CHITOSAN FROM CRAB SHELLS AS CHROMIUM ADSORBENT

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ABSTRACT: *The potential of chitosan extracted from crab exoskeleton as biosorbent for the removal of toxic Cr(VI) on waste water is investigated by doing preliminary adsorption experiment to determine the effect of contact time, pH, initial Cr(VI) concentration, dosage of biosorbent and particle size. Batch adsoption method is employed in the adsoption experiment. The highest removal of Cr(VI) on chitosan was attained at 45 min contact time, pH 2.00, 30 ppm initial Cr(VI) concentration, 30 mg chitosan dosage, and 1.18 mm chitosan particle size. The adsorption capacity of chitosan was 24.52 mg/g (±0.138) under these conditions, in which 51.07% (±0.193) of Cr(VI) is adsorbed. These results suggest that chitosan can be used as a cheap alternative biosorbent for the removal of heavy metals.*

Keywords: chitosan, adsorption, chromium

1. INTRODUCTION

Overexposure to heavy metals causes toxicity to human, as well as to all living organism [1-2]. Hexavalent chromium (Cr(VI)) is known for its carcinogenic effect in humans [3]. Short term and prolonged exposure to Cr(VI) through inhalation, ingestion or topical contact can also cause adverse health effect in human [3-7].

A number of treatment methods for the removal of chromium ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation, and adsorption. Most of these methods suffer from drawbacks such as high operational costs and incomplete removal or the disposal of the residual metal sludge.

Hence, it is important to study other alternative treatment methods for metal bearing-effluents that is efficient and economical. One such as technique is via adsorption process that uses biosorbent that are abundantly available in nature.

In recent years, biosorption by biologically originated materials in removing heavy metals has drawn more and more attention, largely due to the unique properties of these biomaterials being environmentally unreactive, low cost, effective at low metal concentration and easily reusable [8-9]. Biosorption, which involves active and non-active uptake by biomass, is a good alternative to traditional processes. Biosorption removal of toxic heavy metals is especially suited as a 'polishing' wastewater treatment step because it can produce close to drinking water quality [10].

The biopolymer used in this study is chitosan, which is obtained from the deacetylation of chitin (Figure 1). Chitin is the second most abundant natural polysaccharide after cellulose and is composed of β(1→4)-linked 2-acetamido-2-deoxy-β-D-glucose [11]. Chitosan is a copolymer of glucosamine and N-acetylglucosamine and it has an amine functional group, which is strongly reactive with metal ions [10]. Chitosan is more protonated at low pH, therefore it is able to bind anions by electrostatic attraction [12].

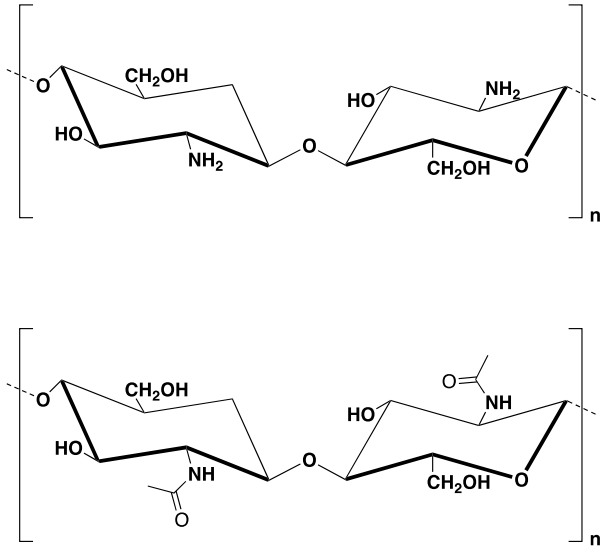

Figure 1. Structure of chitosan (top) and chitin (bottom)

2. EXPERIMENTAL DETAILS

2.1. Chemicals and Instrument

All chemicals were of reagent grade and used as purchased. All weighing were done using a Mettler Toledo AT21 Comparator analytical balance. UV-Vis spectroscopic measurements were performed using Lasani LI-2800 UV-Vis spectrophotometer. The pH was measured using Fisher Accumet pH meter model 610A.

