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Preparation of Lanthanum Impregnated Pumice for defluoridation of water: Batch and column experiments

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ABSTRACT

In this study, a novel low-cost adsorbent Lanthanum Impregnated Pumice (LIP) was developed, to study the synergistic influence of Lanthanum and Pumice on removal of fluoride from water. Lanthanum loading onto Pumice was varied and evaluated for its defluoridation capacity. Characterization studies were performed using SEM, XRD and FTIR analysis. Equilibrium batch studies, continuous flow studies and mechanistic aspects involved in the adsorption process were explored. It was observed that, at an optimal 2.5 wt% loading of Lanthanum on Pumice, the fluoride adsorption capacity was 7.18 mg/g. Characterization studies confirmed the presence of Lanthanum on Pumice after impregnation. BET surface area increased significantly to 21.4 m^2/g after impregnation. pH_{zpc} of the synthesized sorbent, LIP was found to be 7.9. Equilibrium isothermal and kinetic data was tested for suitability with various standard models. Non-linear method of fitting was adopted, using Root Mean Square (RMSE) analysis. Adsorption data fitted well with pseudo-second-order kinetic model, indicating chemisorption, whereas for equilibrium isothermal data, Sips model suited best. Continuous flow studies revealed that a column of 2.54 cm diameter, 30 cm bed depth, flow rate 15 ml/min and influent fluoride concentration of 10 mg/L could treat 36.45 L of fluoride laden water optimally up to permissible limit of 1.5 mg/L. Thomas and BDST models fitted well with the results of column studies. Thus the synthesized low-cost sorbent LIP was able to effectively remove fluoride from water.

1. Introduction

In spite of several technologies available for defluoridation of water, fluorosis is still prevalent among people as a burning issue, since, the available technologies have not yet reached the ground root level. World Health Organization (WHO) has recommended a concentration of not more than 1.5 mg/L in potable water to prevent fluorosis [1]. Bureau of Indian Standards (BIS) has prescribed a required limit of 1.0 mg/L of fluoride and 1.5 mg/L of fluoride as permissible limit [2]. Fluoride within required limits is beneficial to human health, whereas in concentrations higher than permissible limits, it is detrimental [3], as it causes fluorosis, brittleness of bones, dwarfishness etc [4]. Therefore whenever excessively present, fluoride has to be removed from water before consumption. Several methods such as coagulation and flocculation [5], ultra filtration [6], electro coagulation [7], reverse osmosis [8] and adsorption [9] have been tried for removal of fluoride from water. Adsorption is considered to be a feasible technique, compared to other methods, owing to its ease in operation and its household applicability [10]. Adsorbents such as activated alumina [11], activated carbon [12], bauxite [13], brick powder [14], rice husk [15] etc were investigated by several researchers. Among them activated alumina is considered to be the best suited adsorbent for fluoride removal, owing to its affinity for fluoride [16]. However activated alumina performs optimally at a pH of 5.5, whereas, normally encountered groundwater laden with fluoride occurs in a pH range of 6.5–8.0. Hence the pH of water has to be altered before and after treatment with activated alumina, to ensure optimal removal of fluoride. Thus, usage of activated alumina has practical difficulties.

Rare earth metals have good affinity for fluoride [17,18]. Recently various rare earth materials such as Lanthanum oxide [19], Cerium [20], mixed rare earth oxides [21], Lanthanum hydroxide [22] and zirconium [23] have been investigated for adsorptive removal of fluoride from water. Among them Lanthanum has got a good potential for removal of fluoride from water. But, its application in defluoridation of water is still at its infancy. This is because, compounds of Lanthanum occur as fine powders and when used as adsorbents pose practical difficulties in separation of the loaded adsorbent from solution, impede hydraulic flow in a column and cause metal oxides to leach into treated water. Pumice is another adsorbent which is a naturally occurring low-cost material with a good porous structure and has been employed for

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defluoridation of water [24]. It can be potentially utilized wherever abundantly available endemically. So, to overcome the difficulties associated with use of Lanthanum individually as an adsorbent, to utilize its full potential on a practical scale and also to study the synergistic influence of Lanthanum and Pumice, a low-cost adsorbent was developed by impregnating Lanthanum onto Pumice and studied for fluoride removal in the present investigation. Thus, the main objectives of this work are to investigate for fluoride removal using Lanthanum Impregnated Pumice (LIP) by 1) studying the kinetics, equilibrium and isothermal aspects in batch mode, 2) studying the breakthrough time and effective volume treated at different flow rates, bed depths and influent fluoride concentrations in continuous flow mode and by 3) understanding the mechanism involved in adsorption using various models.

2. Materials and methods

2.1. Chemicals

All reagents used in the present investigation were procured from E.Merck Ltd, India and were of analytical reagent grade. 221 mg of sodium fluoride was dissolved in distilled water and made up to 1L in a volumetric flask to prepare a stock fluoride solution of 100 mg/L. Stock solution was diluted appropriately to obtain fluoride solutions of required working concentrations. Pumice was obtained from local market at Hyderabad, India. Lanthanum carbonate was procured from Indian Rare Earths Ltd, India. Lanthanum was thermally impregnated onto Pumice to obtain the sorbent, Lanthanum-impregnated Pumice.

