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Engineering a lignocellulosic biosorbent – Coir pith for removal of cesium from aqueous solutions: Equilibrium and kinetic studies

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ABSTRACT

A novel method of engineering lignocellulosic biosorbent- coir pith (CP) by incorporation of nickel hexacyanoferrate (NiHCF), also referred to as Prussian blue analogue (PBA) inside its porous matrix is reported. Structural characterization confirmed the successful synthesis of NiHCF in the coir pith matrix. Sorption capacity of coir pith (CP) before and after loading of NiHCF was investigated for cesium (Cs) in batch equilibrium studies. Kinetic studies showed that the sorption process was rapid and saturation was attained within 30 min. The applicability of non linear Langmuir, Freundlich and Redlich Peterson isotherms was examined for the experimental data. The present studies revealed that there was nearly 100% increase in the sorption capacity of CP after its surface modification with NiHCF. Owing to its low cost, fast sorption kinetics and high uptake capacity, coir pith loaded with NiHCF (CP-NiHCF) seems to be one of the most promising biosorbents for recovery of cesium from liquid nuclear wastes.

1. Introduction

Advancement of nuclear technology has resulted in large-scale release of radioactive Cs isotopes into environment since ^{137}Cs is among the main fission products in radioactive wastes. The availability of ^{137}Cs into environment poses a threat to the eco-system owing to its long life and unlimited solubility, which causes its migration to the biosphere through ground water and tends to remain in an available form to biota for several decades. Furthermore, the chemical similarity of Cs to K leads it's readily assimilation by terrestrial and aquatic organisms (Bagosi and Csetenyi, 1999; Poinssot et al., 1999). On the other hand, it is well known that radioactive cesium is an excellent γ source for some clinical and biotechnological applications like surgical instrument disinfection, radiotherapy and food sterilization (Ebner et al., 2001). Therefore, separation and recovery of radioactive cesium from waste solutions is a significant issue and has drawn particular attention of researchers.

From past few decades, considerable efforts have been directed towards the development of various physico-chemical methods for removal and recovery of radioactive Cs isotopes from nuclear waste streams involving co-precipitation, coagulation, ion exchange, solvent extraction, electrochemical and membrane processes. Among all, solvent extraction and ion-exchange methods have been most widely used. Solvent extraction methods involving crown ethers, calixarenes and calix crowns have shown great promise for Cs recovery from the waste solutions (Duhart et al., 2001; Mohapatra et al., 2004; Talanov et al., 2002). However, application of these materials in large scale processes is limited due to their high cost. In case of ion exchange separation of Cs,

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inorganic ion exchangers are found to be superior over organic ion exchangers due to their thermal stability, resistance to ionizing radiation and good compatibility with final waste forms (Nilchi et al., 2002). Natural zeolites have also been used for removal of ^{137}Cs from low and intermediate level radioactive waste effluents (Abusafa and Yucel, 2002; Faghihian et al., 1999), but the main disadvantage of their application is the competitive interactions of other monovalent cations, in particular Na^+ and K^+ in waste effluents that can considerably block Cs^+ adsorption (Lehto and Harjula, 1987).

Transition metal hexacyanoferrates, in particular nickel hexacyanoferrate (NiHCF), also referred to as Prussian blue analogue (PBA) is known to be highly selective for cesium adsorption. (Ambashta et al., 2003; Kertesz et al., 2002; Loos-Neskovic et al., 2004; Nilchi et al., 2003). In principal, transition metal hexacyanoferrates and related analogues exhibit an open zeolite type structure (Fig. 1) consisting of a cubic network of iron centers bound by bridging cyanide ligand (Keggin and Miles, 1936), which facilitates the intercalation of alkali metal ions into the cubic network required for maintaining its charge neutrality in solutions. Higher selectivity of NiHCF towards cesium can be attributed to its cubic structure with a channel diameter of about 3.2 Å, which permeates small hydrated ion such as Cs^+, whereas larger hydrated ions like Na^+ gets blocked (Jin et al., 2003; Pyrasch et al., 2003). Although the structural properties of NiHCF are useful for selective separation of cesium, very fine particle size of as synthesized NiHCF, restricts its direct use for column operations. This necessitates the employment of some support materials in column separations or surface modification of NiHCF using techniques such as impregnation. Silica gel and polyacrylonitrile have been successfully used as support materials for hexacyanoferrates during removal of cesium from aqueous solutions (Konecny and Caletka, 1973; Ramaswamy, 1997; Someda et al., 2002).

