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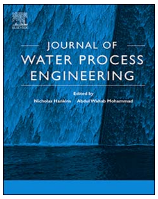

Fabrication of sustainable organometallic polymeric adsorbents for remediation of fluoride from water: A novel approach

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ABSTRACT

In this work, we have synthesised a series of crosslinked porous polymeric adsorbents poly(zirconyl methacrylate-co-methylmethacrylate) (p(ZrDMA-co-MMA)) by polymerising the organometallic vinyl monomer via suspension polymerisation. The novel adsorbents have been investigated for defuoridation of drinking water using batch and continuous mode experiments. The effects of different parameters such as initial fluoride concentration, adsorbent dosage, pH and co-ion concentration were extensively studied to investigate the adsorption capacity in field water.The fluoride adsorption was found to be maximum at neutral pH where 96.54% fluoride removal was achieved.The equilibrium data were fitted well with Freundlich and Langmuir adsorption isotherms, and it was found that fluoride sorption on ZrMA5 followed pseudo-second order kinetics with a correlation coefficient of 0.99. Further, the adsorption kinetics was studied by both reaction based and diffusion-based models, and results indicate both the surface adsorption as well as intraparticle diffusion contributes to rate-determining step. The unique approach to incorporate zirconium metal ions into polymeric moiety in the form of the organometallic vinyl monomer has delivered safe and potable treated water by curbing the commonly encountered problem of leaching of metal ions when metal is loaded/coated/impregnated onto the polymeric moiety.

1. Introduction

Fluoride, one of the micronutrients derived from natural as well as anthropogenic sources is a major public health concern in many regions across the globe. Fluoride is considered beneficial in drinking water at levels of about 0.7 mg/l but turns harmful once it exceeds 1.5 mg/l. The difference between desirable and toxic doses of fluoride is ill-defined, and fluoride may, therefore, be considered as an essential mineral with a narrow margin of safety [1]. Higher levels of Fluoride in drinking water were reported in various parts of India as well as in many countries [2]. The excessive intake of fluoride may cause dental, skeletal infirmities as well as several neurological disorders.

Different types of techniques such as coagulation/precipitation [3], ion exchange [4], membranes and electrodialysis [5] have been reported for the removal of fluoride from drinking water. Among various aforementioned techniques, adsorption is found to be most effective, economical and environment-friendly method due to its high efficiency, low cost, viability and simple design requirements [6]. Many of these modified adsorbents have been prepared by impregnating/loading/coating of some metal ions on native adsorbents such as alum-impregnated activated alumina [7], manganese oxide coated alumina [8], Fe(III)-loaded ligand exchange cotton cellulose adsorbent [9], metal-loaded amberlite resins [10], Al(III)- and Fe(III)-loaded aminomethylene phosphonic acid resin [11]. In this series, some other modified adsorbents using rare earth oxides or transition metals have also been developed including La-impregnated silica-gel [12], La(III) and Y(III)-impregnated alumina [13], zirconium loaded carboxylated orange peel [14] and zirconium(IV)-impregnated adsorbents [15]. However, their usage remained limited due to several shortcomings like short lifespan, the decrease of adsorption capacity after regeneration and the requirement of pH adjustment of influent and eluent. Concomitantly, there occurs major problem of leaching out of metal ions into the treated water which is often impregnated/loaded/coated onto polymeric moiety. This leaching phenomenon puts adsorbent's defluoridation capacity in question as its use results in the release of metal ions in water which is again required to get treated before consumption. The

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Nomenclature

qe	Amount of adsorbate removed from aqueous solution at equilibrium (mg/g)
qt	Amount of adsorbate sorbed on the sorbent surface at any time t (mg/g)
k_1	First-order rate constant of sorption (h^{-1})
k_2	Second-order rate constant of sorption (gm/g h^{-1})
T	Reaction time (h)
X	Mass of solute adsorbed on the adsorbent (mg/l)
M	Mass of adsorbent (g/l)
b	Constant that represents the energy or net enthalpy of adsorption (lm/g)
C_o	Initial concentration of the adsorbate in the solution (mg/l
C_e	Equilibrium concentration of the adsorbate in the solution (mg/l)
q_m	Mass of adsorbed solute completely required to saturate a unit mass of adsorbent (mg/g)
K_F	Freundlich constant indicative of the adsorption capacity of the adsorbent (mg/g)
K_p	Constant of intraparticle diffusion (g m/gh$^{-1/2}$)
n	Experimental constant indicative of the adsorption intensity of the adsorbent
t_b	Service time at breakthrough (h)
C_b	Effluent concentration at breakthrough (mg/l)
N_0	Saturation concentration of the bed (mg/l)
k_a	Kinetic constant (l m/gh^{-1})

leaching of aluminium is observed while using activated alumina, which is undesirable for health [7].

