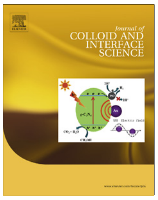
Journal of Colloid and Interface Science 476 (2016) 103–118

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



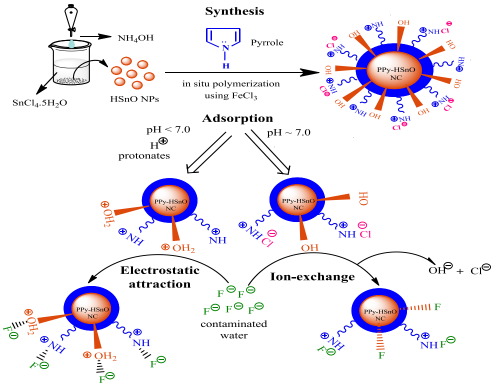
Regular Article

Rapid and efficient removal of fluoride ions from aqueous solution using a polypyrrole coated hydrous tin oxide nanocomposite

Kamya Parashar[a], Niladri Ballav[a], Sushanta Debnath[b], Kriveshini Pillay[a,*], Arjun Maity[a,c,*]

[a] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[b] Saha Institute of Nuclear Physics, Kolkata, West Bengal, India
[c] DST/CSIR National Center for Nanostructured Materials, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 March 2016
Revised 11 May 2016
Accepted 11 May 2016
Available online 12 May 2016

Keywords:
Polypyrrole
Hydrous tin oxide
Adsorption
Fluoride
Isotherms
Rapid kinetics

ABSTRACT

Polypyrrole/hydrous tin oxide nanocomposites (PPy/HSnO NC 1, 2, 3, 4 and 5) were synthesized through encapsulating HSnO by the PPy via an *in situ* polymerization for fluoride removal. The optimized adsorbent i.e. PPy/HSnO NC 3 was characterized using FE-SEM, HR-TEM, ATR-FTIR, XRD, BET, TGA and zeta sizer. Microscopic images revealed the encapsulation of HSnO by precipitating PPy during polymerization. The FTIR and XRD studies confirmed the presence of both constituents. The BET surface area and pH_{pzc} of the adsorbent were estimated to be 65.758 m^2/g and 7.6, respectively. The fluoride adsorption followed pseudo-second-order model and was commendably rapid. The monolayer adsorption capacity was found to be 26.16–28.99 mg/g at pH 6.5 ± 0.1. The thermodynamic parameters indicated the sorption of F^- was spontaneous, endothermic and that physisorption occurred. The calculated activation energy ($E_a \sim 20.05$ kJ/mol) provided further evidence of a physisorption mechanism. Moreover, the adsorbent performed very well over a considerably wide pH range of 3.5–8.5 and in the presence of other co-existing ions. The regeneration of the F^- laden PPy/HSnO NC 3 showed a high desorption efficiency of 95.81% up to 3 cycles. Ground water tested results also demonstrate the potential utility of the PPy/HSnO NC as an effective adsorbent.

1. Introduction

The modern world is facing two prime concerns, exponential population growth, and rapid industrialization. As a result of these,

---

* Corresponding authors at: DST/CSIR National Center for Nanostructured Materials, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa (A. Maity).

E-mail addresses: kriveshinip@uj.ac.za (K. Pillay), maityarjun@gmail.com, AMaity@csir.co.za (A. Maity).

http://dx.doi.org/10.1016/j.jcis.2016.05.013
0021-9797/

various xenobiotic substances are introduced into the ecosystem. Water forms an integral part of the ecosystem and due to its excellent potential as a solvent it acts as an "eternal sink" for many of these pollutants. Consequently, the most dangerous threat that humanity is currently facing is, meeting the rising demands for clean water [1]. Groundwater accounts for 97% of global freshwater and serves as the only economically viable source of potable water for >50% of the world population [2]. However, due to various anthropogenic and naturogenic factors groundwater quality is deteriorating at an alarming rate. According to the World Health Organization (WHO), the essential priority inorganic pollutants of groundwater are fluoride, arsenic, selenium and nitrate [3].

Fluoride (F^-) contamination has been recognized as one of the major health concerns worldwide, especially in several parts of India, China, Sri Lanka, South Africa, Tanzania, Argentina, and Mexico [4]. The prime sources of fluoride contamination are naturogenic in origin and include processes such as weathering, dissolution of fluoride-rich rocks, volcanic ash, and marine aerosols [5]. Some anthropogenic activities such as coal combustion, steel manufacturing, Al, Cu and Ni production, phosphate ore processing, fertilizer production, glass and ceramic manufacturing, glue and adhesive manufacturing, fluoridation of drinking-water supplies also play minor roles [5]. Fluoride can be both beneficial and detrimental to humanity depending on its concentration and exposure duration. As per the guideline values set by WHO, in a small range of 1.0–1.5 mg/L, fluoride strengthens the enamel, causes dental fluorosis above 1.5 mg/L and furthermore prolonged exposure to the much higher concentrations of 4–10 mg/L can even lead to skeletal fluorosis. Disruption of various metabolic functions such as oxidative phosphorylation, glycolysis, coagulation, brain functioning, pineal gland functioning and neurotransmission are also some of the consequences of fluoride toxicity that have been reported by researchers [6]. This fluoride toxicity makes it necessary to develop an effective technology to reduce fluoride levels to the permissible limits in the ground as well as surface water.

