Development of nanohybrid adsorbent for defluoridation from aqueous systems

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HIGHLIGHTS

- The ZAC nanohybrid composite were developed by a simple steps and FESEM image showing highly nanoporous morphology.
- The nanohybrid composite exhibited high fluoride removal in pH range from 3 to 8.
- The adsorbent-desorption study with showed high adsorption capacity after fourth reuse cycles.
- The presence of competitive ions with moderate concentrations had almost no significant effect on the F^- adsorption.
- The adsorption kinetics and isotherms was well described by different kinetic and isotherm models.

GRAPHICAL ABSTRACT
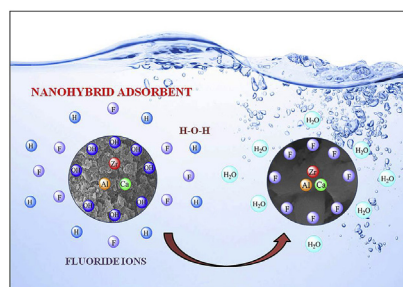
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ABSTRACT

The objective of present study is advancement of an efficient nanomaterial which was investigated to substantiate its efficiency, using kinetic studies to ensnare fluoride in order to make water potable. A new crystalline Zr–Al–Ca nanohybrid adsorbent for fluoride removal was successfully synthesized by a co-precipitation method in this study. The prepared adsorbents were characterized by XRD, FT-IR, TGA, BET and FESEM and EDX. The adsorption properties of the developed adsorbent were studied using batch adsorption method which shown the noticeable fluoride removal efficiency up to 99% at near neutral pH as well as in acidic pH range. The reaction kinetics for adsorption of fluoride was established using reaction based kinetic models which fitted well with Avarami kinetic model as compared to pseudo-first-order, pseudo second-order and power function rate expression. The equilibrium isotherm modelling described adsorption process and Langmuir, Jovanovic, Temkin and Freundlich isotherms provides best fit to experimental data. The fluoride loaded adsorbent was efficiently regenerated by using an alkali solution and has no significant counter ion effect on fluoride adsorption efficiency. Interestingly, the developed nanomaterial has fluoride removal efficacy over varied concentration ranges. It has capability of reanimate and reuse the nanohybrid adsorbent makes it an attractive sustainable material.

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1. Introduction

The occurrence of fluoride in natural groundwater is a global problem and has attracted lot of attentions (Chakrabortty et al., 2016). Small amount of fluoride ingested in water are usually considered to have a beneficial effect on the rate of occurrence for dental caries. The WHO recommendation of fluoride in drinking water is 1.5 mg/L and excessive intake will result in diseases, such as dental/skeletal fluorosis, neurotransmitters and fatal cerebral function (Jadhav et al., 2015). Industrial waste water, coal-fired power plants, beryllium extraction plants, brick and iron works glass and ceramic production, semiconductor manufacturing, electroplating and aluminium smelters have higher fluoride concentrations ranging in thousands of mg/L (Habuda-Stanić et al., 2014). A literature review revealed that India is among the 25 nations around the globe, where health problem arises due to the intake of fluoride contaminated water. In India, seventeen states have been identified as an epidemic for fluorosis. Accordingly, the fluoride removal has emerged as a significantly recognized subject of concern by various scientists globally. Several techniques have been developed for fluoride removals, such as ion exchange, precipitation and coagulation, adsorption, membrane separation, reverse osmosis, and electrodialysis (Tomar et al., 2013). Among these methods, the adsorption method has attracted great attentions in the purification of water with decline trace levels of fluoride, low cost, simple operation and treatment stability. Hence, in the past few years, a number of efficient adsorbents have been developed for the fluoride removal.