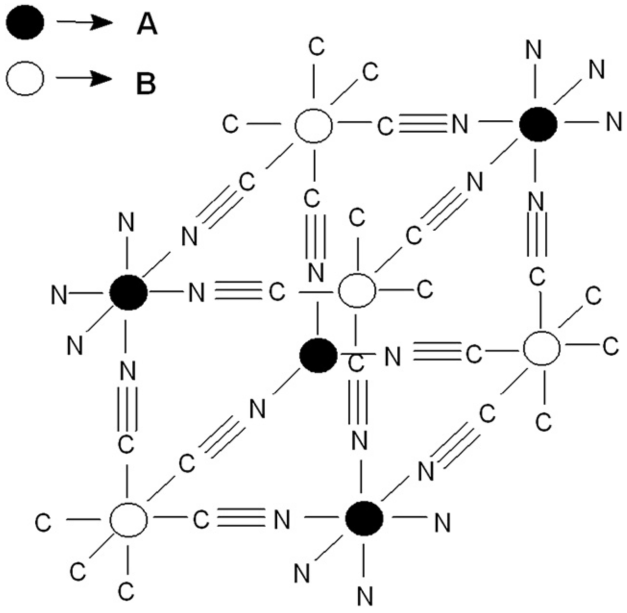

Fig. 1 – The cubic framework structure of Prussian Blue analogues, $A[B(CN)_6].nH_2O$, where the transition metal ions A, B are Ni^{II} and Fe^{III} for nickel hexacyanoferrate, respectively.

Herein, we have introduced the concept of utilizing a lignocellulosic material as a support for NiHCF for separation of Cs. The main idea behind the use of lignocellulosic material as a support was to combine the sorption properties of both NiHCF and lignocelluloses in order to achieve higher Cs sorption. We have employed coir pith- a lignocellulosic waste material obtained from coir processing industries, as a host for synthesis of NiHCF. Recently, coir pith has been emerged as a promising candidate biosorbent for removal of toxic metal ions from aqueous solutions. It is basically a corky tissue available in the husk of coconut fruit along with the coir fiber. The separation of coir fiber from coconut husk produces large amount of coir pith as a waste. Use of this solid waste as a biosorbent would not only be economical, but would also help to reduce the cost of waste disposal and most importantly, provide a potentially inexpensive alternative to the existing adsorbents. The exchange/sorption properties of coir pith are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have an affinity for metal ions (Tan et al., 1993). Sorption properties of coir pith for uranium, cobalt, chromium and nickel has already been studied in our laboratory (Parab et al., 2005, 2006 and 2008). In the present studies, we have made an attempt to estimate the synergistic sorption efficiency of both coir pith and NiHCF towards Cs using CP-NiHCF. This work focuses on synthesis of NiHCF inside porous matrix of coir pith, characterization of the CP-NiHCF and its application for removal of cesium from aqueous solutions.

2. Experimental

2.1. Materials

Coir pith was obtained from Central Coir Research Institute, Kerala, India. It was washed several times with deionised water to remove the soluble impurities, air dried; ground and sieved. Particles with diameter 300–600 μm were further used for sorption experiments. The chemicals nickel chloride ($NiCl_2.6H_2O$) and potassium hexacyanoferrate ($K_3[Fe(CN)_6].3H_2O$) were of A.R. grade and purchased from S.D. Fine Chemicals, India. Deionised water from a Millipore-MilliQ system ($\rho = 18$ MΩ cm) was used throughout the experiments.

2.2. Synthesis of NiHCF in the porous matrix of coir pith

Synthesis of NiHCF has been reported previously (Bagkar et al., 2006, 2008). For the present studies, synthesis of NiHCF inside coir matrix was performed by a modified method comprising two main steps, where the first step involved the loading of $NiCl_2$ on CP and the treatment of $K_3[Fe(CN)_6].3H_2O$ with $NiCl_2$ loaded coir pith was carried out in the second step. In brief, 7.5 g of coir pith was immersed in 100 mL of 0.5 M $NiCl_2.6H_2O$ solution and placed in a rotary shaker (model Julabo sw-20c, Germany) at 27 °C, at 120 rpm, for 6 hrs followed by filtration and washing with deionised water to remove excess of $NiCl_2.6H_2O$. Next, this $NiCl_2$ loaded coir pith was added to 100 mL of 0.5 M $K_3[Fe(CN)_6].3H_2O$ and agitated