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Research paper

Sorption of cesium from aqueous solutions by some Egyptian pottery materials

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ABSTRACT

Removal of Cs(I) from aqueous solutions using low-cost adsorbents such as Egyptian pottery materials under different experimental conditions was investigated. Three kinds of pottery, in addition to their raw materials were tested. Instrumental characterizations of the Egyptian pottery materials were performed by different techniques such as XRF and XRD. The effects of pH, initial metal concentration, shaking time, adsorbent weight and temperature on the removal of Cs(I) from aqueous solutions by the pottery materials were studied. The results indicated that the optimum pH for the removal of Cs(I) was found to be 7.0 for all types of pottery materials. The present study suggested raw pottery materials to be potentially low cost sorbent for the removal of Cs^+ ions from aqueous solutions more than fired pottery materials.

1. Introduction

Cesium radioisotopes such as ^{134}Cs and ^{137}Cs are frequently found in aqueous radioactive wastes originating in nuclear reactors as one of the main fission products of U or Pu (Povinec et al., 2013). As an important source of radioactivity in the radioactive waste, cesium has posed serious environmental threats because of its high solubility and ability to move with aqueous media in the subsurface. Furthermore, as its chemical similarity to potassium, cesium is readily assimilated by terrestrial and aquatic organisms (Stauntona et al., 2002). The removal of Cs^+ from water can be achieved through chemical precipitation and conventional coagulation. However, these approaches cannot reach the emission standards imposed for radioactive wastewater and even generate a large amount of sludge difficult to handle (Galambos et al., 2009). More effective purification methods such as membrane process and ion-exchange column are costly and unsuitable for industrial processing. The adsorption technique has been found to be effective and practical in application for the radioactive wastewater treatment due to its simplicity, high efficiency and the availability of a wide range of adsorbents (Tsai et al., 2009). There are many studies concerning the adsorption of cesium on clay minerals especially illite, smectite, kaolinite and vermiculite (Comans et al., 1991; Comans and Hockley, 1992; Kim et al., 1996; Komarneni, 1978; Poinssot et al., 1999; Sawhney, 1966; Staunton and Roubaud, 1997; Vejsada and Jelínek, 2005; Bergaouia et al., 2005; Benjaminc et al., 2002; Shahwan and Erten, 2004), in addition to bentonite (Galamboš et al., 2011), natural inorganic sorbent (Galamboš et al., 2012), olive pomace (Omar and Attia, 2013) and sand (Zaki et al., 2013).

The adsorption capabilities result mainly from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity (Alkan et al., 2004). There has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite and diatomite for their capacity to adsorb not only inorganic but also organic molecules. Many studies are also aimed to adsorption behavior of various natural clays that could be used as barrier materials in repositories of radioactive waste (Yllera et al., 1998; Lauber et al., 2000; Tsai et al., 2001; Hurel et al., 2002; Murali and Mathur, 2002; Shahwan and Erten, 2002; Khan, 2002).

Pottery was the first manmade material from clay. It is an artificial stone produced by firing clay shapes to a temperature sufficiently high to change the physical and chemical properties of the original clay into a new substance with many of the characteristics of stone (Helal et al., 2006). The neutron activation analysis indicated a high degree of similarity between the compositions of the pottery and clays (Helal et al., 2006; De Sena et al., 1995).

Certain characteristics are common to all types of pottery. They are hard, nonflexible, not affected by heat or cold, fire or water, or by the usual chemicals met within daily life (Helal et al., 2006). Also it is

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resistant to radiation (Helal et al., 2003), does not deteriorate with time, and is durable and virtually indestructible. A survey of the literature has shown that only very small attempt has been made to use pottery or its raw materials to remove heavy metals from aqueous solutions (Helal et al., 2005; Khazali et al., 2007; Al-Sou'od, 2012).

Therefore, the aim of this work is to characterize the pottery materials and investigate the adsorption of cesium on raw and modified Egyptian pottery materials using the batch adsorption method. Egyptian pottery was chosen due to its low cost, its granular structure, insolubility in water, chemical stability and local availability.

2. Experimental

2.1. Sampling and collection

Six pottery materials were purchased from a factory of pottery in the village of Al-Fakharan, AL-Fustat in ancient Egypt and were used without any treatment. According to the data given in Table 1, the collected samples were classified into two groups: (1) samples that were used as raw pottery materials without any treatment and this included: AP, BP and WP. (2) Samples that were used after firing (modified by high temperatures) and these included: AF, BF and WF.

