Cadmium selenide nanoparticles loaded on activated carbon and its efficient application for removal of fluoride from aqueous solution

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Abstract : In the first, cadmium selenide nanoparticles loaded on activated carbon (CdSe-NP-AC) has been synthesized. Then, this new adsorbent successfully has been applied for the removal of fluoride from aqueous solution in batch studies, while the effect of various experimental parameters like initial pH, contact time and temperature on its removal percentage was examined by one at a time optimization method.
Keywords: fluoride ; Cadmium selenide nanoparticles ; Activated carbon.

1. Introduction

Fluoride contamination in the drinking water due to natural reasons and human activities is a major problem worldwide [1,2]. According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 1.5 mg L^{-1} [3]. Long-term ingestion of high-fluoride drinking water can cause fluorosis [4,5], which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones ossification of tendons and ligaments and neurological damage in severe cases [2,6]. Millions of people in the world are affected by fluorosis, especially in Asian countries such as China, India, Pakistan, and Thailand [6–8].

Several methods have been applied to remove excessive fluoride from aqueous environments, such as adsorption [10], precipitation [6], ion-exchange [11], electrodialysis [12] and electrochemical methods [13]. Among them, precipitation and adsorption are two most important techniques used for water defluoridation. Precipitation methods based on the addition of chemicals to the water is simple and economical, and is used principally for the treatment of high-fluoride containing wastewater (typically greater than 10 mg L^{-1}). But, the final concentration of fluoride is generally still above level prescribed by WHO and excess chemicals in treated water are difficult to eliminate. For example, the theoretical lower concentration limit of fluoride in treated water using limestone (CaO) as precipitation reagent is approximately 2 mg L^{-1} [6]. Comparatively, adsorption seems to be the most attractive method for the removal of fluoride below 1 mg L^{-1}. The criteria for the selection of adsorbent mainly include its potential (adsorption capacity) for fluoride removal and the cost. Various low-cost materials such as activated alumina [7,8], clay [14], soil [15], bone char [8,12], light weight concrete [16], fly ash and other materials [13] have been tested for removing fluoride from drinking water, but the fluoride adsorption capacities of those materials are not high enough for wide application [8]. In the past few years, novel adsorbents with strong affinity towards fluoride have been developed for fluoride removal, such as

synthetic ion exchangers calcined Mg–Al–CO$_3$ layered double hydroxides (LDH) [7], zirconium-impregnated collagen fiber [2], Fe–Al–Ce trimetal oxide [17] and iron-aluminum mixed oxide [9]. Rare earth elements also have been investigated as potential adsorbents because of their selective affinity to fluoride, high adsorption capacity, cause little pollution, and easy preparation [18]. These novel adsorbents have shown very promising fluoride adsorption capacities, but some of them are expensive to be considered for full scale drinking water treatment. Furthermore, the adsorption processes of those adsorbents generally involve the passage of raw water through an adsorbent bed and the initial setup cost is high. Therefore, an effective and low-cost adsorbent with high-fluoride adsorption capacity and efficient treatment technology for removal of fluoride from large volume water samples is desirable.

Most of adsorbents for removing fluoride reported in literatures are micron-sized particles. In recent years, nanomaterials have attracted much interest and been widely used as sorbents due to properties such as high surface-to-volume ratio and short diffusion route [19]. Because of comparatively large surface areas, it is likely that nanosized adsorbents with strong affinity towards fluoride can be a useful tool in enhancing the adsorption capacity in drinking water treatment. However, due to their small particle size, isolation of nanosized adsorbents from matrices is difficult for practical application. Magnetic nanosized adsorbents overcome the shortcoming of nonmagnetic nanomaterials and are very promising for application in the field of preconcentration and removal pollutants from environmental samples [20].

2. Experimental

2.1. Instruments and reagents

Stock solution of fluoride (Merck, Darmstadt, Germany) was prepared by dissolving accurately weighted amount of fluoride solid material in double distilled water, while the working solution was prepared daily. The fluoride concentration was determined using respective calibration curve by UV-Vis spectrophotometer perkin Elmer UV-visible spectrophotometer model 35 at 246 nm. The pH measurements were done using pH/Ion meter model-682 (Metrohm, Switzerland, Swiss).