2.2. Adsorbent preparation

Lanthanum carbonate of varying weights was mixed with 0.05 L of distilled water and diluted HCl was added to it drop wise until Lanthanum Carbonate got dissolved completely. Dilute NaOH was added to this solution under constant stirring until precipitates were visually observed. Pumice of 600 µm size and 20 ± 0.2 g weight was added to this mixture. This mixture was mixed for 6 h in a magnetic stirrer. Subsequently, it was decanted, dried and heated at 300 °C for 4 h in a muffle furnace. It was thoroughly washed with distilled water and dried subsequently. The obtained material is LIP and was used as an adsorbent in all further investigations.

2.3. Characterization of adsorbent

X-ray diffractograms were taken for LIP before and after impregnation using a diffractometer, Philips: PW1830 with CuKα radiation run at 20 mA and 30kv. The crystalline/amorphous phases on LIP were analyzed using a software database published by Joint Committee on Powder Diffraction Standards (JCPDS). SEM images were taken using Carl Zeiss, EVOMA15, to observe the morphological features of the adsorbent, before and after impregnation. Spot elemental analysis was performed on LIP to qualitatively ascertain the presence of lanthanum, using Energy-dispersive X-ray spectroscopy (EDX). BET Surface area measurements were done using ASAP 2020, Micrometrics, USA at −196 °C, by analyzing nitrogen adsorption and desorption isotherms. FTIR analysis was made using Perkin-Elmer FTIR spectrometer (Spectrum 100) in the range 400–4000 cm^{-1} in percent transmittance mode at a rate of 4 readings per centimeter.

2.4. Determination of pH_{zpc}

pH_{zpc} was measured using a batch equilibrium method [25]. Six flasks of 50 ml of 0.01 M NaCl each, were taken and pH was varied from 2 ± 0.2 to 10 ± 0.2. One gram of LIP was added to each flask. Similarly, a set of six other flasks were taken without LIP, as blanks. The flasks were agitated for 48 h in a magnetic stirrer and pH was measured. The plots of initial pH Vs. final pH of, adsorbent loaded samples and blank samples were superimposed on each other. The intersection point of these plots is considered as pH_{zpc}.

2.5. Batch adsorption experiments

Teflon flasks of 250 ml capacity and a working volume of 100 ml were used throughout the experiments. Laboratory spiked fluoride solutions of 10 ± 0.2 mg/L were prepared and LIP of dose 4 g/L was added to each flask. These flasks were agitated in a rotary shaker of make Kaizen imperial. The optimum rate of agitation for highest removal of fluoride was determined by varying the speed of agitations at 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200 rpm, at 25 ± 1 °C. Highest fluoride removal was observed at 160 rpm and so all experiments were conducted at this speed of agitation. The findings are presented in Fig. S1. After agitating for 180 min, the contents were withdrawn, filtered in a Whatman filter paper of size 42 and analyzed for fluoride removal using SPADNS method [26]. Fluoride was analyzed using a spectrophotometer, Evolution 201, of Thermo Scientifics. pH adjustments were carried out using dilute NaOH and H_2SO_4. Based on preliminary investigations, a concentration range of 5 mg/L to 70 mg/L was selected and equilibrium isothermal experiments were performed to arrive at the maximum adsorption potential of LIP. Foreign ions such as Cl^-, SO_4^{2-}, PO_4^{3-}, HCO_3^- and NO_3^- of individual concentrations of 250 ± 5 mg/L each, were evaluated, for their influence on defluoridation by LIP. Concentration of Lanthanum was measured using an atomic absorption spectrophotometer AAS, GBS 932 plus.

2.6. Column experiments

Fixed bed down flow column studies were performed using a Pyrex glass column of inner diameter 2.54 cm and depth 1 m. Cotton was placed at the base to support aggregates. It was filled with aggregate of mean size 900 µm to a depth of 30 ± 1 cm at the base of the column. On the top of it, LIP of varying depths of 20 cm, 30 cm and 40 cm was filled. It was further topped up with aggregate of mean size 450 µm and depths varying from 30 ± 1 cm to 50 ± 1 cm, to ensure an equally distributed flow of spiked fluoride onto the sorbent bed. The setup of the column is depicted in Fig. S2. Aqueous fluoride solutions of various concentrations of 5 ± 0.1 mg/L, 10 ± 0.1 mg/L and 15 ± 0.1 mg/L were passed through it. Flow rates of the solution were varied at 10 ± 0.2 ml/min, 15 ± 0.2 ml/min and 20 ± 0.2 ml/min. At regular intervals of time, effluent samples were collected and analyzed for residual fluoride concentration, until the effluent concentration of fluoride equaled the influent concentration.

2.7. Continuous sorption experiments

Analysis of breakthrough curves give an insight into the performance of fixed bed column. The time taken for breakthrough and time taken for complete exhaustion of column gives characteristic information for determining the performance and dynamics of adsorption of a column [27]. Breakthrough of the column is considered to have occurred when the effluent concentration (C_t) has reached about 0.1% of influent concentration (C_o) and exhaustion of column is considered to have occurred, when effluent concentration has reached about 95% of influent concentration [28]. However, from fluoride removal point of view, 15% fluoride removal (ie., up to effluent concentration of 1.5 mg F^-/L) is considered for analysis. A breakthrough curve is obtained by plotting values of (C_t/C_o) Vs. (t) [29]. Effective effluent volume (V_{eff}) can be calculated from Eq. (1) [30].

$$V_{eff} = Q.t_{total} \quad (1)$$

Where Q is volumetric flow rate (ml/min) and t_{total} is flow time (min). The value of total mass of fluoride adsorbed (q_{total}) (mg) can be