2.2. Modification of clay by high temperature to obtain fired clay (modified pottery material)

A ball of clay after suspended in water was pressed to form a bowl or pot, or the clay was rolled into ropes or coils that were then wrapped in upward circles until the desired height was reached. The coils were then often smoothed so that they were no longer distinct. After a piece of pottery was shaped and air dried completely, it was fired to achieve permanency. The hand shaped material was then fired in a kiln at certain temperature obtained by electric furnace, burnt gas, fired wood or other combustibles materials. Electric and gas kiln were used in this study. The manufacturer avoided exposing the clay to rapid heating when the clay put in the oven, which may result in cracking of the clay, and weaken the cohesion of the clay, so it must be fired at different temperature according to each type of clay such as Aswan clay, black clay and white clay The temperature of the kiln was raised gradually from the room temperature up to 850 °C or any other temperature according to the type of pottery material for 12 h. This will produce “bisque” or “unglazed pottery. This initial firing removed the physical, chemical water and modified the raw materials. Later after 48 h when temperature has completely cooled (Rado, 1969), the fired shaped pottery is removed.

2.3. Chemicals

All chemicals used were of analytical grade. Stock solutions of 1000 mg/L Cs(I) ions was prepared from CsCl, by dissolving appropriate amounts of solid salt in double distilled water (18 MΩ) in a measuring flask to give a standard solution of 1000 ppm of the metal ion. From this solution, concentrations of 20, 40, 60,100 and 120 ppm were prepared by dilution.

2.4. Preparation of samples

The pottery materials were washed several times with DDW (18 MΩ) to remove dust and other adhering particles. They were dried in an oven at 115 °C for 24 h until constant weight, manually grounded in a mortar after cooling in a desiccators and sieved through a 200 mesh sieve to get homogeneous particle size for adsorption studies. The dried samples were stored in airtight bottles for further use without any chemical or physical treatment.

2.5. Instrumentation

Characterization of pottery materials was carried out with a number of experimental approaches in order to investigate all the characteristic features. X-ray diffraction (XRD) was used to determine the mineralogical composition of pottery samples as well as qualitative and quantitative phase analysis of multiphase mixtures. XRD patterns were taken by BRUKER X-Ray Diffractometer (Germany) of type AXS D8 ADVANCE with Cu target ($\lambda = 1.540$ Å and $n = 1$) at 40 kV potential and 40 mA current. The XRD pattern was analyzed by using the high score software giving mineral composition.

X-ray fluorescence (XRF) was performed to learn about the main chemical compositions and elemental analysis of the minerals that are present in the pottery. Samples of pottery materials in the form of powder were placed in a polymer holder. The X-ray Fluorescence (XRF) spectrometer JEOL (JSX-3222), Japan, ELEMENT ANALYZER was used to analyze the samples. The system consists of a low power air-cooled X-ray tube as an excitation source. The operating voltage and the current of the X-ray tube were 30 kV and 0.6 mA, respectively. The X-rays from the tube were exposed on a molybdenum secondary exciter and the generated characteristic X-rays of molybdenum were used to excite the elements present in the studied samples. The measurement time for the determination of the main components was 300 s. The characteristic X-rays emitted from the elements present in each sample were collected using a Si (Li) detector and a PC-based multi-channel analyzer. The X-ray Fluorescence (XRF) spectrometer detected elements from sodium to uranium.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Prodigy High Dispersion ICP, Leeman, USA, was used to determine the initial and final metal ion concentration in the solution.

Quantachrome, Nova 1100e series, version 2.1, USA, was used to determine surface areas and pore characteristics of various samples by nitrogen adsorption/desorption isotherms. Density of pottery materials was determined by AccuPyc 1330 v2.02 density meter.

The initial pH was determined with a pottery material: water ratio of 1: 1 ($g\ L^{-1}$) using Cyperscan 500^{pH} pH meter, USA (Kalra, 1995). Loss of ignition (L.O.I) was determined using the dry combustion method at 600 °C (Nwosu et al., 2013). Cation exchange capacity (CEC) was determined by the compulsive exchange method recommended by the Soil Science Society of America, because it was a highly repeatable, precise and direct measure of a soil's CEC (Gillman and Sumpter, 1986).

Table 1
Data of the six pottery materials use.

Sample	Code	Firing temperature (°C)	Source
Aswan powder	AP	–	Village Alfakhareen, Pottery House Abdeen, Ancient Egypt, Al-Fostat, Cairo Governorate.
Aswan fired	AF	900–1100	
Black powder	BP	–	Ezbet Elnamooss, Samannoud City, El-Gharbeya Governorate.
Black fired	BF	800–900	
White powder	WP	–	Village Alfakhareen, Pottery House Abdeen, Ancient Egypt, Al-Fostat, Cairo Governorate.
White fired	WF	up to 1200	

AP, BP and WP = unfired clay (raw pottery materials).
AF, BF and WF = fired clay (modified pottery materials).