Thus, there exists an exigency to develop an adsorbent material which is comprised of chemically stable metal ions to perform defluoridation and concomitantly prevent leaching of these metal ions in treated water. Furthermore, the adsorbent material must be economical, easy to synthesize and implement for large-scale operations as well. Keeping in view this elusive problem of leaching out of metal ions into treated water, in the present study, we have synthesized a series of adsorbents which have zirconium oxide in its structural moiety and thus do not require any post coating/loading/impregnation of metal ions to carry adsorption. We have utilized zirconium due to its non-toxic nature [16]. The novel porous crosslinked poly(zirconyl methacrylate-co-methylmethacrylate) p(ZrDMA-co-MMA) has been prepared in one step synthesis by adopting suspension polymerization and is further implemented to investigate fluoride removing tendency from the water. Firstly, an organometallic vinyl monomer (ZrDMA) has been synthesized using zirconium oxychloride salt and sodium methacrylate. The introduction of metal ions into the copolymeric network is ensured by polymerizing ZrDMA with methacrylate in the presence of suitable porogen via suspension polymerization technique. Adoption of this method has resulted in curbing the leaching of zirconium in water during fluoride removal treatment which makes this novel adsorbent capable of offering a simple, rapid and economically viable solution to effectively remove excess fluoride ions from water and make it potable. The feasibility of fluoride removal has been systemically evaluated under different experimental parameters such as initial fluoride concentration, adsorbent dose, pH, and co-existing ions to predict the adsorbents performance for fluoride removal in field water samples.The high regenerability of above reported adsorbent makes it a promising candidate for the commercial-scale application. To the best of our knowledge, no such adsorbent has been developed having zirconium oxide intact in the polymer moiety.

2. Experimental

2.1. Materials

All chemicals were of laboratory reagent grade. Methyl methacrylate (MMA 99.0%), Methacrylic acid (MAA ≥ 98.0%), and Ethylene glycol dimethacrylate (EGDMA > 97.0%) were purchased from Tokyo Chemicals Industry, Japan. All of these chemicals were used after purification by passing through a basic alumina column. Benzoyl peroxide (BPO) obtained from SD Fine Chemicals was re-crystallized with chloroform before use. Zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), Sodium fluoride (NaF), Sodium hydroxide (NaOH), and Polyvinyl alcohol (PVA Cold, MW-125000) long-term from Sigma-Aldrich, Germany.

2.2. Synthesis of polymeric adsorbent

2.2.1. Synthesis of zirconyl methacrylate monomers (ZrDMA)

The monomer zirconyl methacrylate (ZrDMA) was prepared by the double decomposition of zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) and sodium methacrylate (MANa). In brief, to a suspension of 352 g of sodium methacrylate and 225 g of anhydrous sodium bicarbonate, there was added 480 g of $ZrOCl_2{\cdot}8H_2O$ under constant stirring at room temperature. A white colored precipitate of ZrDMA gets settled at the bottom with the completion of the reaction. This precipitate is dried under vacuum after washing with deionized water. Further, the dried product is washed with dichloromethane to remove any unreacted reactants. The solid powder of ZrDMA was obtained after removing the solvent under reduced pressure in a rotary evaporator. (Yield − 96%, Melting point- 227–232 °C)

2.2.2. Synthesis of crosslinked p(ZrDMA-co-MMA)

The crosslinked p(ZrDMA-co-MMA) adsorbent was synthesized by the suspension polymerization method using ZrDMA and MMA as monomers, EGDMA as a crosslinking agent, BPO (1% *w* of the total monomer) as the initiator and xylene (30% *w* of total organic mixture) as the porogen. The monomer mixture was dispersed in an aqueous phase containing 3% *w/v* of PVA as stabilizers in a suspension medium at 80 ± 2.0 °C under stirring after purging with nitrogen. The polymerization was carried out in a three-necked round bottom flask which was accoutring a mechanical stirrer, a reflux condenser and a thermocouple for temperature sensing. The whole mixture was stirred at a constant agitation rate of 240 rpm to keep dispersed monomer droplets in suspension with an aqueous phase. At the initiation of polymerization, the temperature of reaction mixture was maintained at 80 ± 2.0 °C for 2 h, and it was later increased to 90 ± 2.0 °C for next 2 h till the completion of the reaction. The resultant polymeric beads were given several washes with hot deionized water to remove the adhering stabilizers from beads surface. The air-dried beads were extracted using *n*-hexane as the solvent in Soxhlet extractor. The soxhilated beads were then sieved using standard sieves of different mesh sizes and the particles which got sieved through a standard sieve of −18 + 52 BSS mesh size were used for further analysis and application. A series (MA-ZrMA5) of such adsorbents was prepared using different composition of ZrDMA monomer.

2.3. Adsorption study

The defluoridation efficiency of developed adsorbent was performed using batch and column method. For the defluoridation study, stock solution (1000 ppm) of sodium fluoride (NaF) was used to prepare various solutions of lower concentrations.