

THE INFLUENCE OF PHYSICAL CONFIGURATION ON THE PERFORMANCE OF CHITOSAN–POLY(ACRYLIC ACID) HYDROGEL BEADS AS ADSORBENT FOR LEAD(II)

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ABSTRACT

Polymer composites of various configurations have been utilized as adsorbent materials to remove heavy metals from the aquatic environment. In this study, the influence of physical configuration on the prevailing adsorption mechanisms and capacity of adsorbents was elucidated by using chitosan–poly(acrylic acid) (CS–PAA) hydrogel beads in the dry and wet states and comparing their ability to remove Pb(II) from solution. In the production of the beads, crosslinking with glutaraldehyde (GLA) led to the formation of a semi-interpenetrating polymer network (semi-IPN) with enhanced capacity for metal chelation. Meanwhile, the successful integration of CS and PAA was verified by attenuated total reflectance-infrared (ATR-IR) spectroscopy which showed the presence of functional groups contributed by both polymers. Vacuum drying was employed to produce the hard and rigid dry polymer beads. Scanning electron microscopy (SEM) showed that the beads had a convoluted polymer surface covering a homogeneous, compact, and impermeable inner structure. Owing to the non-porous nature of the dry beads, Pb(II) uptake was limited to 37.85 mg/g. However, the use of the wet configuration enabled the internal polymeric material to contribute to the adsorption process through intraparticle diffusion, thereby increasing lead uptake. Intraparticle diffusion was confirmed to occur in three stages and the lead removal increased by 128.48% to 86.48 mg/g. This significant improvement underscores the influence of physical configuration in dictating the prevailing adsorption mechanisms and how it can be used to maximize the adsorptive capacity of polymer composites for the heavy metals in the environment.

Keywords: chitosan, poly(acrylic acid), semi-IPN, hydrogel beads, intraparticle diffusion

1. Introduction

Water pollution poses a continuing and ever-growing threat to the global environment by reducing the suitability of natural water for human use and other vital processes. Among pollutants, heavy metals are of particular concern because of their severe toxicity to human beings and other wildlife, even in relatively low concentrations (N. Li & Bai, 2006; Rivas, Quilodrán, & Quiroz, 2005). More than 20 metals are considered toxic and one of the most toxic is lead (Hajdu *et al.*, 2012). Yet despite its established toxicity, lead continues to be discharged into the environment because it is used in vital industries.

Stringent discharge regulations worldwide have pushed engineers to develop treatment technologies that remove lead from wastewaters and industrial effluents. Among these, adsorption is recognized as the most efficient, promising and widely used fundamental approach in the treatment of wastewaters (Foo & Hameed, 2009) and has proven attractive owing to its simplicity, effectiveness, technical and economic feasibility, and social acceptability (X. Li, Li, Zhang, & Ye, 2012; Nouri, Ghodbane, Hamdaoui, & Chiha, 2007; Vuković *et al.*, 2011; Zhang *et al.*, 2010). In particular, biosorption – the use of inactive and dead biological materials as adsorbents (N. Li & Bai, 2006; Romera, González, Ballester, Blázquez, & Muñoz, 2007) – is of particular interest because of the wide availability of biocompatible, biodegradable, and

renewable macromolecular polymers which are environmentally safe (Febrianto *et al.*, 2009; Garg, Gupta, Bala Yadav, & Kumar, 2003; Hajdu *et al.*, 2012).

Chitosan (CS) is one of the most abundant biopolymers in nature (Dai, Yan, Yang, & Cheng, 2010) and has found extensive use as biosorbent due to the presence of amine (-NH₂) and hydroxyl (-OH) functional groups that form complexes with different substances, especially metal ions (Dai *et al.*, 2010; X. Li *et al.*, 2012; Ngah & Fatinathan, 2010). Use of CS to form hydrogels requires crosslinking in order to improve mechanical strength and stability in acidic media. The use of glutaraldehyde (GLA) as crosslinker, however, consumes amino groups leading to a decrease in adsorption capacity (Kandile & Nasr, 2009). To offset the decrease in performance, poly(acrylic acid) (PAA), a polymer with a carboxyl group in each repeating unit, may be added to form a semi-interpenetrating network (s-IPN) with increased capacity to adsorb pollutants from solution.

In this study, CS-PAA hydrogel beads were synthesized and its performance as adsorbent material for lead was evaluated. Whereas previous researches have shown the applicability of using either dry or wet hydrogel beads for the removal of heavy metals, no study has focused on comparing the efficiency of similar materials in different configurations. By using adsorption assays, this study will show the influence of physical configuration on the lead removal capacity of CS-PAA hydrogel beads and the mechanisms responsible for the observed behavior.

2. Materials and methods

2.1. Materials

CS ($\geq 75\%$ deacetylated, from shrimp shells) and PAA (average molecular weight = 450,000) were purchased from Sigma Aldrich. NaOH was obtained from Alfa Aesar while GLA, Pb(NO₃)₂, H₂SO₄, and HCl were purchased from Fisher Scientific. The chemical reagents used were analytical grade and used without further purification. All aqueous solutions were prepared using deionized (DI) water.

