Research article

Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent

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ABSTRACT

Water pollution by industrial and anthropogenic actives has become a serious threat to the environment. World Health Organization (WHO) has identified that lead and fluoride amid the environmental pollutants are most poisonous water contaminants with devastating impact on the human race. The present work proposes a study on economical bio-adsorbent based technique using exhausted coffee grounds in the removal of lead and fluoride contaminants from water. The exhausted coffee grounds gathered from industrial wastes have been acid-activated and examined for their adsorption capacity. The surface morphology and elemental characterization of pre-and-post adsorption operations by FESEM, EDX and FTIR spectral analysis confirmed the potential of the exhausted coffee ground as successful bio-sorbent. However, thermodynamic analysis confirmed the adsorption to be spontaneous physisorption with Langmuir mode of homogenous monolayer deposition. The kinetics of adsorption is well defined by pseudo second order model for both lead and fluoride. A significant quantity of lead and fluoride is removed from the synthetic contaminated water by the proposed bio-sorbent with the respective sorption capabilities of 61.6 mg/g and 9.05 mg/g. However, the developed bio-sorbent is also recyclable and is capable of removing the lead and fluoride from the domestic and industrial waste-water sources with an overall removal efficiency of about 90%.

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1. Introduction

Water is an essential element for the survival of humankind. However abundant it is distributed across the earth, about only 2.5% of it is freshwater, of which only 0.03% on the surface and 0.75% in the form of groundwater is potable (Gleick, 1993; Harder, 2013). An analysis of the availability of clean drinking water has projected that about 1/3rd of world's population is inaccessible to safe drinking water (Chartres and Varma, 2010). In addition to this, the industrial and human activities such as mining and etc., pose a devastating impact on the quality of available drinking water through discharge of non-biodegradable pollutants. Among these lead and fluoride are regarded as the poisonous pollutants.

Lead is a naturally occurring heavy metal with a density of 11400 kg/m3. It is commonly found as a bluish mineral

contaminant in association with elements such as oxygen and Sulphur (Wuana and Okieimen, 2011). Lead is considered as the toxic metal owing to its lethal dosage character, assimilation and half-life period activity in the human body causing neurocognitive disorders (Needleman et al., 1990). The maximum permissible concentration of lead (Pb^{2+}) for safe consumption of drinking water as recommended by World Health Organization is about 0.05 μg/L (WHO, 2004; Teoh Yi et al., 2013). Lead is known to enter the human organic system through absorption in the gastrointestinal tract or inhalation and any excess intake of lead can damage nervous, kidneys and reproductive system (Amarasinghe and Williams, 2007; Saraiva et al., 2007). Besides the geological and industrial effluent sources, pharmaceutical studies have reported the consumption of fluoridated water to cause an increase in lead concentration in blood cells (Masters and Coplan, 1999; Masters et al., 2000; Macek et al., 2006).

Similar to lead, fluoride is also a naturally occurring mineral, generally released into the groundwater from mineral resources

such as fluorite and rocks sources: shale, basalt and granite (Banks et al., 1995). In spite of its benefits in the formation of enamel on teeth (Kumar and Moss, 2008; Jackson et al., 1973; Grynpas et al., 2000; Fawell et al., 2006; Underwood, 1997) within the permissible concentration range of 1.5 mg/L (WHO, 2004), consumption of any excess is reported to cause dental and skeletal fluorosis; an irreversible demineralization of tooth tissues and bones, damage of kidney, brain and nervous system and in extreme conditions to death (Susheela, 2001; Barbier et al., 2010; Ganvir and Das, 2011; Gazzano et al., 2010).

With the stringent norms imposed by environmental regulatory bodies on recycling and reuse of these toxicant contaminated water, many researchers have attempted to remove the lead and fluoride by adsorbing them on zeolites (Perić et al., 2004; Onyango et al., 2004), activated carbon (Acharya et al., 2009; Ravulapalli and Kunta, 2017) and modified alumina (Mahmoud et al., 2010; Tripathy et al., 2006). Despite their high adsorption capacity, these adsorbents do not enjoy the commercial success owing to their high manufacturing costs. In this context, the application of industrial and agricultural wastes such as red mud (Gupta et al., 2001; Çengeloğlu et al., 2002), spent tea (Xiaoping Yang and Xiaoning Cui, 2013; Cai et al., 2015), chitosan (Anantha Ratna Kumari and Kota Sobha, 2016; Viswanathan et al., 2009), sawdust (Choong Jeon and Jung Hwan Kim, 2009; Asheesh Kumar Yadav et al., 2013) and rice husk (Khalid et al., 1998; Ganvir and Das, 2011) have been identified as an economical substitute in removal of lead and fluoride.

