

Chromium Ion Adsorption Using Chitosan from Mussel

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Abstract : Heavy metals discharge associated with industrial activities constitute serious environmental problems, most especially water pollution. Many materials have been identified for the adsorption of these heavy metals and chitosan, a derivative of natural polymer chitin, has been identified as one of such materials. This study was carried out to investigate the removal of chromium (VI) from chromate solution using chitosan from mussel shell, obtained from Gubi dam in Bauchi Nigeria. Chemical method was used to extract the chitosan from the chitin. The chitosan had degree of deacetylation (DDA) of 60.69% and 60.66% as calculated from elemental analysis and FTIR spectra of chitosan respectively and surface area of 2.77m²/g. The chitosan was used for removal of Cr⁶⁺ from dichromate-deionised water solution with initial Cr⁶⁺ concentration of 0.62 mg of Cr⁶⁺ per litre of water and the adsorption isotherm established. Optimum chitosan dosage was found to be 2.5 g at 28°C with a Cr⁶⁺ removal of 82.3%. The time required for equilibrium to be attained was 80 minutes for batch adsorption study. The Langmuir isotherm was the best fitted isotherm with an R²-value of 0.983.

Keywords : Adsorption, Chitosan, Chromium, Isotherms, Mussel.

I. Introduction

In the past century there has been a rapid change in industrialization. This has led to an increase in the complexity of toxic effluents. Several industries such as tannery, mining, petrochemicals etc. generate waste waters containing metals [1,2]. Efficient removal of toxic metal ions from these wastewaters is an important and widely studied research area where a number of technologies have been developed over the years [3].

A wide range of physical and chemical processes for the removal of these metals from such waters are precipitation, ultrafiltration, adsorption, ion exchange, reverse osmosis, oxidation, ozonation etc. Among these, the adsorption method has been proven to be an excellent method due to its advantages over the other processes mentioned [4]. Adsorbent such as chitosan, activated carbon, zeolites etc. have been reported as used for the adsorption of heavy metals from waste water.

Chitosan can be obtained by deacetylation of chitin through enzymatic or alkaline method during the course of deacetylation; parts of polymer N-acetyl links are broken with the formation of D-glucosamine units, which contain a free amine group, increasing the polymer's solubility in aqueous means [5].

A lot of achievements have been recorded with respect to chitosan and its use as an adsorbent in trapping heavy metals from waste water. Chemically Modified Chitosan beads from chitosan flakes were used to adsorb mercury ion by Chung and Wolfgang [6], and they reported that 2.3 mmol of mercury ion was removed per gram of chitosan beads [6]. Saifuddin [7] reported the removal of chromium (VI) ion using chitosan coated oil palm shell charcoal, and chromium removal of 154mg Cr (VI) ion/g of composite was achieved. It was also discovered that by using biopolymer crab shell chitosan, the degree of sorption of manganese, Zinc, Nickel, Iron, Lead, Chromium and Cadmium by the adsorbent follows the order Mn>Cd>Zn>Ni>Fe>Pb>Cr [8]. Dhanesh and Anjali [9] used commercial chitosan for the adsorption of chromium (VI) ion and reported that the adsorption process was dependent on contact time, pH of the solution and the initial concentration of the sorbate.

Despite all these works no work has been reported in the use of chitosan from mussel shells for adsorption of heavy metals. However, it was reported that the properties of chitosan are raw materials and source dependent [10]. Since the shells of mussel are not biodegradable, they constitute environmental nuisance along dams where they exist and they are not usually properly disposed, therefore the need to investigate their use as adsorbent in heavy metal removal. The isotherm of adsorption was also studied to establish the isotherm that the generated adsorption data fits best and therefore describe the nature of the adsorption process.

II. Materials And Method

2.1 Chitosan Extraction

The mussel shells used for the chitosan extraction were gotten from the Gubi Dam bank of Bauchi, north eastern part of Nigeria. The chitosan extraction was done in four steps as used in Abdulkarim *et al* [11]; pre-treatment, demineralization, deprotenization and the deacetylation steps.