2.2. Hydrogel beads production

Hydrogel beads were prepared by mixing appropriate amounts of CS and PAA powders in 0.5 % (wt) HCl solution to obtain a solution that was 2% (wt) CS and 1.5% (wt) PAA. PAA was initially dissolved in acidic solution by magnetic stirring for 1.5 h in an Erlenmeyer flask before adding CS powder until complete dissolution. To ensure homogeneity, the solution was stirred for 20 h more then left to stand for another 22 h. To form the hydrogel beads, the solution was placed inside syringes fitted with 23G1 Precision Glide needles (BD) and dropped into 1.5 M NaOH solution stirred at 100 rpm using a variable speed pump injector. Contact with the basic media led to immediate hydrogel bead formation and resting for 14 h ensured complete solidification. To remove excess NaOH, the beads were washed with copious amounts of water. The rinsed beads were stored directly in DI water. Prior to adsorption studies, the beads were cross-linked with 2% (vol) GLA solution for 3.5 h and washed with copious amounts of DI water to wash off excess GLA. To produce dry beads, the crosslinked beads were dried in a vacuum oven at 50°C then kept in a desiccator until constant weight.

2.3. Analyses and adsorption assays

Functional groups were identified through Attenuated Total Reflectance–Infrared Spectroscopy (ATR-IR) using a Nicolet iS10 Mid Infrared FTIR Spectrometer (Thermo Fisher Scientific). Processing of the data was done using Omnic 8 software (Thermo Fisher Scientific). To obtain scanning electron microscope images (SEM) using JSM-6010LA (Jeol, USA), the dry beads were coated with gold using Denton Desk V (Denton Vacuum LLC, NJ) at 0.05 Torr and 40 mA for 30s.

Adsorption assays were conducted using 40 mL Pb²⁺ solutions (100 ppm) prepared by dissolving Pb(NO₃)₂ powder in Millipore water. Tests were conducted at room temperature in conical tubes mounted sideways on a platform shaker (New Brunswick Scientific) set at 190 rpm for 20 h. Pb²⁺ concentration was measured using an AAnalyst 200 Atomic Absorption Spectrometer (Perkin Elmer). Lead removal capacity (Q) was calculated using $Q = V(C_o - C_e)/m$ where C_o (mg/L) and

C_e (mg/L) are the initial and final Pb^{2+} concentrations in solution, respectively, V (L) is the volume of Pb^{2+} solution, and m (g) is the polymer mass.

3. Results and discussion

3.1. CS – PAA blending

The blending of CS and PAA was designed to harness the synergistic interaction between the two polymers in its ability to act as adsorbent for heavy metals. To confirm the successful integration of the two polymers and identify active functional groups, the FTIR spectra for CS and CS-PAA were obtained (Fig. 1). Due to crosslinking with GLA and the ionic interaction of the positively-charged amino groups in chitosan and negatively-charged carboxyl groups of PAA, the polymers had formed a semi-interpenetrating network (s-IPN) (Hu *et al.*, 2002; Lee *et al.*, 1999) (Fig. 2).

The peaks exhibited by the FTIR spectra for CS and CS-PAA are consistent with those reported in literature (Dai *et al.*, 2010; Liu *et al.*, 2012; Xu, Xu, Zhao, & Luo, 2013; Yan *et al.*, 2012). For CS, the overlapping peaks observed around 3355 cm^{-1} indicate the stretching vibrations of $-OH$ and $-NH$. Peaks at 1633 cm^{-1} and 1378 cm^{-1} correspond to the bending vibration of the primary amino group and $C-H$ stretching vibration of the alkyl group of the polymeric structure, respectively, while the peak at 1070 cm^{-1} indicate $-C=O$ stretching vibration. When PAA was added to CS, a sharp peak at 1709 cm^{-1} was observed showing the stretching vibration for $-COOH$. Additional peaks at 1566 cm^{-1} and 1409 cm^{-1} were also observed, corresponding to the asymmetric and symmetric vibrations of $-COO^-$, respectively. These peaks indicated the successful blending of PAA and CS.

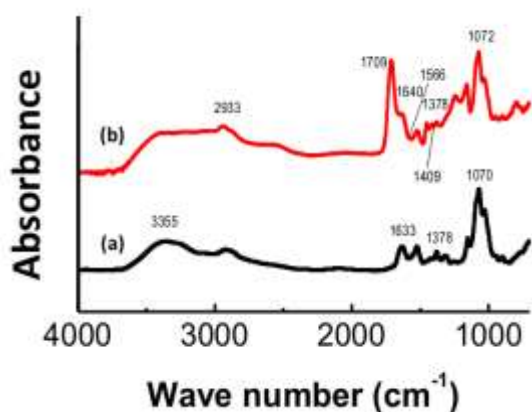


Figure 1: ATR-IR spectra of CS (a) and CS-PAA (b).