All chemicals such as KOH, HCl, KCl, Cadmium perchlorate, sodium sulfite, selenium powder and soluble sodium citrate were of analytical grade(Merck, Darmstadt, Germany) and used without further purifications from Merck, Darmstadt, Germany.

2.2. Preparation of CdSe-AC

Cadmium selenide nanoparticles were prepared according to a previous work [21]. In order to coat the particles, 5mL of CdSe solution (5% m/v) was added to about 5 g of damped nanoparticles in a beaker. The solution was stirred for 1min by a glassy rod and the beakerwas then placed on the magnet. After complete precipitation of CdSe-NP-AC occurred the solution was decanted and ferroflouid was washed with distillated water for several times (3 times on average) to eliminate extra amount of activated carbon from nanoparticles.

3. Results and discussion

3.1. Effect of contact time

Effect of contact time for the removal of fluoride by the adsorbents at showed rapid adsorption of dye in the first 15 min, the adsorption rate decreased gradually and the adsorption reached equilibrium in about 4 h. Aggregation of dye molecules with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated dye molecules in the adsorbents. This is the reason why an insignificant enhancement in adsorption is effected in 7 days as compared to that in 4 h. Since the difference in the adsorption values at 4 h and at 7 days is very small, further experiments were conducted for 4 h contact time only. The adsorption curves were single, smooth and continuous leading to saturation and indicated the possible mono-layer coverage on the surface of adsorbents by the dye molecules.

3.2. Effect of pH variation

The effect of pH on the adsorption of fluoride (2.0 µg mL^{-1}) by 0.4 g of damped CdSe-NP-AC at 25 ^{0}C showed (Fig. 1) that the adsorption and removal of fluoride remains constant at pH range from 3 to 9. The mean pH value (6) was used as optimum pH for further works. The volume of phosphate buffer used in 50 mL of test solution was optimized and it was found that 1 mL of buffer solution can be used as the optimum volume. Higher volumes of buffer solution decreased the adsorption and also the removal of fluoride.
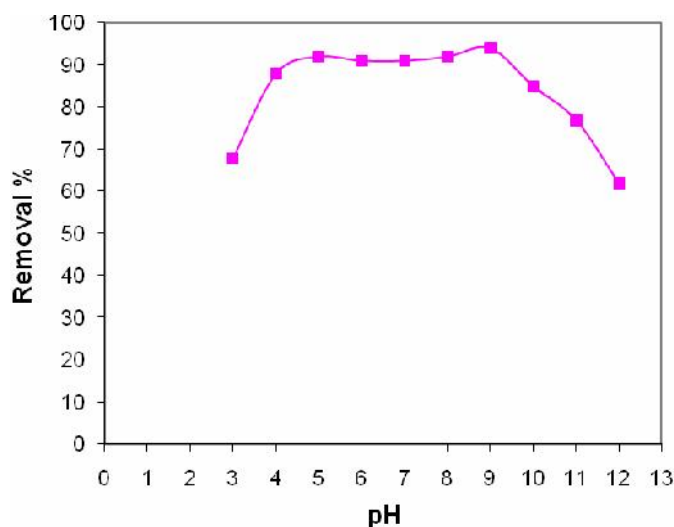
Fig. 1. Adsorption of fluoride on CdSe-NP-AC as a function of pH.

3.3. Effect of temperature

The adsorption of fluoride $(2l\ g\ mL^{-1})$ in a 50 mL solution using 0.3 g of damped CdSe-NP-AC at pH 6 under different temperatures showed that the adsorbed amount of fluoride remained almost constant at different temperatures and the removal was greater than 91%.

4. Conclusions

A fast, simple and new magnetic removal of fluoride from aqueous solution has been successfully developed with CdSe-NP-AC as adsorbent. The adsorbent could be manipulated magnetically and exhibited high adsorption capacity and fast adsorption and desorption rates for the removal of fluoride due to the high specific surface area and the absence of internal diffusion resistance. The adsorption behavior could be described by Langmuir isotherm. In addition the proposed procedure offered higher removal and recovery percents and also shorter adsorption–desorption times of the dye compared with most of the previously reported methods.

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