

Synthesis of nano-hydroxyapatite from a biogenic waste for the removal of manganese from wastewater

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ABSTRACT

A novel Hydroxyapatite (HAp) nanopowder prepared from a biogenic waste, the shell of a gastropod (SS), by hydrothermal method was used as adsorbents (SSHAP nanopowder) for adsorption of manganese ion in wastewater. The SSHAP produced was characterized using FTIR and SEM. Also, the surface area of the nanopowder was determined using BET. The effects of contact time, pH, initial ion concentration and adsorbent dosage were investigated. The initial ion concentration, pH and played important role on the adsorption capacity of the SSHAP nanopowder. Increasing the initial ion concentration increases the removal efficiency. Also, as the pH increases, the removal efficiency increases. However, as the adsorbent calcining temperature increases, the removal efficiency decreases. 79 % removal efficiency of manganese was obtained at 200 mg/L initial manganese concentrations, pH 6 and 120 °C adsorbent calcining temperature. The equilibrium removal process of manganese ions by the nano-HAp was described well with the Langmuir isotherm

model, resulting in the maximum adsorption capacity of 3.163 mg/g of manganese ions on SSHAP nanopowder. The results of the thermodynamic and kinetic investigations indicated that the adsorption reactions were spontaneous ($\Delta G^\circ < 0$), endothermic ($\Delta H^\circ > 0$) and the pseudo second order model fitted better the adsorption kinetics of manganese on the SSHAP. The main mechanism for manganese ions removal using the SSHAP was suggested to be a complex compound formation on nano-HAp surface.

Keywords: Nano-Hydroxyapatite, adsorption capacity, manganese, wastewater treatment.

1 INTRODUCTION

Manganese is one of the three toxic essential trace elements which means that it is not necessary for humans to survive, but it is not only necessary for human survival, but it is also toxic when too high concentration are present in a human body. After absorption of manganese in the human body, it will be transported through the blood to the liver, the kidneys, the pancreases and the endocrine glands. Manganese effects occur mainly in the respiratory tract and in the brain.

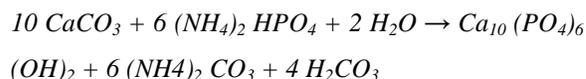
The development of potential low-cost adsorbents with high adsorption capacity levels is essential to facilitate the application of adsorption processes for heavy metal removal. The efficiency of this technique depends on nature of adsorbent. The adsorbent such as activated carbon [1], clay [2], activated alumina [3], chitosan [4], silica [5], zeolite [6], agro-waste [7] and Hydroxyapatite [8] were used for heavy metal removal.

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp] is the main mineral constituent of teeth, bones and phosphate mineral rocks. HAp was reported to be efficient in the removal of many toxic metal ions [20-21]. Natural sources are more cost-effective and safer over cross-reaction and other immunological reaction compared to synthetic HAp.

In the present studies, nano HAP, derived from the shell of a gastropod shell (African land snail, *Achatina achatina*) (SSHAP nanopowder), is being evaluated in abstraction Mn from aqua system. The choice of the shell of this phylum of mollusca as a precursor to the synthesis was predicated on the fact that snail shell (SS) consists mainly of Calcium carbonate [22]. The HAP shall be synthesized from the SS via the hydrothermal method and characterized.

The SS were crushed and subsequently grounded in an agate mortar. The powders were washed in distilled water. After drying, powders were heated to 900 °C for 1h. Produced powders were then mixed with 2.5 times of diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$ (Merck No.1205) by weight and distilled-deionized water. The resulting mixture was converted to nano HAp by hydrothermal method, which was carried out in a stainless steel reactor at 200 °C for 6 hours. Precipitated product was washed

with distilled water and dried at 80 °C for 24 h. The chemical reaction that was generated is as follows:



2 BATCH ADSORPTION STUDIES

Batch adsorption experiments were carried out in aqueous solutions with controlled initial Mn^{2+} concentrations (50-200 mg/L) and pH values. Aqueous solution of different concentrations were prepared by dissolving of appropriate amounts of nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, Merck No. 6725) in distilled –deionized water, and 0.1 mol/L HCl or 0.1 mol/L ammonia solutions were used for pH adjustment. All the experiments were performed by agitating of the Mn solution at the desired concentration and temperature. Samples were taken at appropriate time intervals and then filtered through 0.45 μm filters and the Mn was determined in the liquid phase using atomic absorption spectrophotometer. All experiments were carried out in duplicate.

3 RESULTS AND DISCUSSION

3.1 Infrared spectral analysis

FTIR analysis of the new adsorbent was performed, and the percentage transmission for various wave numbers is presented in Figure 1. The FTIR spectra of thenano HAP shows the presence of absorption bands at 562, 597, 962, 1032 and 1095 cm^{-1} corresponding to the PO_4^{3-} groups of the hydroxyapatite. The band around 3650, 3572 cm^{-1} and peaks around 632 cm^{-1} is due to the OH group. However, the appearance of peaks at 1460, 1418 and 870 cm^{-1} indicates the presence of trace contamination

of residual carbonate in HAp.

