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Removal of Cr(VI) ions using Fe-loaded chitosan carbonized rice husk composite beads (Fe-CCRCB): Experiment and quantum chemical calculations

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ABSTRACT

This present investigation deals with the preparation of cross-linked Fe-loaded chitosan rice husk carbon composite (Fe-CRHCB) for the adsorption of Cr (VI) ions. The surface properties of Fe-CRHCB were characterized by Brauner, Emmett and Teller (BET) analyser, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), and Fourier Transform Infrared Spectroscopy (FTIR). The chemical processes occurred during the synthesis of adsorbent and the adsorption process involving the adsorbent and adsorbate were studied through quantum chemical method, which elucidates the reactivity and stability of the interacting system via the highest occupied molecular orbital and the lowest unoccupied molecular orbital energies with its energy gap. Quantum chemical studies were carried out for each stage of adsorbent synthesis, as well as for the interaction of adsorbent with Cr (VI) ions. The interaction of molecules is described by global scalar properties such as chemical potential (μ), electronegativity (χ), chemical hardness (η), chemical softness (S) and electrophilicity index (ω). From these global scalar properties, it was observed that the interaction occurred at each stage of reaction during the adsorption process. Hence, it can be concluded that Fe-CRHCB is an efficient adsorbent for the adsorption of Cr (VI) ions.

1. Introduction

Hexavalent chromium in the wastewater from various industries such as chrome plating, electroplating, leather tanning, mining, dyes and pigments, steel fabrication, canning industries and others accumulates in the ecosystem, which causes serious risk to the environment and endangers public health [1]. Due to its severe toxicity, the Environmental Protection Agency of Cincinnati, OH, USA sets the tolerance limit for the discharge of Cr(VI) ions into surface water at 0.1 mg/L and in potable water at 0.05 mg/L [2]. Thus, it is mandatory to remove Cr(VI) ions before discharge. Adsorption is one of the efficient methods due to its simplicity, sludge free operation, easiness in handling, availability of various adsorbents, regenerative and more efficient in removal of heavy metals at lower concentration levels [3]. Activated carbon is a common adsorbent because of its high surface area and easy availability [4]. Several investigators have reported on the adsorption of heavy metals using activated carbon prepared from waste biomass such as rice husk [5–9], wood [10], and sugarcane bagasse [11]. Rice husk is chosen as a precursor for the preparation of activated carbon because of its availability, and it constitutes organic materials and hydrated silicon.

In recent years, surface modified activated carbon has been prepared to improve the adsorption capacity and removal efficiency of metals ions [12–14]. Chitosan, a biopolymer of glucosamine, has received considerable attention for the removal of transition metal ions and organic species due to its excellent metal chelating property and availability [15–18]. Recent investigations show that the amine and hydroxyl groups in chitosan chelates Fe (III) ions, and more than one polymer chain are involved in the formation of complexes [19–21]. Metalloorganic chelating materials are more effective when it is cross-linked after metal complexation. Cross-linking agents like glutaraldehyde, epichlorohydrin and others are used to enhance the stability of chitosan in acidic medium by forming Schiff base reactions [22, 23].

Recently, quantum chemical studies have been performed massively to compliment the experimental evidence. Quantum chemical studies and molecular simulation involve a large number of molecular quantities characterizing the shape, structure, reactivity, stability and binding properties of a complete molecule, as well as molecular fragments and substituents [24, 25]. Density functional theory (DFT) is one of the quantum chemical calculations that is used in different applications to investigate the electronic structure of a system, in particular atoms and molecules. Thus, it can properly describe the intermolecular interactions, especially van der Waals forces (dispersion), charge transfer excitations, transition states, global potential energy surfaces and some

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other strongly correlated systems, which could be used for better understanding of the system performances [26].