Among current trends in water de-fluoridation techniques such as, chemical precipitation/coagulation, ion exchange, adsorption, reverse osmosis, and electrodialysis; adsorption is most sought after and extensively employed. It is more efficient, convenient and very feasible due to the simplicity of its design [6]. It is also a financially viable technique provided that low-cost adsorbents which can effectively remove F^- around the neutral pH of drinking water are used.

The very fundamental step for implementing adsorption in water research is to provide media that can rapidly adsorb a reasonable amount of pollutant. So far several adsorbents have been applied in water defluoridation; such as activated alumina, mixed metal oxides-hydroxides, iron, calcium, carbon and to some extent conducting polymers based materials [6]. Among these adsorbents, all the other materials are hugely explored and exploited for their defluoridation capabilities except for conducting polymers (polyaniline and polypyrrole). Since the last few decades, quite a substantial amount of research has been carried out on the physical and chemical characteristics of conducting polymers. Among available conducting polymers, polypyrrole (PPy) is most sought after, due to its ease of preparation, high environmental stability and electrical conductivity [7]. A literature review has revealed that PPy can exhibit both anion and cation exchanging properties depending on the type and size of dopant ions present in the polymerizing solution during its synthesis. Due to their high mobility in the polymer matrix, these doped counter-ions can be easily exchanged with other ions [8]. Furthermore, PPy prepared by both chemical and electrochemical polymerization reactions usually carries charges in the polymer, i.e. some of the nitrogen atoms in PPy are positively charged [9], and they become major active sites for adsorption of anions such as F^- ions. The defluoridation potential of PPy was first studied and reported by Karthikeyan et al. [7,10]. However, the major disadvantage associated with PPy is its tendency to aggregate due to strong π-π^* interactions between PPy main chains [11]. To prevent the aggregation, PPy can be modified with inorganic nanomaterials to create organic/inorganic hybrid nanocomposites. Due to the higher surface area and shorter diffusion path lengths, and combined merits of both the constituents, PPy based inorganic nanocomposites will give rise to the most suitable adsorbents for fluoride removal with significant adsorption capacity and faster kinetics. Some prior studies have also been conducted to evaluate the defluoridation potential of PPy based hybrid nanocomposites by Bhaumik et al. and Karthikeyan et al. using PPy-Fe_3O_4 magnetic nanocomposite and PPy-Alumina based composite respectively [12,13]. Furthermore, adsorbent materials such as synthetic hydrous oxides/mixed oxides of some polyvalent metals such as Sn(IV), Zr(IV), Fe(III) and Ti(IV) were also applied in removing fluoride from the contaminated water [14]. Hydrous tin (IV) oxide among all other oxides is economically most viable and has not been extensively studied for F^- removal, despite the fact that it has strong anion exchanging properties as reported by White et al. [15]. Moreover, Manna et al. [16] and Biswas et al. [17] had also studied the adsorption of As(III), As(V) and F^- ions respectively on hydrous tin oxide and Fe(III)-Sn(IV) bimetal hydrous oxides, respectively. Thus, there is still an ample scope for investigating and improving the F^-adsorbing properties of tin dioxide composites.

The primary purpose of the present work was to increase the fluoride adsorption capacity of PPy by synthesizing a series of PPy/HSnO nanocomposites with hydrous tin oxide using *in situ* polymerization technique. The as-synthesized and optimized nanocomposite was characterized for its physico-chemical properties. The effect of parameters such as contact time, solution pH, initial concentration, temperature and competing anions interference on the adsorptive performance of optimized nanocomposite was assessed. Adsorption kinetics and isotherms have been studied and modeled to evaluate the mechanism involved in the fluoride sorption onto the optimized nanocomposite. Moreover, the regeneration and reusability of the adsorbent was established using suitable regenerant. Finally, to check the feasibility of the study, ground water (drinking water) was tested using the synthesized adsorbent.

2. Materials and methods

2.1. Materials

Pyrrole monomer (98%), sodium fluoride (NaF, >99%), tin tetrachloride pentahydrate ($SnCl_4{\cdot}5H_2O$, >99%), iron (III) chloride anhydrous ($FeCl_3$, >97%), and all other chemicals of AR grade were purchased from Sigma-Aldrich, USA. Pyrrole monomer was then purified by vacuum distillation under reduced pressure and refrigerated in a dark and airtight bottle before use. All stock and working solutions were made in ultrapure deionized water (resistivity > 18.5 MΩ cm) obtained from gradient water purification system (Milli-Q, Millipore, USA). Sodium hydroxide (NaOH, >99%) and hydrochloric acid HCl of concentration (1–0.1 M) were used to adjust the pH of working solutions.

2.2. Adsorbent preparation

2.2.1. Synthesis of hydrous tin oxide (HSnO)

The method for synthesizing hydrous tin oxide is the same as reported elsewhere with just a slight modification [14,15]. In brief, a tin precursor salt was neutralized using a base via a precipitation