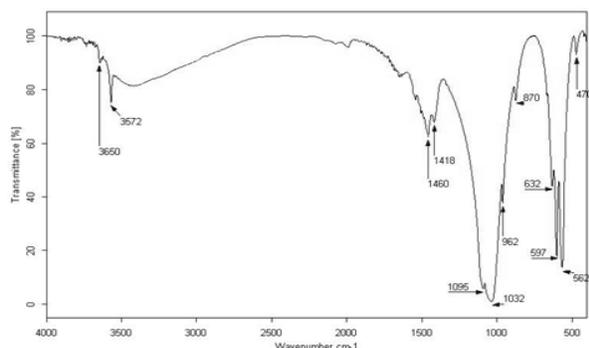


Figure 1 FTIR spectra of SSHAP

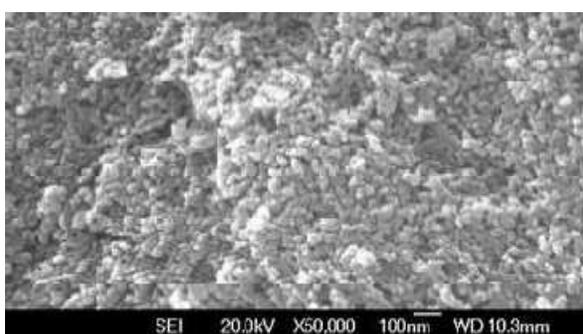


Figure 2 Scanning Electron Microscope of SSHAP

SEM was applied to characterize size and morphology of the SSHAP nanopowder. Typical SEM image of the HAP nanopowder are shown in Fig. 2. It shows that nanoparticles are sphere-like shaped or ellipsoidal particles with nano-size. Mean diameter calculated from the SEM image was estimated as ca. 10.3 nm.

3.2 Effect of contact time and initial Mn^{2+} concentration

The effects of contact time on the SSHAP– Mn^{2+} interaction were determined by studying the time-concentration profile, at fixed SSHAP:1 dosage (1 g, temperature (303 K) but varying Mn^{2+} concentrations (50, 100, 150 and 200 mg/L) and contact time (20,40, 60, 80, 100 and 120 min). The amount of adsorbed Mn^{2+} increased with contact time for all the initial Mn^{2+} concentration and attained

equilibrium within 60 min, showing that the adsorption occurred quickly (Fig. 3). The reason for the rapid adsorption of the Mn^{2+} ion might be that the SSHAP colloidal particles have a small average particle diameter and little internal diffusion resistance. However, the absolute amount of Mn^{2+} adsorbed per unit mass of sorbent increased with increase in the initial Mn^{2+} concentration. The increase became gradual until a point where there is no change in the amount adsorbed i.e a constant value when the amount of dye desorbed is proportional to the amount of dye on the adsorbent inferring dynamic equilibrium. The time required to attain this state of equilibrium is termed equilibrium time, and the amount of Mn^{2+} adsorbed at equilibrium reflects the maximum adsorption capacity of the adsorbent under the operating conditions.

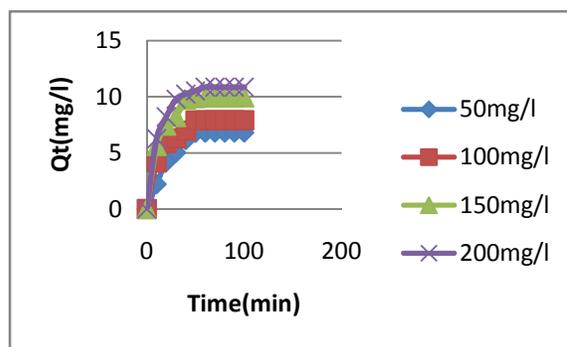


Fig. 3. Time-concentration profile of the sorption of Mn^{2+} on SSHAP.

3.3 Effect of solution pH

Figure 4 showed the percentage removal of Mn^{2+} versus pH over a range of pH 3.0 to 11.0. The percentage adsorption of Mn^{2+} increased with an increase in pH up to pH 6 and then decreased. This is due to the fact that pH affects concentration of the counter ions on the

functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. When the pH of the adsorbing medium increased from pH 3 -6, there was a corresponding increase in deprotonation of the adsorbent surface leading to a decrease in the H^+ ion on the surface of the adsorbent. This creates more negative charges on the adsorbent surface which favours adsorption of positively charged species and the positive sites on the SSHAP surface [13]. The optimum removal efficiency was at pH 6.

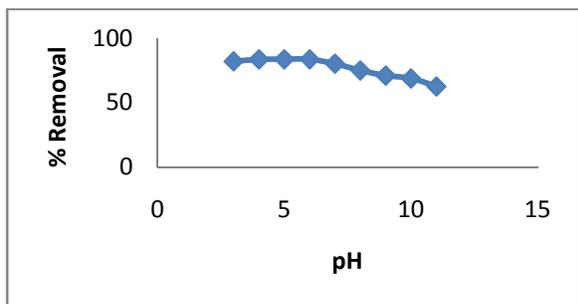


Figure. 4 Effect of solution pH on the % removal of Mn^{2+}

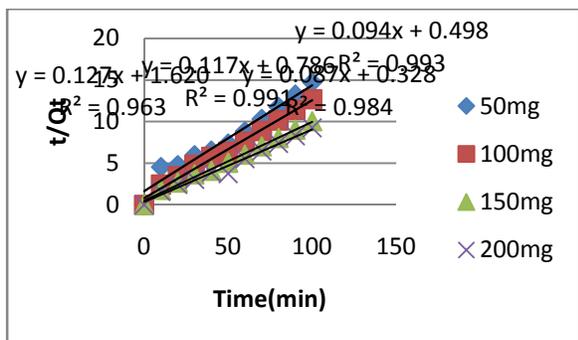


Figure 5 Pseudo second order model plot for the adsorption of Mn^{2+} onto SSHAP at 30° C at different initial concentrations.

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