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Reduction of hexavalent chromium by green synthesized nano zero valent iron and process optimization using response surface methodology

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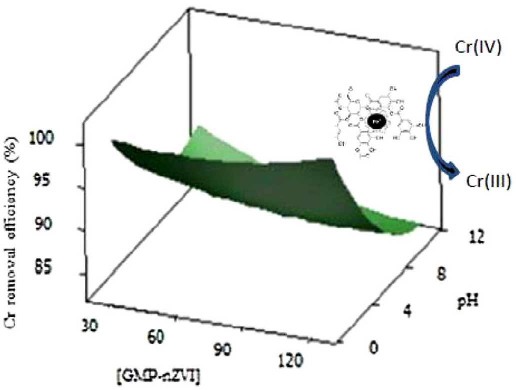
HIGHLIGHTS

- Response surface methodology (RSM) was applied to evaluate chromium removal efficiency of mango peel nano-zero valent iron.
- GMP-nZVI can effectively remove chromium (VI) from the aqueous solution.
- pH played the greatest role in chromium removal.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the most promising applications of zero-valent iron in environmental applications is its viability in reduction processes. Chromium (VI) is a reducible contaminant. In this study, GMP-nZVI (mango peel nano-zero valent iron) was analyzed for its ability to remove chromium from aqueous solution. To determine the optimum operating conditions for removing Cr(VI), response surface methodology (RSM) was applied. GMP-nZVI can effectively remove chromium (VI) from the aqueous solution. EDS and XPS analyses confirmed the reduction of Cr (VI) to Cr (III) and the subsequent adsorption on the surface of GMP-nZVI. Response surface methodology highlighted the role of GMP-nZVI concentration, pH and the initial chromium load in the reduction of chromium (VI) of which pH is the

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greatest contributor (61%). Compared to the commercial forms of nanoparticles, GMP-nZVI indicated improved efficiency in removing Cr(VI), suggesting the role of surface structures in protecting against corrosion.

1. Introduction

Mechanistically, nZVI reactivity is a function of surface area; consequently, mobility of the particle is essential for the successful reduction of Cr (VI). However, formation of passive layers such as magnetite (Fe_3O_4), green rust, goethite (FeOOH), and ferric hydroxide [$Fe(OH)_3$] on the zero-valent iron particle, greatly impacts upon the rate of reduction (Mitra et al., 2011). In addition, a potential challenge to application is the limitation in transport of nZVI in media such as soil and groundwater due to several physico-chemical factors, which leads to the aggregation and settling of particles. Therefore, the radius of influence in the subsurface is limited to few meters. Various approaches have been suggested to promote transport and hence treatment effectiveness. For example, Quinn et al. (2005) reported the use of surfactant-stabilized and biodegradable emulsion forming droplets on zero-valent iron particles. In another study, carbon-supported iron nanoparticles (Hoch et al., 2008) that were modified with polyelectrolyte mixtures support mechanical stability to the nanoparticles (Hydutsky et al., 2007) thereby significantly enhanced transport leading to the rapid remediation of Cr(VI).

Synthesis of iron nanoparticles by means of a biological approach has the advantage of protecting the effect of aggregation via the coatings of polyphenol ingredients. Presumably, the coating improves transport characteristics of the iron nanoparticles Chrysochoou et al. (2012b) carried out a batch column study evaluating the transport characteristics of zero-valent iron synthesized using green tea. The study reported improved transport of nanoparticles whereby 73% of the iron mass was detected in the outflow. Factors such as pH, type and concentration of nZVI, and the geochemical nature of the environment influence the rates of Cr(VI) reduction. In this experiment, GMP-nZVI was tested for its ability to remove chromium from aqueous solution. The polyphenol–iron complex structure on the surface of GMP-nZVI was assumed to protect against surface corrosion thereby enhancing the reduction process. While designing a technological approach for environmental remediation, a thorough understanding of the influences and optimization of the operating conditions that lead to desirable performance is crucial. The conventional approach for optimization of operating conditions requires determining the influential variables in each and every combination of the number of variables by changing them one at a time and keeping all others as constant. This approach is daunting due to the very large number of experiments required which would be expensive and time-consuming. Technically the approach is limited in its ability to reveal the influence of interactions between the independent variables. As an alternative to determine the optimum operating conditions for the removal of Cr(VI), response surface methodology (RSM) was applied. The approach is a powerful experimental design which is based on both mathematical and statistical techniques. It delineates the individual and interaction effects of independent variables ($x_1, x_2, \ldots, x_k$) on the response (y) by generating a mathematical model. Four factors, specifically initial concentration of chromium, concentration of GMP-nZVI, temperature and pH are selected as independent variables influencing the reduction process. A central composite design method was used to evaluate the most efficient treatment conditions of these independent factors.

2. Methods and materials

2.1. Chemicals

Potassium dichromate ($K_2Cr_2O_7$), 1,5-diphenylcarbohydrazide (DPC) and phthalic acid were purchased from Sigma Aldrich, Australia. 300 mL DPC reagent was prepared by dissolving 12 g of phthalic acid and 0.75 g diphenylcarbazide in 300 mL of 95% ethanol. All the reagents used were analytical grade. Commercial nZVI and nano Fe–Ni particles were obtained from Guangzhou Jiechuang Trading Co. Ltd (Guangzhou, China).

2.2. Synthesis of GMP-nZVI

Mango peel was used to prepare the aqueous extract for the synthesis of nZVI. After a thorough washing of the mango peel using deionized water, it was air dried in the shade for two weeks and then the dried peel was ground to fine powder. The extraction was carried out by boiling 12 g of the powder in one liter of deionized water for 12 h at 80 °C. The extract was centrifuged for 10 min at 4000 rpm and filtered using Whatman paper (pore size of 25 μm). Mango peel extract was added drop-wise into the aqueous solution of iron chloride (0.05M $FeCl_3 \bullet 6H_2O$). The synthesis was carried out at room temperature and freeze dried for analysis by X-ray photo-electron spectroscope (XPS). Due to the iron–polyphenol complex formation (core/shell), the use of XRD has a limit in distinguishing the details of the particle composition on the surface and the inner structure. Thus, X-ray photo-electron spectroscope was used to reveal the elemental compositions and oxidation