The mechanism behind the fluoride adsorption is commonly dependent on interactions occurring between adsorbent and fluoride, as well as hydrogen bonding and additional types of interactions involving fluoride ions. Therefore, high attention has been paid to the research and development of a new adsorbent (Singh et al., 2013, 2015. 2017; Bazrafshan et al., 2016). Hybrid nanoadsorbents are trending in many recent studies for removal of various pollutants from aqueous systems. Advantage of using hybrid material is to improve adsorption efficiency unlike conventional adsorbent. By taking in consideration about hybrid materials, high attention has been paid to the research and development of new adsorbent for substituting conventional adsorbent material for various applications (Boldaji et al., 2009; Mahvi, 2008; Madan et al., 2017, 2016a, b, 2015; Waghmare et al., 2014; Rai et al., 2013; Kumar et al., 2012, 2013; Gulipalli et al., 2011, 2009a,b; Wasewar et al., 2006, 2008, 2009a, b, 2010; Wasewar, 2010; Rajoriya et al., 2007). Activated alumina extensively used as a fluoride adsorbent but it has relatively trivial adsorption capacity and gets saturated (Du et al., 2014; Rai et al., 2013). It has been reported in various recent articles that the fluoride adsorption capacity of activated alumina can be enhanced by chemical modification of its surfaces. Fluoride ion is classified as hard base, due to high electro negativity and small ionic size. So, it has a strong affinity towards electropositive multivalent metal ions like Ca^{2+}, La^{3+}, Fe^{3+}, Zr^{4+}, Ce^{4+} etc. Impregnation of positively charged cations (such as Ca^{2+}, La^{3+}, Fe^{3+}, Zr^{4+} and Ce^{4+}) onto the adsorbent helps to develop positive charges on the adsorbent surface which attracts fluoride ion (F^-). CaO loaded mesoporous Al_2O_3 based adsorbents was reported for removal of F^- from water. It was observed that, fluoride solution of 5 mg/L and 10 mg/L was treated with CaO loaded Al_2O_3, the fluoride concentration of treated water became <1 mg/L, which is under the permissible limit of fluoride in drinking water. The fluoride adsorption capacity of CaO loaded Al_2O_3 were found higher than Al_2O_3 respectively. Because of Ca may react with fluoride ions to form CaF_2 precipitates which exhibited good fluoride removal efficiency over a wide range of pH.

The aim is to develop new adsorbent is to improve fluoride removal efficiency and make it as low cost and readily available. For synthesising new hybrid material zirconium (Zr), aluminium (Al) and calcium (Ca) were selected. Motivation behind selecting Zr, Al and Ca is availability and high fluoride removal efficiency of materials. To know synergetic effect on fluoride removal, new hybrid adsorbent were developed.

In present experimental work, successful attempt was made to develop an efficient nanohybrid adsorbent for removal of fluoride from aqueous system. This is particularly significant in the light of recent reports on toxic fluoride contamination in the rural areas. A series of experimental conditions, with different initial pH, contact time, adsorbent dose and initial fluoride concentration and temperature, were performed. Various kinetic models are illustrated by means of the experimental data in order to explain the adsorption mechanism.

2. Material and methods

2.1. Adsorbent preparation

The ZAC adsorbent was synthesized by co-precipitation method. Analytical grade Aluminium chloride ($AlCl_3$), Calcium chloride dihydrate ($CaCl_2.2H_2O$), supplied by Merck and Zirconium oxychloride ($ZrOCl_2.8H_2O$) supplied by LOBA chemie were used to prepare adsorbent. The other chemical used in experiment (Sodium fluoride (NaF), Sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Nitric acid (HNO_3), Sulphuric acid (H_2SO_4), Phosphoric acid (H_3PO_4) and Ammonium hydroxide (NH_4OH)) were of Analytical grade supplied by Merck. $AlCl_3$ (0.7 M), $CaCl_2.2H_2O$ (0.1 M) and $ZrOCl_2.8H_2O$ (0.1 M) were dissolved in a calculated amount for preparing a mixed solution. Ammonia solution was added dropwise at a rate of three drops per minute to the solution until the pH of the solution reached to 9.5 which led to precipitation of a mixed solution. The obtained precipitate was centrifuged and washed with millipore water until pH of the filtrate was in the range of 7 to 6.5. The obtained precipitate was then dried in hot air oven for 72 h at 60 °C and ground into a fine powder using mortar and pestle. The adsorbent was stored at room temperature in an airtight container. In similar fashion, two more variants of the adsorbent were synthesized with $CaCl_2.2H_2O$ (0.15 M and 0.05 M) and $ZrOCl_2.8H_2O$ (0.05 M and 0.15 M) with constant $AlCl_3$ (0.7 M). Because alumina is highly porous and excellent support for loading of various metals hence aluminium were used with higher concentration than the rest of involved material in synthesis. Zirconium is rare earth metal which has ability to remove fluoride but economically impractical and calcium can also ensnare fluoride but up to certain limits. (Tomar et al., 2013). Initially three adsorbent prepared and termed as ZAC-1 (0.15:0.7:0.05), ZAC-2 (0.05:0.7:0.15), ZAC-3 (0.1:0.7:0.1) A schematic representation of the synthesis process is depicted in (Fig. 1).

2.2. Characterization of adsorbent

The crystallinity and structure of synthesized sample were characterized by X-ray diffraction (XRD) analysis on XPERT-PRO Diffractometer system (PAN analytical) with Cu Kα radiation. The applied current and accelerating voltages were 40 mA and 45 kV, respectively. Fourier Transfer Infrared Spectrometry (FTIR) for the analysis of chemical bonds on the surface of synthesized material was obtained using Shimadzu Corporation IRAffinity-1 (Japan). For sample preparation, potassium bromide (KBr) disc was prepared using 2 mg of sample and 100 mg of KBr then spectra were obtained within the range of 4000 to 400 cm^{-1}. The thermogravimetric