2.2. Sample Collection and Preparation

Crab exoskeleton samples were collected in Barangay Tuna-an, Municipality of Lala, Lanao del Norte where crab fattenings are located. The meat and other parts of crabs were removed and the remaining exoskeleton was washed with tap water to remove dirt and other unwanted materials that may interfere in the extraction of chitosan. The cleaned exoskeleton was dried by hanging in a net under the sun to avoid the growth of unwanted molds.

Using a blender the dried crab exoskeleton was crashed and

pulverized. It was then washed thoroughly with deionized water with repeated soaking, stirring and decanting until all dirt and unwanted impurities were removed. The clean pulverized crab exoskeleton was oven-dried at 80 ^{o}C for a few hours until stable weight was attained. The dried pulverize crab exoskeleton was then sieve into particle sizes 0.245 mm, 0.4 mm and 1.18 mm.

2.3. Preparation of Chitosan

Chitosan was prepared by deacetylation of chitin, which is naturally found in crab exoskeleton. The purification method of chitin was based on the detailed methods of Bader, 1997 [13]. Further isolation of chitosan from chitin was done following the procedure obtained from the work of Hadi, 2013 [14]. These are briefly discussed in the following sections.

2.3.1. Calcium Carbonate Removal (Demineralization)

Removal of calcium carbonate from the sample of different particle size was done separately. Each sample (25.0 g) was treated with HCl solution (250 mL of 0.68 *M*) by slow addition and the mixture was stirred for 6 h at room temperature until the gas stops to evolve. The sample was then filtered. Additional HCl (10.0 mL of 0.68 *M*) was added to check if calcium carbonate is completely removed. If no further generation of gas (bubbling) occurs the calcium carbonate is completely remove. The crab exoskeleton was then filtered and washed with deionized water.

2.3.2. Protein Removal

In the removal of protein, NaOH solution (250 mL of 0.62 *M*) was added to the previously demineralized sample. The sample was soaked with NaOH solution (250 ml of 0.62 M) for 16 h at ambient temperature. The sample was filtered and washed with deionized water to neutral pH, until the filtrate is almost clear and colorless. The resulting residue is the purified chitin, which was oven dried at 100 ^{0}C.

2.3.3. Preparation of Chitosan from Chitin by Deacetylation

In the deacetylation of chitin, NaOH (250 mL, 50 % (w/v)) was added to 25 g of the previously prepared chitin and was heated at 50 ^{0}C for 4 h. The sample was placed under the hood for 30 min. The cooled sample was washed with NaOH (250 mL, 50 % (w/v) and filtered to retain the solid matter, which was the chitosan. The prepared chitosan was oven dried at 100 ^{0}C.

2.4. Adsorption

Batch equilibriation method was carried out for the adsorption experiment. The parameters: pH, contact time, initial metal ion concentration, adsorbent dosage, and particle size, was each varied, one at at ime, while setting other parameters constant (set conditions, Table 1). All experiments were conducted at 25 ^{0}C.

2.5. Spectrophotometric Determination of Residual Cr(VI)

Several concentrations of Cr(VI) were prepared from the $K_2Cr_2O_7$ stock solution for the calibration curve. Each solution of $K_2Cr_2O_7$ (5 mL) was added with 2.5 mL of 1,5-diphenylcarbazide solution. The solution was transferred to a 50 mL volumetric flask and diluted to mark with deionized water. The resulting solutions were allowed to stand for 10 min to allow full color development.

1,5-diphenylcarbazide solution was prepared by dissolving 40 mg of 1,5-diphenylcarbazide in ethanol (20 mL of 95% (v/v)). The resulting solution was added with H_2SO_4 (80 mL, 1.44 *M*).

The absorbance of the standard solution was determined using double beam UV-Vis spectrophotometer at 540 nm [15]. The concentration of Cr(VI) in solution was based on a standard curve (Figure 2).

