



## Sorption studies of manganese and cobalt from aqueous phase onto alginate beads and nano-graphite encapsulated alginate beads



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### ABSTRACT

Comparative sorption study of dissolved manganese and cobalt ions onto alginate beads (ABs) and thermally activated nano-carbon beads (NCBs) was performed. Acidic functionalities dominate over sorbent surface. Elemental analysis confirmed that divalent calcium replacement with heavy metal ions might be a possible sorption mechanism. Optimum metal uptake was observed at pH 8. Most of the metal ions (80–92%) were sorbed within 4 h, followed by a slower sorption stage. Mn(II) and Co(II) recovery was greater than 99% with 0.1 N HCl, and NCB could be repeatedly utilized for Mn(II) and Co(II) sorption with negligible loss in sorption capacity.

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### 1. Introduction

Divalent heavy metals such as manganese Mn(II) and cobalt Co(II) in trace quantities serve as essential elements and are required to promote biological activities in both human beings and plants. However, these heavy metals can have a deleterious impact if present in greater than trace amounts. Unlike organic compounds, heavy metals are non-degradable and persistent; therefore, it is essential to remove or minimize them to a permissible amount.

Manganese is widely used in dry batteries, ceramics, ferroalloys, smelting, welding and electrical coils. Though it is an essential nutrient for human metabolism, it also acts as a potent neurotoxin at higher exposure levels [1]. Epidemiological studies revealed that the over exposure of human beings to Mn(II) can adversely affect physiological systems such as nervous, immune, and reproductive systems in adults [2]. During the perinatal period, both a deficiency and an excess of Mn(II) are problematic. Owing to the hazardous effects of Mn(II), it is essential to stringently assess and control its presence in environmental resources. The maximum permissible levels for Mn(II) as set by World Health Organization (WHO) are 0.1 [2] and 0.05 mg/L [3] in drinking and ground water, respectively, while the United States Environmental Protection

Agency (USEPA) has set 0.05 mg/L as a maximum permissible level for Mn(II) in drinking water [4].

The applications of Co(II) in electronic, metallurgical and paint industries have been well defined [5]. Cobalt is essential for human health under permissible limits as it is one of the constituents of vitamin B<sub>12</sub> [5]. However, Co(II) may cause bronchial infection, diarrhea, cardiomyopathy and dermatological disorders if present in amounts greater than the permissible limits [6], which are set at 0.05 and 0.002 mg/L for irrigation and drinking water, respectively [7].

Conventional treatment techniques such as chemical precipitation, reverse osmosis, electrolytic removal, ion-exchange and adsorption have been engineered for the abatement and remediation of heavy metals from water systems. Operational ease, economic feasibility and effectiveness even at lower (<10 mg/L) sorbate concentrations make adsorption a preferred method. Additionally, the related sludge production and disposal issues are minimal during adsorption. Adsorbents such as *Shewanella putrefaciens* [8], calcareous soils [9], brown seaweeds [10], natural clinoptilolite [11], activated carbon [12], vermiculite [13], poly (protoporphyrin-co-vinylpyridine) [14], hierarchical CaCO<sub>3</sub>-maltose meso/macroporous hybrid material [15], lemon peel [16], red macroalgae [17], EDTA-modified chitosan-silica hybrid materials [18], *Rhytidadelphus squarrosus* [19], *Garcinia mangostana* L. fruit shells [20] and granular activated carbon [21] have been recently reported for Mn(II) and Co(II) removal from aqueous phase.

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High surface area to mass ratio and porosity, imparts excellent adsorbent characteristics to nano-materials. The advent of nanotechnology has provided immense scope and opportunities to fabricate the desired nano-sized adsorbents specifically for water decontamination. Nanosorbents such as *Pleurotus ostreatus* nano-particles [2], oxidized multi-walled carbon nanotubes [22], carbon nanotubes [23] and magnetic multi-walled carbon nanotube/iron oxide composites [7] have been reported for the removal of Mn(II) and Co(II) from aqueous media. Though these materials showed high metal removal rate, separation from the aqueous phase is an issue of concern due to their nano-scale size. Utility of nano-sorbents on an industrial scale could cause choking and fouling of industrial columns, limiting their application.

We have encapsulated nanographite carbon in an alginate matrix (referred to as nano carbon beads or NCBs) and utilized them for cobalt [Co(II)] removal in a previous study. Slow sorption kinetics and low Co(II) sorption capacity were the major demerits observed [24]. In the present study, thermal activation of both ABs and NCBs was performed through drying, to overcome the problems observed in the previous study. A comparative study was carried out for the sorption of Mn(II) and Co(II) on both ABs and NCBs. Kinetics, isotherms and thermodynamics parameters were studied. The economic feasibility of the sorption process was confirmed by batch mode desorption and regeneration studies.

## 2. Experimental

### 2.1. Chemicals and reagents

The chemicals and reagents used were of analytical reagent grade or as specified. Sodium alginate was obtained from Sigma–Aldrich and was used without further purification. Stock solutions of Mn(II) and Co(II) (1000 mg/L) were prepared with reagent grade manganese sulfate ( $\text{Mn}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$ , Sigma–Aldrich) and cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , Sigma–Aldrich) in deionized (DI) water, respectively and were further diluted as desired. Calcium chloride ( $\text{CaCl}_2$ ), HCl and NaCl were obtained from Sigma–Aldrich.

