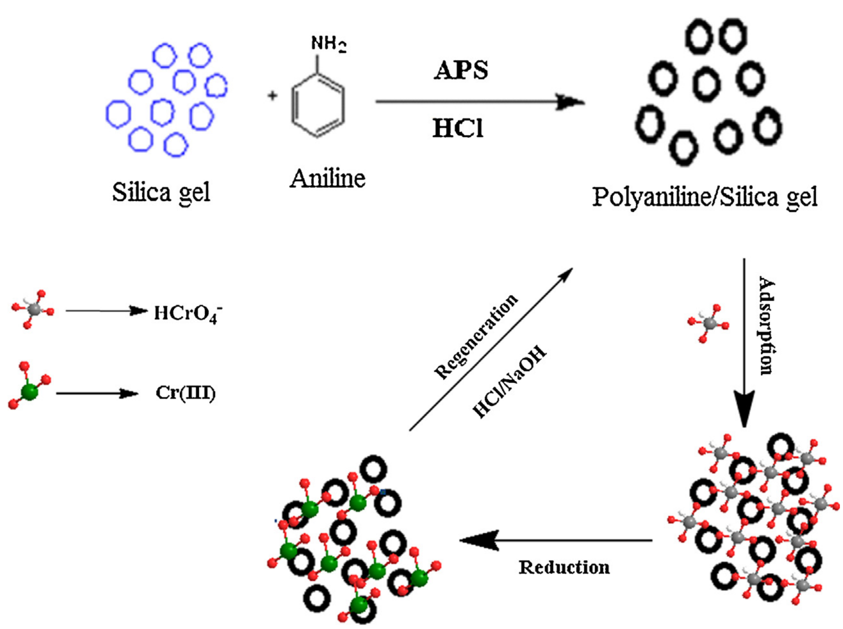
Silica gel (60–120 mesh) was heated to 110 °C for 3 h to activate the surface. The PANI coated silica gel was prepared via in situ polymerization as reported by Fedorova and Stejskal [34]. In a typical synthesis of PANI/SiO_2 composite, 10 g of silica gel was suspended in 200 mL of DD water and stirred for 2 h at 303 K. Subsequently, to this mixture 0.02 M of aniline in 150 mL of 0.5 M HCl was added and the stirring was continued at 0–4 °C. After 1.5 h, 0.025 M of APS in 150 mL was added at 0–4 °C and the resulting mixture was left at 0–4 °C. After 24 h, PANI coated SiO_2 was filtered and washed several times with DD water. Finally, the composite was washed with acetone and dried in hot air oven at 60 °C. The proposed preparation of PANI/SiO_2 composite is represented in Scheme 1.

2.3. Sorption experiments

Batch equilibrium studies were conducted at ambient temperature (28 °C ± 2) in which 0.1 g of adsorbent material (PANI/SiO_2) taken in a conical flask was added with 50 mL of solution containing various amounts of Cr(VI) ions. All the experiments were carried out by without adjusting the solution pH 4.2. The contents in the flask were agitated thoroughly using a thermostated shaker rotating at a speed of 200 rpm for 60 min. After 60 min the PANI/SiO_2 composite was filtered from the solution. The concentration of Cr(VI) ions in the filtrate after adsorption was measured by a UV-spectrophotometer (Pharo 300 Merck) using 1,5-diphenyl carbazide method at the wavelength of 540 nm. All experiments were conducted in duplicate to ensure accuracy and reproducibility. The adsorption capacity of the composite was calculated using the following mass balance Eq. (1):

$$\text{Sorption capacity (SC)} \quad q = (C_0 - C_e)V/W \quad (\text{mg/g}) \tag{1}$$

where q is the adsorption capacities of PANI/SiO_2 composite (mg/g), V is the volume of Cr(VI) ion solution (mL), C_0 is the initial



Scheme 1. Reaction scheme.