Table 1. Experimental parameters for adsorption

Parameters	pH	Particle Size, mm	Dosage, mg	Initial Cr(VI) concentration, ppm	Contact Time, min
pH	2 3 4 5	0.245	30	30	35
Particle Size, mm	3	0.245 0.450 1.180	30	30	35
Dosage, mg	3	0.245	10 20 30	30	35
Initial Cr(VI) concentration, ppm	3	0.245	30	10 20 30	35
Contact Time, min	3	0.245	30	30	35 45 55 65 75

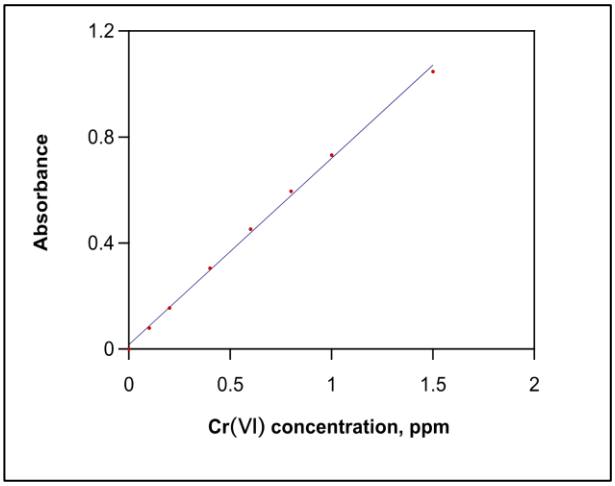

Figure 2. Calibration curve for determination of Cr(VI)

2.5.1. Measurement of Residual Cr(VI)

In the determination of concentration of Cr(VI) from the adsorption experiment, the analyte solution was prepared in the same manner as the standard solution.

2.6. Adsorption Capacity of Chitosan

The adsorption capacity of extracted chitosan was determined by conducting adsorption experiment using the observed conditions in which highest removal of Cr(VI) attained. Cr(VI) solution (250 mL, 30 ppm) was prepared from the stock solution of Cr(VI) (500 mL, 500 ppm). The prepared solution (50 ml) was added to 250 ml Erlenmeyer flask, one containing 30 mg of chitosan adsorbent (1.18 mm) and the other without chitosan. Both flasks were agitated for 45 min in a mechanical shaker. After the adsorption process, the solutions were filtered and 5 mL aliquot of each solution were added with 2.50 mL 1,5-diphenylcarbazide. The resulting solutions were then diluted to 50 mL with deionize water and subjected to spectrophotometric analysis.

3. RESULTS AND DISCUSSION

The effect of various parameters (contact time, pH, initial Cr(VI) concentration, chitin dosage, and particle size) on the removal of Cr(VI) in aqueous solution using extracted chitosan was studied to determine the optimal conditions.

3.1 Effect of pH

The effect of pH of Cr(VI) solution on the adsorption of Cr(VI) on chitosan was studied by varying the pH from 2.00 to 5.00. It was observed that that adsorption of Cr(VI) on chitosan is highly pH dependent: as the pH increases the amount of Cr(VI) removed by chitosan decreases (Figure 3).

Cr(VI) ions exist as $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ in aqueous solution. The relative concentration of various Cr(VI) species depends on pH and total Cr(VI) concentration [16]. Above pH 6, CrO_4^{2-} dominates. Below pH 6, $HCrO_4^-$ dominates when Cr(VI) concentrations are relatively low, and $Cr_2O_7^{2-}$ becomes more significant as Cr(VI) concentration increases [16-17].

