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Synthesis, optimization and characterization of mesoporous Mg-Al-Fe tri-metal nanocomposite targeting defluoridation: Synergistic interaction of molar ratio and thermal activation

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ABSTRACT

In the present study, the synthesis of a novel tri-metal nanocomposite (TMNC) Mg-Al-Fe using co-precipitation method was optimized by a 3^3 factorial design. The physicochemical properties were characterized by XRD, FESEM, EDX, HRTEM, FTIR, BET, and TGA. The influence of process parameters viz. molar ratio of bivalent to trivalent metals, the molar ratio of trivalent metals, and the calcination temperature on the preparation of TMNC targeting fluoride adsorption was also elucidated. The substantial variation of adsorption capacity from 1.20–4.98 mg/g established the vital role of optimum molar ratio and calcination temperature in the preparation of TMNC. It was observed that the adsorbent with bivalent to trivalent metal molar ratio of 5 and calcined at 400 °C exhibits maximum Langmuir adsorption capacity of 90.68 mg/g. The high surface area and mesoporous structure of the mixed metal nanocomposite obtained at optimum preparation conditions play an essential role in enhancing its fluoride removal capability.

1. Introduction

Overexploitation of groundwater resources is causing an alarming situation of geogenic fluoride contamination. Fluoride (F^-), a naturally occurring element in minerals, sediment deposits, surface water stream, and groundwater aquifers, is an inherent constituent of the living biota. Fundamentally at low concentrations, fluoride has potential benefits on human health but its intake in an excess amount may cause irremediable dental and skeletal fluorosis. This makes fluoride one of the noxious water pollutants whose concentration has to be monitored regularly. Additionally, malnutrition aggravates the ill effects of fluoride especially in the case of teenagers of rural and semi-urban areas [1,2]. Considering the adverse impact of fluoride World Health Organization has set the upper limit of fluoride in drinking water to 1.5 mg/L [3]. Although the concentration of fluoride in groundwater is within the permissible limit, extensive industrial activity, weathering, and erosion of geologic formations have elevated the fluoride concentration posing a challenge towards human health. Fluoride contamination has mostly been reported in parts of India, China, and southwest of the United States [4,5]. Fluoride can enter the food chains through consumption of drinking water, and cereals and uptake by plants. Long-term ingestion of excess fluoride may also trigger diseases like cancer, osteoporosis, arthritis, brittle bones, brain damage, thyroid disorder, Alzheimer syndrome, and other neurological disorders [6,7]. The elimination of fluoride from drinking water is of prime importance and hence an economical, efficient, and cost-effective method needs to be developed to purify water [2,6–12]. Several technologies such as, coagulation-precipitation [13,14], induced crystallization [15], ion exchange [16,17], reverse osmosis [18,19], membrane filtration [20], nanofiltration, electrocoagulation [21–23], sorption and adsorption [2,24–29] have been employed to tackle the menace of fluoride contamination in drinking water. Among all, adsorption is the most widely accepted technique due to its simple operation, ease of design, high selectivity, and cost-effective approach [30–33]. The basic mechanism of adsorptive removal of fluoride is mainly dependent on the selective interaction of adsorbent and fluoride in addition to hydrogen bonding between them [34]. In recent years, potential advancements have led to the research and development of multivalent metal (Mg, Fe, Al, Ca, La, Zr, and Ce) based nano-adsorbents to enhance the fluoride adsorption capacity at the same time decrease the overall cost [4,6–10,34–36]. The better adsorptive interaction of fluoride with multimetal nanocomposites can be attributed to the ionic interaction between electronegative fluoride and electropositive metals like Mg^{2+}, Fe^{3+}, Al^{3+}, Zr^{4+}, Ce^{4+}, and La^{3+}. The interaction can also be catalyzed by the similarity in ionic radii of fluoride to that of metal ions. Previously, Wang et al. reported the use of Mg-Al-Zr tri-metal composite to

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enhance fluoride adsorption capacity [8]. The research group led by Zhang G. also utilized Ce-Fe and Fe-La bi-metal oxide for efficient removal of fluoride from aqueous solution [37,38]. Similarly, Wang et al. synthesized Mg-Fe-La tri-metal composite for the removal of fluoride from water [6]. Wu et al. also reported the Fe-Al-Ce tri-metal hydrous oxide with high fluoride adsorption capacity [39]. It is evident from the previous studies that the dearly-won rare earth metals (Ce and La), which are exploited to improve the fluoride adsorption capacity, increase the cost of adsorbent. Mg-Al-Fe tri-metal nanocomposite (TMNC) has attracted our attention for the adsorptive removal of fluoride for its (hard acid) strong binding affinities towards F^- (Lewis acid-base interaction) and comparatively lower cost than rare earth metals.

