Fluoride adsorption by doped and un-doped magnetic ferrites 
CuCe$_x$Fe$_{2-x}$O$_4$: Preparation, characterization, optimization and modeling for effectual remediation technologies

Muhammad Abdur Rehman$^{a,b}$, Ismail Yusoff$^a$, Yatimah Alias$^b$

$^a$ Department of Geology, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia
$^b$ Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

**HIGHLIGHTS**

- A series of doped and un-doped magnetic ferrites adsorbents has been prepared by W/O micro-emulsion.
- The adsorption, electrochemical and magnetic properties of the adsorbents was compared.
- A fluoride adsorption model was developed based on central composite design of experiments.
- Effect of concomitants HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$ and Arsenic on fluoride adsorption.
- Response surface method for adsorption of fluoride.

**ABSTRACT**

A series of doped and un-doped magnetic adsorbents CuCe$_x$Fe$_{2-x}$O$_4$ ($x = 0.0$–$0.5$) for fluoride were prepared with the micro-emulsion method. Fluoride adsorption was optimized for solution pH, temperature, contact time, and initial concentration and was monitored via normal phase ion chromatography (IC). The effect of concomitant anions was also explored to perform and simulate competitive fluoride adsorption in real water samples. Optimal adsorption was discovered by a simple quadratic model based on central composite design (CCD) and the response surface method (RSM). The adsorption, electrochemical and magnetic properties were compared between doped and un-doped ferrites. Doped ferrites ($x = 0.1$–$0.5$) were found to be superior to un-doped ferrites ($x = 0$) regarding the active sites, functional groups and fluoride adsorption. The characterization, optimization and application results of the doped ferrites indicated enhanced fluoride adsorption and easy separation with a simple magnet.

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1. Introduction

Fluoride is a necessary nutrient for dental health because it increases dental resistance to the attacks of acids formed by bacterial plaque and prevents the formation of cavities. However, when fluoride is present in public water supplies beyond certain limits, it is injurious to health [1–3]. The maximum allowable fluoride concentration level (MCL) of 1.5 mg/L has been set for drinking water by World Health Organization (WHO). The consumption of excess fluoride can cause impaired physical growth and intelligence, skeletal fluorosis, osteoporosis, arthritis, and even cancer in extreme cases [4–8]. Adsorption is considered the most efficient method due to its reduced cost, environmental friendliness and ease of operation. A number of adsorbents have been developed for fluoride adsorption [9–11]. The criteria for selecting a suitable adsorbent is based on the desirable properties, large specific surface area, larger number of active functional sites, pore size and volume, stability, and magnetic separation capability [12,13]. However, some obstacles remain in the development of adsorbents for fluoride adsorption, such as instability, matrix effects, mechanical strength and poor adsorption capacity. Therefore, more efforts should be devoted toward new classes of adsorbents with high de-fluoridation capacity.

Recently, magnetic adsorbents with high adsorption capacity and environmental friendliness have been developed and...
These anions may strongly compete for ferrites active sites during adsorption. Fig. 7(B) shows the effect of HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and As on Ce-doped ferrite ($x = 0.2$). The adsorption of fluoride was unaffected by the lower concentration of the anions. However, the higher concentration, as usually encountered in industrial wastewater, adversely affected the fluoride removal process. Fig. 7(C) demonstrates the effect of HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and As on ferrite ($x = 0.3$) at pH 7.0. For this particular adsorbent, the 10 mM NO$_3^-$ exhibited a 45% decrease in fluoride adsorption, as indicated by the orange color. The presence of chlorides has a mild effect, even at a concentration of 10 mM. An arsenic concentration of 30 mg/L in the solution also exhibited a 39% decrease in fluoride adsorption. Fig. 7(D) shows the effect of HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and As on the last member of the ferrite series ($x = 0.5$). The elevated levels of HCO$_3^-$, NO$_3^-$, and As were mapped in the danger zone of the graphs. In some regions with higher concentration of competing anions, careful pretreatment is mandatory before adsorption. However, lower concentration levels may not cause any concern during the fluoride removal process. Hence, this adsorbent is suitable for the de-fluoridation of the surface and ground water because the chloride, bicarbonate, nitrate, sulfate and arsenic levels are lower than those given above.

4. Conclusion

In summary, by using a straightforward doping of cerium into magnetic ferrite, we successfully fabricated a series of novel magnetic adsorbents for fluoride adsorption and water remediation technology. Compared with undoped parent material, superior results were obtained, and the present enhancement in adsorption behavior contributed to the active functional groups created after doping, the increased surface area with suitable porosity and the electro-magnetic properties. However, the presence of some concomitant species that are usually found in high concentration in industrial effluents reduced the efficiency of the present series of adsorbents due to competition for adsorbent active sites, which led to a decline in fluoride removal. These ferrite-based adsorbents for fluoride open new vistas for a broad range of applications and may lead to better insights into energy efficient magnetic adsorbents, electrochemical sensors and photo catalysts for environment remediation.

Acknowledgments

We gratefully thank Bright Spark (BSP) University of Malaya, and High Impact Research MoE Grant UM.C/625/1/HIR/MoE/SC04/01 from the Ministry of Education Malaysia, University Malaya Center for Ionic liquids (UMCIL) and IPPP grant # PC215-2014B for funding the cost of chemicals and analysis.