



Development of novel in situ nickel-doped, phenolic resin-based micro–nano-activated carbon adsorbents for the removal of vitamin B-12

Rishabh Saraswat^a, Neetu Talreja^a, Dinesh Deva^b, Nalini Sankararamakrishnan^a, Ashutosh Sharma^{b,c,*}, Nishith Verma^{a,c,*}

^aCenter for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208 016, India

^bDST Unit of Soft Nanofabrication, Indian Institute of Technology Kanpur, Kanpur 208 016, India

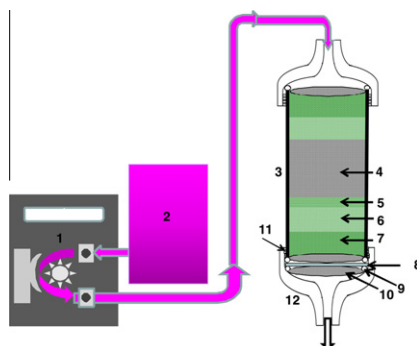
^cDepartment of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208 016, India

HIGHLIGHTS

- Synthesis of Ni-doped activated carbon spheres and carbon micro–nanoparticles.
- Synthesized materials used as efficient adsorbents for vitamin B-12.
- A specially designed column for breakthrough study on micro–nanoparticles.

GRAPHICAL ABSTRACT

A specially designed packed column was developed for applying micro–nanoparticles based adsorbents to the aqueous flow without entrainment or channeling in the column. The breakthrough analysis revealed that the VB₁₂ uptake in the bed was comparable to the equilibrium adsorption data obtained from the batch study. This indicates an effective bed design allowing a uniform flow distribution and minimal particle entrainment and loss by flow. The simple methodology for developing micro–nanoparticles based adsorbents and applying them in the column under dynamic conditions has potential for a wide range of bio-separation and bio-purification applications.



ARTICLE INFO

Article history:

Received 10 March 2012

Received in revised form 13 May 2012

Accepted 14 May 2012

Available online 23 May 2012

Keywords:

Vitamin B-12

Adsorption

Carbon micro–nanoparticles

Biochemical engineering

Environment

Packed bed

Polymerization

ABSTRACT

Activated carbon spheres (ACSs) and carbon micro–nanoparticles derived from nickel (Ni)-doped phenolic beads (~0.8 mm) were synthesized as efficient adsorbents for vitamin B-12 (VB₁₂). Ni was incorporated in an intermediate step during a suspension polymerization. ACSs were synthesized by the carbonization and activation of Ni-doped polymeric beads. Carbon micro–nanoparticles (average size ~200 nm) were synthesized by milling polymeric beads followed by carbonization and activation. Adsorption tests were carried out under both batch and dynamic (flow) conditions. The latter tests were carried out in a specially designed and fabricated micro-column packed with carbon micro–nanoparticles. The adsorption loading of VB₁₂ on the adsorbents was determined to be ~300 mg/g, corresponding to an aqueous phase concentration of 500 ppm, which is comparable to or larger than the literature data. The method of in situ synthesis of metal incorporated carbon micro–nano-adsorbents and their use in a micro-column under the flow conditions has much potential for bio- and pharmaceutical separation and purification applications.

© 2012 Elsevier B.V. All rights reserved.

* Corresponding authors. Fax: +91 512 2590104.

E-mail addresses: ashutos@iitk.ac.in (A. Sharma), nishith@iitk.ac.in (N. Verma).

1. Introduction

Vitamin B-12 (VB₁₂), which is a highly valued pharmaceutical compound, is the largest and most complex water soluble vitamin – essential for the normal growth of human health [1,2]. VB₁₂ is industrially produced by fermentation driven by micro-organisms. The recovery of pharmaceutical compounds by adsorption from crude sources or downstream from the fermentation process is considered to be more energy efficient compared to membrane-filtration and conventional separation techniques such as chromatography and extraction [3].

Polymeric resin-based adsorbents have been extensively used for the removal of pharmaceutical compounds from water. Some common examples of precursors for such polymeric adsorbents are styrene, methyl acrylate, and phenol [4–13]. However, these adsorbents generally have low adsorption capacities for large molecules and compounds such as vitamins and proteins [3–5].

Polymers doped with metals, metal oxides, and inorganic ion exchangers have also found various applications. Polymer/inorganic hybrid composites have been developed as adsorbents for pharmaceutical compounds through the dispersion of inorganic nanoparticles within a polymer-matrix [14]. Styrene/divinylbenzene-based gel-like materials (~150 μm) doped with iron have been prepared for cell labeling [15]. Iron particles have also been incorporated into polystyrene-beads (average size ~80 μm) and this powdery material produced has been used as a scavenger resin [16]. Similar micron sized styrene-based particles (~7 μm) that incorporate Fe-particles have been synthesized by suspension polymerizations for bio-applications, including protein purification and recovery of enzymes [17].