The shells obtained were washed thoroughly with distilled water and dried in an oven to constant weight at a

temperature of 35°C. Then 100g of the sample was taken out of the shell sample for the extraction process. The dried shells were size-reduced and soaked in 0.68 M HCl (1:10 w/v) at ambient temperature (approximately 30°C) for 6 hours after which it was washed in the acid until no bubbles were seen and no colour change was observed. The sample was then washed with distilled water until a relatively neutral pH was obtained and then the demineralized shells were dried to constant weight. The demineralized mussel shells were dried weighed and soaked in 0.62 M NaOH solution (1:10w/v) at ambient temperature (approximately 30°C) for 16 hours. After which the shells were then washed thoroughly with water followed with distilled water until a neutral pH was obtained. The chitin was then dried to constant weight and ground and screened with 150µm sieve. The chitin obtained was then deacetylated in 25 M NaOH (1:10 w/v) for 20 hours at 75°C. After deacetylation, the chitosan is then washed thoroughly with water followed by distilled water. The resulting chitosan was then dried to constant weight and characterized. The characterization revealed that the mussel shell contained 15.14% chitosan as obtained from the proximate analysis result. The DDA was evaluated after the characterization using Kasaai Equation (Equation 1) [12] and Equation 2 respectively,

$$DDA\% = \frac{6.857 - \left(\frac{C}{N}\right)}{1.7143} \times 100 \quad (1)$$

$$DDA\% = 60.69\%$$

$$DDA = 100 - \frac{A_{1655}}{A_{3450}} \times 115 \quad (2)$$

$$\text{But } A_{1655} = -\log\left(\frac{T_{1655}}{100}\right) \quad \text{also } A_{3450} = -\log\left(\frac{T_{3450}}{100}\right)$$

Where T and A are the transmittance and adsorbance at the respective wavelengths

DDA = 60.66% (From FTIR Analysis)

2.2 Adsorption Studies

0.5g of K₂Cr₂O₇ salt was weighed and added to 1000 ml of deionized water to simulate chromium ion contaminated water for treatment using chitosan. The initial concentration of 0.62 mg/L of Cr (VI) ion in solution was detected by the spectrophotometer. 100ml of the solution was taken from the bulk solution prepared above and 0.5g of chitosan sample was added to it, the mixture was stirred continuously for 5 minutes at room temperature (28°C). The mixture was allowed to settle after which the clear solution was filtered then a pillow of chromaVer 3 was added to the mixture and shaken thoroughly. The concentration of chromium (VI) was determined using the DR 2000 spectrophotometer. This procedure was repeated for chitosan dosage of 1.0g, 1.5g, 2.0g, 2.5g, 3.0g, and 3.5g, respectively. Optimum dosage of chitosan during the experiment was noted by checking the mass of chitosan that gave the least residual concentration of Cr (VI) in the solution.

III. Results And Discussion Of Results

The mussel shell and the chitosan as reported by Abdulkarim *et al* [11] has the following characteristics; the mussel shell has a mineral content of 51.62%, a chitin composition of 23.25% and the chitosan composition of 15.14%. The chitosan extracted has a degree of deacetylation of 60.69% and 60.66% calculated from the elemental analysis and the FTIR spectra of chitosan respectively. The carbon-nitrogen ratio of the chitosan extracted was 5.9.

Figure 1 shows the variation of final concentration of chromium (VI) ion with the increase in chitosan dosage. At a room temperature of 28°C and a contact time of 5 minutes, the equilibrium concentration was reached with chitosan dosage of 2.5g after which increased dosage makes no reasonable difference, thus this dosage was selected as the optimum dosage, and the Cr⁶⁺ ion concentration (0.11mg/l) was taken as the equilibrium concentration. The percentage uptake at this point was 82.3%.