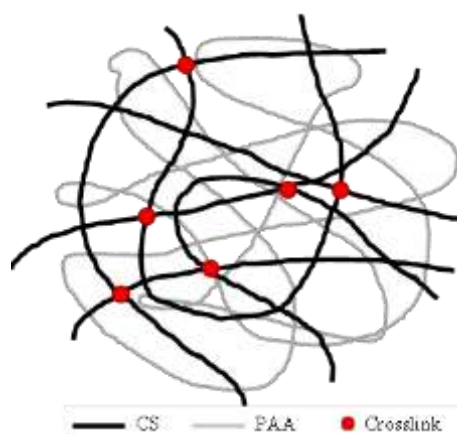


Figure 2: CS and PAA s-IPN after crosslinking with GLA.

3.2. Performance of dry hydrogel beads

Vacuum-dried hydrogel beads were hard and rigid and adsorption assays revealed they were able to remove 37.85 mg/g of lead(II) from solution. An SEM image was obtained to show the surface morphology and help understand the effect of physical configuration on the adsorption process (Fig. 3). The image shows a surface structure made up of a convoluted layer of polymeric material covering an internal structure that was compact, homogeneous, and impermeable. The surface structure is seen to aid the adsorption process by increasing the actual surface area available for adsorption. However, the internal structure did not contribute to adsorption since the non-porous configuration did not allow diffusion to take place and contribute to the removal. Thus, removal was limited to surface adsorption by the functional groups of CS and PAA.

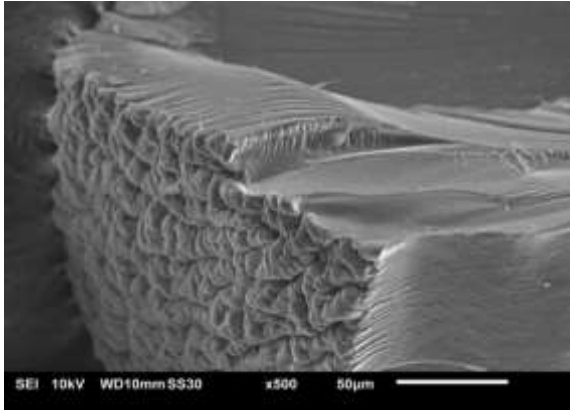


Figure 3: SEM image of dry hydrogel bead showing surface and internal structure

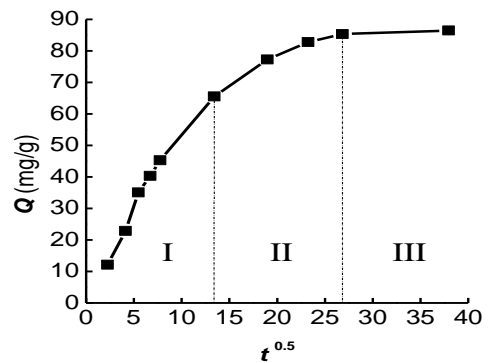


Figure 4: Intraparticle diffusion kinetics for lead(II) uptake.

3.3. Performance of wet hydrogel beads

The use of wet hydrogel beads was able to significantly improve removal by 128.48% to 86.48 mg/g lead(II). The marked improvement is due to the presence of an additional removal mechanism, assumed to be intraparticle diffusion since this mechanism is possible in the hydrated state. To investigate, the kinetic data were fitted to the intraparticle diffusion model using $Q = k_p t^{0.5} + C$ (Basha, Murthy *et al.* 2009) where k_p is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) obtained from the plot of Q_t vs $t^{0.5}$. For processes merely controlled by intraparticle diffusion, the plot forms straight lines.

Fitting of the experimental data into the intraparticle diffusion model did not result in a linear plot indicating that intraparticle diffusion is not the rate-limiting step. However, the shape of the plot suggested that the adsorption mechanism was quite complex and multi-stage (Tan, Chen, & Hao, 2012). Tests for multi-linearity revealed the existence of three distinct regions with different rate diffusion coefficients (Fig. 4): Region I, characterized by the rapid external diffusion and adsorption at the surface ($k_{p1} = 6.19$, $R^2 = 0.986$); Region II, characterized by slow intraparticle diffusion ($k_{p2} = 1.49$, $R^2 = 0.957$); and Region III, characterized by an even slower intraparticle diffusion ($k_{p3} = 0.83$). Since k_{p1} is the highest among the values, the transfer of the lead ions from the bulk phase to the surface occurred fastest. The lower k_{p2} value meant that the penetration of the lead ions into the inner matrix occurred more slowly while the lowest k_{p3} value resulted from the depletion of lead ions in the solution and the establishment of equilibrium at this stage.

4. Conclusion

The results of the present study have shown that physical configuration is a determinant for the performance of hydrogel beads in removing lead(II) from water by dictating the prevailing adsorption mechanisms that occurred in the adsorption system. In the dry state, the mechanism of adsorption was limited to surface adsorption by the functional groups present on the surface of the beads that served as sites for chelation. By this removal mechanism, the CS-PAA hydrogel beads were able to remove only 37.85 mg/g lead(II). In the wet configuration, intraparticle diffusion augmented the surface adsorption and this enabled the internal polymeric material to contribute to the removal of the lead ions leading to enhanced removal. As a consequence, lead removal jumped to 86.48 mg/g. The dramatic increase in performance served to underscore the influence of physical configuration on the performance of hydrogel beads as adsorbent materials.

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