Among these, coffee grounds are the most common beverage consumed in the form of cappuccino, espresso and/or instant coffee, resulting in high amounts of exhausted coffee grounds waste (Caetano et al., 2013). In spite of the low surface area in comparison with the activated carbon, the exhausted coffee grounds encompass a wide range of valuable organic components that better promote their sorption capacity (Pujol et al., 2013). The exhausted coffee grounds in recent times are used extensively in removal of contaminants such as dyes (Roh et al., 2012; Shen and Gondal, 2017), cadmium (Azouaou et al., 2010), Cr (VI) (Krishna Mohan et al., 2017) and Pb (II) (Lavecchia et al., 2016) from industrial wastewater. Therefore, an attempt is made to study the potential of the novel and robust sorption technology using exhausted coffee grounds in treating the water for removal of lead and fluoride. Further, the adsorption characteristics of the exhausted coffee grounds and its associated kinetics are analyzed for their application at variable operating conditions.

2. Experimental methodology

2.1. Adsorbent and chemical reagents

The exhausted coffee grounds (ECG) used in the present study are gathered from waste disposal pits of the soluble coffee manufacturing plant at CCL Products (India) Ltd., Guntur, Andhra Pradesh, India and the elemental composition of the coffee grounds has been presented in Table 1. The analytical grade chemical reagents such as Lead Nitrate, Sodium Fluoride, 2-(p-Sulphophenylazo)-1,8-Dihydroxy-Naphthalene-3,6-disulfonic acid trisodium salt (SPADNS) reagent, Zirconium oxy chloride octa Hydrate, Nitric acid, Sodium hydroxide and Hydrochloric acid are acquired from SD Fine Chemicals Pvt. Ltd., and Merck & Co., India.

2.2. Preparation of adsorbent

The exhausted coffee grounds obtained from coffee manufacturing plant are ground and sieved to 200 ASTM mesh

Table 1
Chemical composition of the coffee grounds.

S.No.	Elements	% (w)
1.	K_2O	28.77
2.	P_2O_5	23.60
3.	CaO	14.45
4.	MgO	11.26
5.	SO_3	7.07
6.	SiO_2	3.55
7.	Al_2O_3	2.94
8.	Fe_3O_3	2.42
9.	CuO	1.95
10.	Cr	0.011

(75 μm). The sieved ECG are then rinsed with double distilled water to clean any foreign components and dried at 383 K. Thus obtained coffee grounds are added with HCl and boiled for 2 h on a water bath to activate the sorption sites (Djati Utomo and Hunter, 2006). Then the Activated-Exhausted-coffee Grounds (AECG) are removed from the water bath and rinsed with the distilled water until the remaining HCl on the AECG is removed. The adsorbent is then dried at 383 K in a hot air oven for overnight and used as an adsorbent in the removal of lead and fluoride from the synthetic contaminated water. The AECG are characterized for their morphology and elemental mapping before the removal of contaminants in batch adsorption operations.

The stock synthetic contaminated water has been prepared by adding 1.598 g of lead nitrate in 1000 mL (1000 mg/L) and 0.221 g of sodium fluoride in 1000 mL (100 mg/L) using double distilled water and characterized for lead (Pb(II)) using Atomic Adsorption Spectroscopy (AAS 500) instrument at operational conditions of 217.00 nm wave length, 416.25 V high voltage, slit of 0.4 nm by flame absorption method at a flow rate of 1200 (mL/min) and Lamp current of 5.0 mA (APHA, 1985). Further, the fluoride (F^-) concentration is analyzed using SPADNS method (APHA, 1985).

2.3. Adsorption studies of lead and fluoride

The lead and fluoride present in the synthetic contaminated water are removed by using AECG at a pH range from 2 to 12 by batch operations (Metcalf and Eddy, 2003; Gerard Kiely, 1998; Trivedy, 1995). 100 mL of synthetic contaminant water with a known concentration of lead and fluoride have been taken into a conical flask to which varied amounts of AECG (0.5–4.0 g) have been added. The resultant mixture is then placed in an orbital shaker operated at various temperatures ranging from 303 K to 333 K in steps of 10 K for different specific time intervals till the equilibrium is attained, but not exceeding 5 h. Once the equilibrium condition is reached, the AECG are removed from the orbital shaker and separated using Whatman No.1 filter paper. The resultant filtrate are analyzed for lead (Pb(II)) and fluoride (F-) using AAS and SPADNS method respectively (APHA, 1985).

The adsorbed amount (mg/g) and percentage removal of Pb^{2+} and F^- is calculated by using equations (1) and (2).

$$\text{Adsorbed amount: } (q_e) = \frac{(C_i - C_e)}{m} * V \tag{1}$$

$$\text{Percentage removal:} (\%R) = \frac{(C_i - C_e)}{C_i} * 100 \tag{2}$$

where C_e is the equipoise concentrations of the Pb^{2+} and F^- solutions (mg/L), C_i is the initial concentrations of the Pb^{2+} and F^- solutions (mg/L), V is the volume of the Pb^{2+} and F^- solutions in liters and m is the mass of the adsorbent in grams.