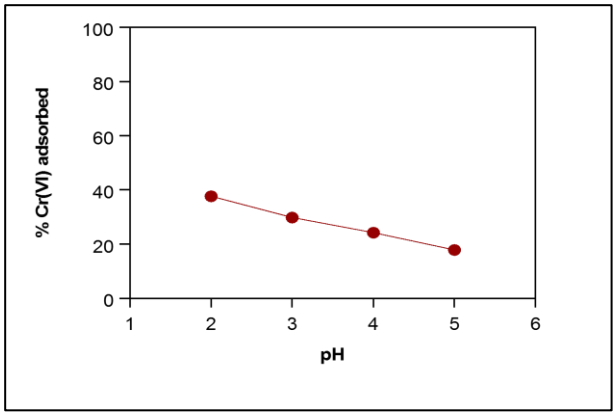

Figure 3. Effect of pH on the adsorption of Cr(VI) on chitosan

The highest adsorption was observed at pH 2.00 which indicates that the active form of Cr(VI) ion is $HCrO_4^-$. Furthermore, chitosan is more protonated at lower pH, and therefore is able to bind anions by electrostatic attraction [12]. The increase in the removal of Cr(VI) as pH decreases suggests that binding of Cr(VI) may have occurred through electrostatic attraction to the positively charged functional groups on the surface of the adsorbent [18]. A pH of 2.00 is selected as the pH at which optimal removal of Cr(VI) is observed.

3.2. Effect of Contact Time

The effect of variation of contact time on the adsorption of Cr(VI) using the biosorbent chitosan was studied for a minimum contact time of 35 min and maximum contact time of 75 min, with 10 min interval. Figure 4 shows that the amount of Cr(VI) adsorbed is constant within the time selected for the experiment. It can be assumed that the adsorption of Cr(VI) on chitosan may have attained equilibrium. The contact time for all other adsorption experiment was set at 45 min.

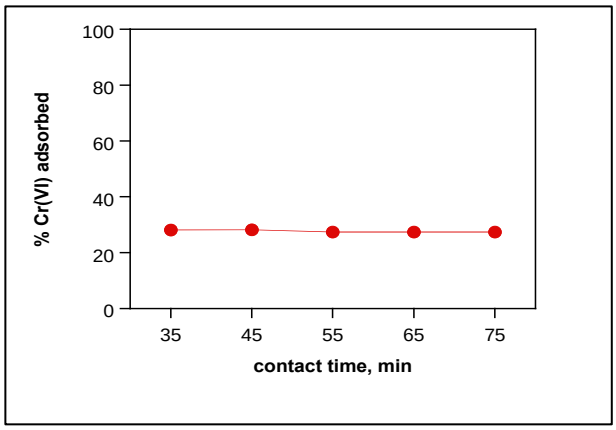

Figure 4. Effect of contact time on the adsorption of Cr(VI) on chitosan

3.3. Effect of Initial Cr(VI) concentration

The effect of amount of Cr(VI) was studied by varying the initial Cr(VI) ion concentration from 10, 20, and 30 ppm. The initial concentration of metal ions provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases. Increasing the initial metal ion concentration enhances the driving force between aqueous and solid phase and increases the number of collision between adsorbent and adsorbate [19]. It can be observed (Figure 5) that at lower initial Cr(VI) concentration the amount of Cr(VI) adsorbed on chitosan is relatively small (4.7 %) and at high initial Cr(VI) concentration the Cr(VI) ion removed increases (28.5 % at 30 ppm Cr(VI)). A concentration of 30 ppm is established as the initial metal ion concentration for the adsoption process.

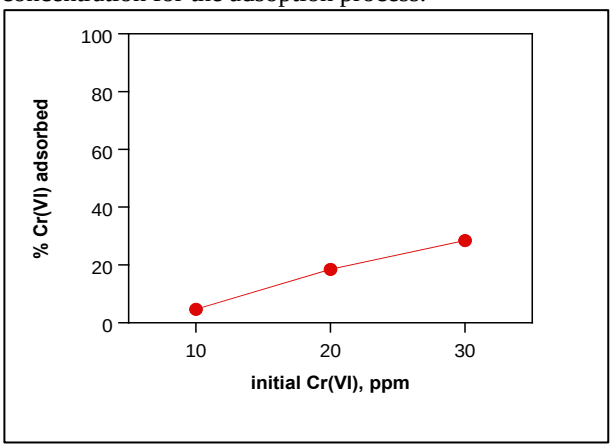

Figure 5. Effect of initial amount of Cr(VI) on the adsorption of Cr(VI) on chitosan

3.4 Effect of Chitosan Dosage

The effect of chitosan dosage on Cr(VI) adsorption was studied by varying the amount of chitosan from 10, 20, and 30 mg. The amount of Cr(VI) ion adsorbed increases as the amount of adsorbent increases (Figure 6). This can be reasoned by the fact that there is subsequent increase in available active sites present on chitosan with increasing dosage, thus enhancing the adsorption capacity of chitosan for Cr(VI). A 30 mg chitosan dosage is selected as the dosage at which highest adsorption of Cr(VI) in aqueous solution is observed.

