



## Enhancing adsorption of nitrate using metal impregnated alumina

Shikha Jain<sup>b</sup>, Amit Bansiwala<sup>a</sup>, Rajesh B. Biniwale<sup>a</sup>, Sachin Milmille<sup>a</sup>, Sera Das<sup>a</sup>,  
Sangeeta Tiwari<sup>b</sup>, Praveen Siluvai Antony<sup>a,\*</sup>

<sup>a</sup> CSIR–National Environmental Engineering Research Institute, Nagpur 40020, India

<sup>b</sup> Amity Institute of Applied Science, Amity University, Noida 201303, India



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### ABSTRACT

The adsorption capacity and selectivity are vital for designing economically feasible treatment system for drinking water. This work is aimed at enhancing the selectivity of nitrate adsorption through metal impregnation. Impregnation of Mg, Fe, Co, Ni, Zn and Cu on alumina was investigated. Nickel impregnation was found to be the best, with an increase in 13 times the nitrate adsorption capacity compared to unmodified alumina. The optimal pH for nitrate adsorption using nickel-modified alumina was in a wide range from 3 to 7. The nitrate adsorption capacity was not influenced by the presence of fluorides and phosphates, whereas carbonates and sulphates were found to decrease the adsorption capacity by 50%. The adsorbents were also tested on drinking water samples from Madhya Pradesh, India. The nitrate adsorption capacity of nickel-impregnated alumina was still 10 times higher compared to the bare adsorbent.

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### Introduction

Among various pollutants present in the water, attention is now being focused on nitrate [1,2]. Nitrate pollution is typically contributed by untreated human wastes, landfill leachate, fertilizers, effluents, etc. [1,3–7]. The high water soluble nature of nitrate and lack of awareness is ascribed to the widespread contamination of nitrate [8]. Various reports in terms of health and hygienist have been reported due to the excess presence of nitrate in drinking water. Eutrophication and algae growth in lakes and ponds are caused due to the excess contamination of nitrate [9,10]. The occurrences of methemoglobinemia in infants have also been reported due to nitrate contamination in drinking water [1,11–15]. Evidences of diabetes, hypertension and blood pressure have also been reported [1,9,13,14,16]. Looking at the above deleterious nature of nitrate, a maximum contaminant level of 50 mg L<sup>-1</sup> and 45 mg L<sup>-1</sup> was set by WHO and USEPA, respectively [3,10].

Various methods such as biological, chemical and physical process have been reported for the removal of nitrate [10,17,18]. Various advantages and limitations are associated with these methods. For instance, reverse osmosis is considered effective, but

not economic [1,12,19–21]. Biological methods on the other hand economic, but are restricted by the secondary biomass generated [1,19,20]. Seeing the various pitfalls of these methods, research is now focused on to develop low cost and effective technique for nitrate removal [8]. Among all removal methods, ion exchange and adsorption methods are considered relatively superior by virtue of their low cost, energy requirements, design and regeneration [21–23]. The present work focuses on removal of nitrate from drinking water through adsorption.

Myriad of adsorbents have been reported for adsorption of pollutant ions from drinking water. Among these varieties, metal oxides, clays, layered double hydroxides, synthetic polymers, hybrid materials, commercial resins, alumina beads and activated carbon are known for their good adsorption properties [24–29]. Although the nitrate adsorption capacities were high in many adsorbents, their selectivity compared to other anions is relatively poor, thereby decreasing the working capacity of the adsorbents installed. Considering this, the present researches were focused on selectivity as a key parameter. Our work mainly addresses the selectivity of nitrate adsorption, keeping the capacity and regeneration as additional factors.

The adsorption capacities, selectivity of adsorbents are generally tuned by surface modification techniques such as acid treatment, metal impregnation and functionalization. Among these methods, metal impregnation has been reported to be one of the stable surface modification techniques [10,12]. In addition, metal impregnated adsorbents are expected to exhibit good

Abbreviations: WHO, World Health Organization; USEPA, United States Environmental Protection Agency; IC, ion chromatograph; mM, millimolar.

\* Corresponding author. Tel.: +91 712 2249885x439; fax: +91 712 2249900.

E-mail addresses: [sa\\_praveen@neeri.res.in](mailto:sa_praveen@neeri.res.in), [praveen.neeri@gmail.com](mailto:praveen.neeri@gmail.com) (P. Siluvai Antony).

## Nomenclature

### Variables

$Q_e$	Amount of nitrate adsorbed at equilibrium ( $\text{mg g}^{-1}$ )
$Q_{\text{max}}$	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )
$K_L$	Langmuir adsorption constant ( $\text{L g}^{-1}$ )
$C_e$	Concentration of nitrate at equilibrium ( $\text{mg L}^{-1}$ )
$n$	Heterogeneity factor
$K_F$	Freundlich adsorption constant ( $\text{mg g}^{-1}$ ) ( $\text{L mg}^{-1}$ ) <sup>1/n</sup>
$Q_t$	Amount of nitrate adsorbed at time $t$ ( $\text{mg g}^{-1}$ )
$K_{\text{ads}}$	Rate constant of adsorption ( $\text{min}^{-1}$ (pseudo first order)) ( $\text{g mg}^{-1} \text{min}^{-1}$ (pseudo second order))
$h$	Initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ )
$t$	Time (min)
$R^2$	Correlation factor

regeneration capacity compared to bare adsorbents. However, the effect of metal impregnation on nitrate adsorption selectivity has never been exploited [9,21,30,31].