From the DFT technique, one can easily understand the reactivity and stability of the interacting system via the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital energies with its energy gap. Therefore, detailed examination of relative energies (i.e. HOMO/LUMO) and structural interaction can be used to build up a picture of interactions occurring in the adsorption process [27–30]. Hence, this present investigation deals with the preparation of cross-linked Fe-loaded chitosan activated carbon beads for the adsorption of Cr(VI) ions (Fe-CRHCB). The surface properties of Fe-CRHCB were characterized by Brauner, Emmett and Teller (BET) analyser, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX) and Fourier Transform Infrared Spectroscopy (FTIR). Quantum chemical calculations were carried out for each stage of adsorbent synthesis, as well as for the interaction of adsorbent with Cr(VI) ions. The interaction of molecules is described by LUMO energy, HOMO energy, LUMO–HOMO energy gap, chemical potential (μ), electronegativity (χ), chemical hardness (η), chemical softness, (S) and electrophilicity index (ω).

2. Experimental

2.1. Chemicals

Raw rice husk was obtained from a local rice mill. Chitosan was purchased from Pelican Biotech Industry, India. The chemicals used in this study such as nitric acid, sulphuric acid, acetic acid, sodium hydroxide, acetone, and $FeCl_3$ were supplied by Merck, India. Potassium dichromate was used for the preparation of Cr(VI) stock solution. Glutaraldehyde was used as a cross-linking agent and supplied by Merck, India. Double distilled water was used to prepare all the solutions.

2.2. Preparation

Rice husk was thoroughly washed with distilled water and dried in a hot air oven at 100 °C for 5 h. The dried sample was treated with 70% concentrated nitric acid (1:1 by weight) at 70 °C for 1.5 h. After acid treatment, the sample was kept overnight, and then subjected to carbonization under a controlled atmosphere of nitrogen from ambient temperature to 600 °C at a constant heating rate of 5 °C min^{-1} in a horizontal tubular furnace for 4 h. The prepared carbonized rice husk (CRH) was cooled in a desiccator and stored. The Fe-loaded chitosan (Fe–C) gel was prepared by dissolving 1 g of chitosan in 50 mL of 0.1 M $FeCl_3$ and kept in a rotary shaker for 2 h. 1 g of CRH was added to the Fe–C gel and kept in a rotary shaker for 3 h at 200 rpm. The Fe-loaded chitosan carbon gel solution was dropped into 0.5 mol/L of NaOH solution, which was maintained for 12 h and washed with distilled water to remove excess NaOH. Then, 7.5% glutaraldehyde in ethanol was added to the beads, which was maintained for 24 h, then washed and dried. The size of the obtained beads was 0.5 mm.

2.3. Characterization

The BET surface area of Fe-CRHCB was measured by using GeminiV2.00 Micromeritics, India. The morphological structure of Fe-CRHCB using SEM and EDAX was observed by the Quanta 200 FEG scanning electron microscope, Ametek, India. FTIR spectra were recorded using Thermo Scientific Nicolet iS50 FT-IR Spectrometer, Thermo Fisher, India to identify the functional groups present in the adsorbents.

3. Theoretical background

Any chemical system involves the interaction of molecules based on hydrogen bonding, electrostatic interaction and HOMO/LUMO interaction. In quantum chemical calculation, the interaction of molecules is described by LUMO energy, HOMO energy, LUMO–HOMO energy gap, chemical potential (μ), electronegativity (χ), chemical hardness (η), chemical softness (S) and electrophilicity index (ω) [31]. The electronic structure principles in static and dynamic situations give a theoretical basis of chemical potential, electronegativity and electrophilicity index [32].

3.1. LUMO and HOMO energies

LUMO energies are related to electron affinity and characterize the susceptibility of molecule towards attack by nucleophiles. Electron affinity (EA) refers to the capability of a ligand to accept one electron from a donor. However, to influence the interacting systems, covalent or hydrogen bonding may take place, which can result in a partial charge transfer.

$$EA = -\xi_{LUMO.} \quad (1)$$

HOMO energies are related to ionization potential (IP) and characterize the susceptibility of molecule transfer by electrophiles. Hard nucleophiles have low HOMO energy, whereas hard electrophiles have high LUMO energy. The operational definition of LUMO and HOMO in density functional theory (DFT) is given by Eqs. (1) and (2) respectively.

$$IP = -\xi_{HOMO} \quad (2)$$

Fig. 1. (a): SEM image of CRH. (b): SEM image of Fe-CRHCB.