In recent times, owing to its highly developed porous structure and large surface area, activated carbon (AC) derived from polymeric resins has been used as a potential adsorbent for VB₁₂ [18,19]. Being chemically inert and stable, AC has also shown excellent biocompatibility relative to its inorganic or organic counterparts without requiring special coatings [20,21]. There have also been studies on the modification of AC as a way to improve its adsorption capacity for VB₁₂, for example, by coating it with poly-methyl methacrylate [22], blending it with ferrocene [19], and treating it with supercritical water [23]. Recently, carbon nanotubes (CNTs) have been suggested as potential adsorbents for VB₁₂ removal [24].

The method of in situ incorporation of metals during a polymerization step to produce metal-doped polymeric beads (~0.8 mm) is relatively new [25,26]. By this study, iron- and aluminum-doped polymeric beads could be produced. Carbonization and activation of the metal-doped polymeric beads produced activated carbon spheres (ACSs), which were used as adsorbents for the removal of arsenic and fluoride ions from wastewater. Such carbon-based materials had metal nanoparticles uniformly dispersed within their micro-meso porous structures. Ball-milling of the iron/aluminum-doped polymeric beads, followed by carbonization and activation produced carbon micro-nanoparticles (~100 nm) whose adsorption performance with fluoride and arsenic ions were even more encouraging. Inspired by these studies, we have carried out the present study on the synthesis of nickel (Ni)-doped, carbon-based adsorbents for the recovery or removal of VB₁₂. ACSs and micro/nanocarbon particles are derived from Ni-doped phenolic beads. ACSs are synthesized by carbonization and activation of the beads, whereas carbon micro-nanoparticles are synthesized by milling the beads followed by carbonization and activation.

The present study has three novelties. (1) Ni-salts are successfully incorporated in situ in the phenolic precursor during a polymerization step to produce spherical beads (~0.8 mm). (2) A special packed bed column is designed and fabricated for using carbon micro-nanomaterials (~200 nm) as adsorbents under flow

(dynamic) conditions, and (3) Ni impregnated carbon micro/nanobeads are shown to be effective for the removal of VB₁₂.

2. Materials and methods

2.1. Chemicals

All reagents used in the experiment were high purity grade. Phenol, hexamethylene tetraamine (HMTA), formaldehyde (37–41%), triethylamine (TEA), 95% hydrolyzed poly vinyl-alcohol (PVA) (MW = 95,000), nickel nitrate (99%), 1-heptane sulfonic acid sodium monohydrate, and cyanocobalamin as VB₁₂ were purchased from Merck (Germany) and used as received. All solutions were prepared in water obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Synthesis of Ni-doped phenolic beads

Ni-doped phenolic resin beads were synthesized by a suspension polymerization. A 2 l round bottom flask made of glass was used as a reactor for polymerization. The three-neck reactor was equipped with a condenser–reflux assembly, a thermometer and a half round stirrer.

Phenol was used as a monomer and 50 g of it was mixed with 60 ml of formaldehyde in the flask. To this mixture, 1.5 ml of TEA was added as a catalyst. The reaction mixture was stirred at a constant speed of 250 rpm for 3 h at room temperature (30 °C ± 1 °C) to prepare a homogeneous solution. Next, 200 ml of distilled water was added to the solution. Subsequently, the solution turned milky white. The speed of the stirrer was increased to 380 rpm. After 30 min, 3.5 g of HMTA was added as a cross linking agent and water flow in the reflux–condenser was initiated. The flask was simultaneously heated at a rate of 3 °C per min until the temperature reached 100 °C. Subsequently, 3 g of PVA was added as a suspension stabilizing agent. The time that PVA was added was found to be critical to the quality (shape and yield) of the synthesized beads. After approximately 35 min, a yellowish gel-like substance began to appear with the simultaneous formation of froth in the reactor, which was the indication of the incipience of polymerization. At this stage, 7.5 g of NiNO₃-crystals were added to the reaction mixture, and the color of the suspension mixture turned light green. Stirring was continued. The formation of solid beads started after approximately 1 h. After another 2 h, heating was stopped and the reactor was allowed to cool with continued stirring. The stirring was stopped when the temperature of the reactor reached room temperature.

The product was filtered and washed three times with distilled water, followed by methanol and acetone. The materials produced were dried in still air for 12 h and then sieved into beads of different sizes. In a typical experiment, the yield was approximately 30 g (~50% w/w), with an average size of the synthesized beads of 0.8 mm.

2.3. Synthesis of activated carbon spheres and micro-nanoparticles

The Ni-doped phenolic resin spherical beads were carbonized at 950 °C for 1 h under nitrogen flow in a horizontal tube furnace. The carbonized beads were then activated at 900 °C for 1 h using steam (50 sccm) to produce ACSs. Upon carbonization and activation, approximately 40% weight-loss was observed, and the average particle size decreased to ~0.5 mm. Carbon micro-nanoparticles were prepared by milling the Ni-doped polymeric beads in a nano-ball mill (Retsch planetary ball mill, PM100, Germany). Ball-milling was carried out at 350 rpm for 24 h using 10 mm-Tungsten carbide grinding balls (25 nos) in a 250 ml grinding jar. The milled particles

Download English Version:

<https://daneshyari.com/en/article/149700>

Download Persian Version:

<https://daneshyari.com/article/149700>

[Daneshyari.com](https://daneshyari.com)