Hence, this paper is intended at examining the influence of various metal ions on selectivity of nitrate adsorption. The alumina was taken as reference adsorbent. Mg, Fe, Co, Ni, Zn and Cu impregnation were chosen for this study based on their surface modification capabilities elsewhere reported [8,32–35].

## Materials and methods

### Materials

All the reagents used in this study were purchased from Merck. The chemicals used in this study were NaOH,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  (anhy), HCl and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

### Metal impregnation method

Various protocols were followed for the impregnation of metal ions on alumina. A metal loading of 5 wt% was targeted. Accounting for the losses of metal ions during synthesis, 15 wt% was taken for loading. The actual amount of metal loaded were estimated experimentally using ICP–OES. For impregnation of magnesium on alumina, 6.275 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was taken in 25 mL of DI water and the pH was adjusted to 9.5 using NaOH. Later 5 g of alumina beads were added to it and shaken for 3 h. The beads were then dried at 110 °C and calcined for 8 h at 300 °C. It was then washed, dried and used in experiments [22]. For modification by iron, 5 g of alumina was immersed in 25 mL of DI water containing 3.73 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The pH was adjusted to 7.0 using NaOH and kept for 6 h stirring. The mixture was then filtered and calcined at 550 °C for 6 h. After calcination, the adsorbents were washed until the pH reached 7. The beads were later dried at 110 °C and used [34]. For nickel impregnation, 5 g of alumina was mixed with 25 mL of DI water containing 3.04 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and then kept for 24 h shaking. It was then filtered, washed and dried at 110 °C. In case of cobalt impregnation, 5 g of adsorbent was kept in 25 mL of solution containing 3.03 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and kept in shaker for 24 h. It was then filtered, washed and dried at 110 °C. For modification by zinc, 5 g alumina beads were boiled with 1.56 g of  $\text{ZnCl}_2$  in 25 mL of solution until dryness followed by calcination in muffle furnace at 700 °C for 3 h. The obtained beads were washed using HCl and then with DI water and finally dried [21]. In case of copper impregnation, alumina beads were kept in 25 mL of DI water having 2.95 g of

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Then the pH of solution was adjusted up to 6.0 using NaOH. It was then agitated and calcined at 400 °C for 4 h. Later, the beads were washed and dried for use [35].

### Characterization and analysis

The metal impregnated alumina was characterized using XRD, FTIR, SEM-EDAX and ICP–OES.

### Equipments

X-ray diffraction studies were carried out using Rigaku desktop X-ray diffractometer operated at 30 kV and 15 mA, with Cu  $K\alpha$  as the radiation source. The samples were scanned with step scan 0.02° and scan speed 5°/min. Scanning was done in range of 2 $\theta$ , 5–80°. XRD of bare and modified alumina beads were done to check for phase changes of alumina beads before and after impregnation of metal ions. Fourier transformed infrared spectroscopy (FTIR) was performed using Bruker Vertex 60 by making pellets of alumina in KBr [36] to know about various bonds present in alumina before and after adsorption [37].

Scanning electron microscope (SEM) analysis was performed using Zeiss EVO 40 equipped with EDAX to study the surface morphology of bare and modified alumina bead [38,39]. Elemental spectra of metal impregnated alumina was obtained using an energy dispersive X-ray analyzer (EDAX) [40]. Inductively coupled plasma with optical emission spectroscopy (ICP–OES) was performed using Thermo Fischer iCAP 6300 duo to quantify the actual amount of metal loaded on alumina. The alumina beads were digested before analysis to dissolve the metals. For acid digestion, 150 mg of alumina beads were mixed with 3 mL of 65%  $\text{HNO}_3$  and 5 mL of 37% HCl and kept in MARS 6–microwave acid digester of CEM at 175 °C for 20 min. The solution was diluted 100 times prior to analysis.

Ion chromatograph of Dionex ICS-3000 was used to quantify nitrate in the adsorption experiment. Standards of different range (5, 10, 25, 50, 100 and 200 ppm) were prepared for calibration and 30 mM KOH was used as an eluent. AS-11HC anion column was used throughout the analysis.

### Analysis

The metal impregnated alumina was screened for nitrate removal using 100  $\text{mg L}^{-1}$  of nitrate solution with 0.1 g dose. The best adsorbent was sorted out based on per gram of metal ion loaded on the adsorbent. The adsorbent was also tested on drinking water samples collected from three different places in Mehatwara situated in Sehore district of Madhya Pradesh, India.

## Results and discussion

The screening study was carried out on the basis of nitrate adsorption capacity and the selectivity study was performed on the best adsorbent after optimizing the experimental conditions.

### Screening

The nitrate adsorption capacity of bare and metal impregnated alumina is shown in Fig. 1. Ni-impregnated alumina exhibited significantly better adsorption capacity compared to Co, Cu, Mg, Zn and Fe impregnated ones. The adsorption capacity of alumina is increased 13 times due to Ni impregnation compared to bare adsorbent. The adsorption capacity of Ni modified adsorbent was found to be 13  $\text{mg g}^{-1}$  of adsorbent. Adsorption capacity of Cu and Mg impregnated alumina were moderate in the range of 2–8  $\text{mg g}^{-1}$ . It is also evident from Table 1 that the preferential metal impregnation for nitrate adsorption follows the order of  $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$ .

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