### 2.2. Preparation of adsorbent

Graphite nano-carbon (GNC) was prepared following a previously reported procedure [25]. In brief, a plastic electrolytic cell containing de-ionized (DI) water as an electrolyte was used for GNC preparation. Three graphite electrodes (two anodes and a cathode) were immersed in the electrolyte. A two-stage working process consisting of activating the anodes in the initial stage and generating GNC in the final stage was used. A graphite nano-carbon colloidal solution (pH 3) with nano-sized graphite carbon (3000 mg/L) was obtained through electrolysis for 15 min. Fifty grams of sodium alginate (5%, w/v) was solubilized in a GNC colloidal solution (1000 mL) under magnetic stirring for 12 h to obtain a homogeneous colloidal suspension. The suspension was then dropped into 1000 mL of 0.05 M  $\text{CaCl}_2$  solution using a 5.0 mL syringe through a 1.7 mm diameter needle to form NCBs. The beads were incubated for 24 h in a  $\text{CaCl}_2$  solution under ambient temperature conditions to complete the cross-linking reaction, and the NCBs were further rinsed several times with DI water to remove residual GNC particles and non-cross linked calcium ions from the surface. To compare the adsorption performance between non-impregnated and GNC-impregnated beads, pure ABs were prepared separately as a control. Wet NCBs and ABs were thermally activated at  $323 \pm 5$  K in oven by varying the drying time as thermal activation promotes hydrophobicity over the carbonaceous sorbent surface. Initially, wet ABs and NCBs weighed approximately 0.210 g. A drastic decrease in AB and NCB weight to 0.018 g (91.43%) and 0.015 g (92.86%), respectively, was observed

after 24 h of drying. Further increase in drying time to 48 h showed no significant effect on weight loss. Therefore, 24 h-dried ABs and NCBs were utilized for sorption studies. The diameter of the dried beads was approximately 1.0 mm. Activated beads were sealed in polybags and were stored in a desiccators to avoid exposure to dirt and moisture.

### 2.3. Characterization of adsorbent

For spectroscopic characterization of ABs and NCBs, the samples were well-dried and ground. Surface morphology of dry ABs and NCBs was assessed through variable pressure field emission scanning electron microscopy (VP-FE-SEM, Carl Zeiss, Germany). Energy dispersive X-ray analysis (EDX, Hitachi, SU-70) was employed to confirm Mn(II) and Co(II) sorption over AB and NCB surfaces. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer spectrometer (BUCKS-HP9 2FX, UK). The IR absorbance was recorded in the range  $4000\text{--}400$   $\text{cm}^{-1}$  using single reflection and a resolution of  $4$   $\text{cm}^{-1}$ . ASAP2010 (Micro metrics, USA) was used to determine the pore area and porosity of ABs and NCBs. The active sites present on the sorbent surface were determined by Boehm's acid-base titration experiments [26].

### 2.4. Batch sorption/desorption studies

The sorption performance of NCBs was studied in batch mode and compared with ABs using Mn(II) and Co(II) as model sorbates. The studies were performed in 50 mL capped glass tubes. The sorbate solutions (20 mL) of desired concentrations were equilibrated with 0.05 g of sorbents (ABs and NCBs) in a shaker at 100 rpm. The suspensions were filtered after attaining equilibrium and the residual metal concentration in the filtrate was determined using inductively coupled plasma (ICP, Thermo Jarrell Ash, USA) spectrometry.

The sorption capacity at equilibrium ( $q_e$ , mg/g) was determined using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the supernatant initial and equilibrium concentrations (mg/L), respectively,  $V$  is the volume of solution (L) and  $m$  is the mass of sorbent (g).

The pH studies were conducted in a pH range of 2–8 under ambient temperature ( $298 \pm 2$  K) conditions. The initial pH of the sorbate solution ( $C_0 = 50$  mg/L) was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. Contact time studies were carried out at a 20 mg/L initial sorbate concentration under ambient temperature conditions, while the isotherm and thermodynamic studies were performed using a wide range of sorbate concentrations. For desorption studies, the sorbates ( $C_0 = 25$  mg/L) were initially sorbed over ABs and NCBs. At equilibrium, the sorbent was separated from the sorbate system and washed with DI water to remove the unadsorbed metal traces from the surface. The sorbed metal ions were eluted using 0.1 N HCl, 0.1 N  $\text{HNO}_3$  and 0.1 N  $\text{H}_2\text{SO}_4$ . Regeneration studies were conducted for five consecutive cycles using 0.1 N HCl as an eluent.

## 3. Results and discussion

### 3.1. Characterization of sorbents

Morphologically, ABs and NCBs were found to be spherical. Alginate beads appeared pale yellow, while NCBs were black in color due to the encapsulation of GNC. Scanning electron microscopic observations were obtained to characterize the porous structure and rough surface of ABs and NCBs. Microscopic images

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