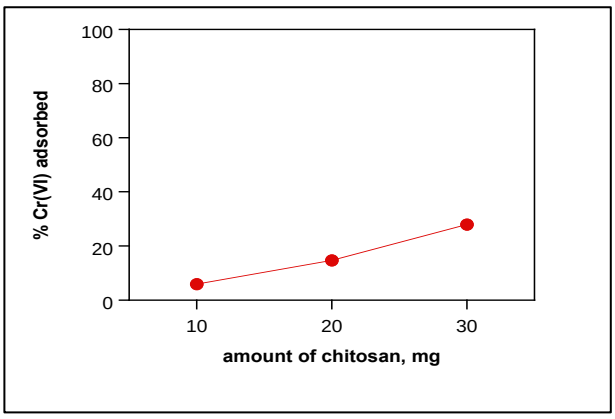

Figure 6. Effect of chitosan dosage on the adsorption of Cr(VI)

3.5 Effect of Particle size

The effect of particle size on the adsorption of Cr(VI) on chitosan is evaluated by varying the particle size. The amount of Cr(VI) adsorbed on chitosan increases as the particle size increases (Figure 7). Although it would be expected that as the particle size increases the adsorption of Cr(VI) on chitosan would decrease due to the increase in surface area of the adsorbent, the number of micro pores also increases with increasing particle size. The increase in the number of micro pores increases the number of accessible sites, hence increasing the amount of Cr(VI) adsorbed. As such, 1.18 mm chitosan particle size is established as the particle size for the adsorption process.

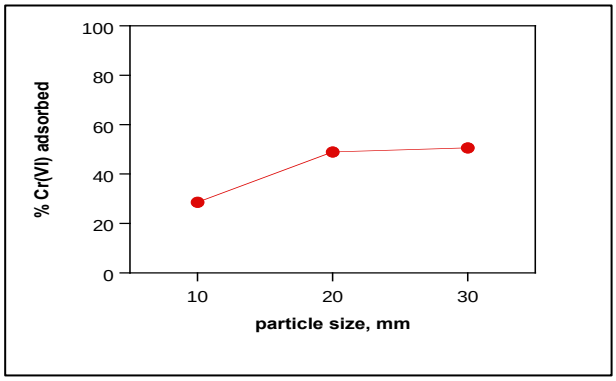

Figure 7. Effect of chitosan particle size on the adsorption of Cr(VI)

3.6 Adsorption Capacity of the Extracted Chitosan

Based on the adsorption experiment it can be deduced that the adsorption of Cr(VI) on chitosan as biosorbent is dependent on the varied parameters (pH, amount of chitosan, particle size, initial Cr(VI) concentration and contact time).

The maximum adsorption capacity of chitosan was determined by using the established conditions at which maximum adsorption of Cr(VI) was observed: 30 ppm initial Cr(VI) concentration, 30 mg chitosan adsorbent dosage, pH 2.00, 45 min contact time, and 1.18 mm particle size. Under these conditions, the adsorption capacity, q_e, was found to be 24.52 mg/g (±0.138) of Cr(VI) adsorbed per gram of the adsorbent, in which 51.07% (±0.193) of Cr(VI) was adsorbed on the extracted chitosan.

4. CONCLUSIONS

Adsorption of Cr(VI) on chitosan was found to depend on pH, chitosan particle size, amount of Cr(VI), and amount of chitosan. Other possible parameters that may affect the adsorption study may also be evaluated such as the agitation speed, temperature and age of the crab.

The use of waste crab shells is an economical and environmentally friendly alternative in the removal of Cr(VI) in aqueous systems, such as in wastewater. This may be extended to other metal ions as well.

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