Co-precipitation is the most accepted technique for TMNC preparation due to its simplicity (i.e., one pot synthesis) [10,39–42]. The synthesis of TMNC follows the co-precipitation of metals ions followed by aging to form mixed metal composites at a constant or variable pH. Synthesis of TMNC with different metal ratio was reported by many researchers, viz. 20:1:4 (Mg: Al: La) [32], 1:2:1 (Mg: Al: Zr) [8], 5:1 (Mg: Fe + La) [6]. Nonetheless, the effect of molar concentration on the performance of the tri-metal composites based on the defluoridation capacity has not been reported yet. The effect of thermal activation on the performance of the composites has been well reported in the literature [8]. However, a fundamental understanding of the synergistic effects of influencing parameters and a critical analysis of the overall optimum synthesis procedure is not well defined and remains elusive. The present study stems from this clear research dawdle and bridges the gaps to identify effects of molar ratio and thermal activation on tri-metal composite morphology, fluoride removal, and other crucial parameters.

A central smattering of process parameters on the physicochemical properties of TMNC and its defluoridation mechanism can improve the process to design an effective adsorbent for removing trace levels of fluoride from aqueous solution. Previous studies establish the usefulness of multivariate optimization techniques to optimize the effect of different process parameters on the scavenging potential of adsorbents [43–47].

The contribution of the study aims to develop an efficient Mg-Al-Fe TMNC for successful removal of fluoride from aqueous solution. The multivariate optimization technique was employed to investigate the interactive effect of process parameters (i.e., molar ratio and calcination temperature) on the physicochemical properties of the as synthesized Mg-Al-Fe TMNC, and determine the most optimal process parameters.

2. Materials and methods

2.1. Materials

All the chemicals were of analytical grade and used without any further purification. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium hydroxide (NaOH), and sodium fluoride (NaF) were purchased from Merck, India. Deionised (DI) water was used for preparing the analytical standards and working solutions for all the experiments. Standard stock fluoride solution of 1000 mg/L was prepared by dissolving 2.21 g of NaF in 1000 mL water at room temperature. The working solution for the experiments was prepared by diluting the appropriate volume of the stock solution.

2.2. Experimental design for TMNC optimization

In order to evaluate the optimum condition for TMNC preparation and investigate the interactive effect of the influencing process parameters, a multivariate optimization technique using response surface methodology (RSM) was employed. RSM is a combination of the mathematical and statistical tool used to improve the experimental process, investigate the effect of dependent and independent variables and develop numerical relation among the variables through a regression model.

Optimization of the three factors at three levels was conducted considering adsorption capacity as a response in the process. The three levels were coded as −1, 0, +1 for low, central, and high values, respectively. The bivalent to trivalent metal ratio (Mg: Al + Fe), trivalent metals ratio (Al: Fe), and calcination temperature were selected as independent variables. The importance of considering an optimum range of molar ratio for the preparation of TMNC provides useful insights into the mechanism of nanocomposite formation facilitating better fluoride removal and has rarely been reported in previous literature [6,8,32].The range and level of the variables are coded (X_i) according to Eqs. (1(a)/(1(b) and summarized in Table 1. The preliminary experiments proposed a calcination temperature limit of 200 to 600 °C.

$$X_i = \frac{(Z_i - Z_0)}{\Delta Z} \tag{1(a)}$$

$$X_i = \log_5 Z_i \tag{1(b)}$$

where, Z_i denotes the actual value of the independent variables, Z_0 denotes the actual value of the independent variables at the central point, and ΔZ is the step change of the respective variables.

The experimental model for the chosen optimization technique was developed (Table 2) using Design Expert 8.0.7.1 (Stat-Ease, Inc. USA). Taking into account the probable interactive effect of the process parameters, a generalized quadratic model applicable for 3-level and 3-factor design approach was utilized to set up a numerical relationship between the process parameters and response.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum \sum_{i<j} \beta_{ij} X_i X_j + \sum_{i=1}^{n} \beta_{ii} X_i^2 + e \tag{2}$$

where, Y is the response of the model; β_0 is a constant; β_i, β_{ii}, β_{ij} are the linear, quadratic, and second-order interaction coefficient of the process parameters, respectively; X_i, X_j are the independent variables in coded term; n is the number of the studied factor; and e is the error term. Analysis of variance (ANOVA) was evaluated by performing a statistical analysis of the model.

2.3. Preparation of Mg-Al-Fe tri-metal composite

Mg-Al-Fe TMNC was synthesized by simple co-precipitation method. A precursor solution containing $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ was prepared by dissolving suitable amounts of metal nitrate salts in 300 mL of DI water as per the molar ratio provided in Table 1. In another beaker NaOH (2 M) solution was prepared by dissolving a calculated amount of NaOH in 300 mL water, which was stoichiometrically sufficient to precipitate the metals present in the precursor solution. The dropwise addition of two solutions was carried out simultaneously into a beaker containing 300 mL of deionised water under the continuous stirring of 350–400 rpm. The temperature was maintained at 60 °C and the drop rate of the precursor solution was 60(±5) drops per minute. Meanwhile, the drop rate of the NaOH solution was maintained to provide a constant pH of 11(±0.1) to the precipitating mixed metal solution. The resulting slurry was then

Table 1
Experimental matrix of independent variables and their corresponding level.

Factors	Level		
	−1	0	+1
Mg: (Al + Fe) (A)	2	5	8
Al: Fe (B)	1/5	1	5
Calcination temperature (°C) (C)	200	400	600