Establishment of adsorption isotherms for Cr (VI) removal using chitosan

The isotherm study in this work is illustrated in Figures 2 and 3 for Langmuir and Freundlich isotherms respectively. The Langmuir isotherm was built under the assumption that the adsorption takes place in a monolayer on a uniform surface with a finite number of adsorption sites. Once these adsorption sites are occupied, no further adsorption can take place. The Langmuir isotherm equation is shown as Equation 3

$$q_e = \frac{k_L b C_e}{1 + k_L C_e} \quad (3)$$

Where, b is the Langmuir constant related to the energy of biosorption (L/mg), k_L is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g), C_e is the equilibrium solute concentration (mg/L) and q_e is defined by Equation 7. The Langmuir adsorption isotherm can be transformed to linear form thereby allowing the parameters to be estimated graphically or with linear regression. One of the linearized forms of the equation is shown as Equation 4

$$\frac{C_e}{q_e} = \frac{1}{k_L b} + \frac{1}{k_L} C_e \quad (4)$$

Using Equation 4, Figure 2A was plotted, such that $\frac{C_e}{q_e}$ is plotted against C_e from where the parameters shown

in Table 1A were calculated.

The Langmuir adsorption isotherm equation is often used to describe the sorption of solute from solution. Table 1A shows the R-square value from the Langmuir plot and other constant. An important parameter determined also is the R_L .

$$R_L = \frac{1}{1 + b C_o} \quad (5)$$

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L is a positive number whose magnitude determines the feasibility of the adsorption process [13]. From Table 1A, the R-square value is 0.983 signifying a good fit, and an R_L value of 0.314. Thus from the above categorisation by Srividya and Mohanty, it can be said that the adsorption process is favoured and it is a physical process since it is reversible.

The second isotherm considered was the Freundlich isotherm. It is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows:

$$q_e = a_f C_e^{b_f} \quad (6)$$

$$q_e = \frac{v (C_o - C_e)}{m} \quad (7)$$

Where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g) calculated from Equation 7, v (L) is the volume of solution for in which the adsorption is taking place, a_f Freundlich isotherm constant, m is the mass of the adsorbent (gram), C_e solution phase ion concentration at equilibrium, mg/L; and b_f is the heterogeneity parameter. It is expected that b_f has an inverse relationship with the heterogeneity. Freundlich equation is strictly valid only for ion adsorption at low concentration. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The linearized Freundlich equation is shown as Equation 8.

$$\ln q_e = \ln a_f + b_f \ln C_e \quad (8)$$

Equation 8 was used to plot Figure 3). The R-square value in Table 1 is very low (0.0254), thus the data does not fit well with the Freundlich isotherm but important parameters like n and b_f were determined. The n or $1/b_f$ value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $1/b_f = 1$, then adsorption is linear; if $1/b_f < 1$, then adsorption is a chemical process; if $1/b_f > 1$, then adsorption is a physical process [14]. For this work, as shown in Table 1A, $n=1.217$ which means the adsorption is physical and this further confirms the deduction made from the Langmuir isotherm.

IV. Conclusion

The optimum chitosan dosage for the removal of 0.51 mg/L of chromium (VI) which is 82.3% of the initial concentration (0.62 mg/L) was determined to be 2.5 g at 28°C. The data obtained from chromium (VI) removal from Chromium solution fits best with the Langmuir isotherm with an R^2 -value of 0.983 which is clearly higher than that of the Freundlich isotherm of 0.0254, thus the adsorption process of chromium (VI) on chitosan follows the Langmuir isotherm.

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APPENDIX

Table 1: Freundlich and Langmuir constants determined from the isotherms plotted and evaluated parameters

Isotherm	R ²	Slope	Intercept	b _F	a _F	n	k _L	B	R _L
Langmuir	0.983	0.0176	0.005	-	-	-	56.82	3.52	0.314
Freundlich	0.0254	0.822	1.7997	0.822	6.048	1.217	-	-	-

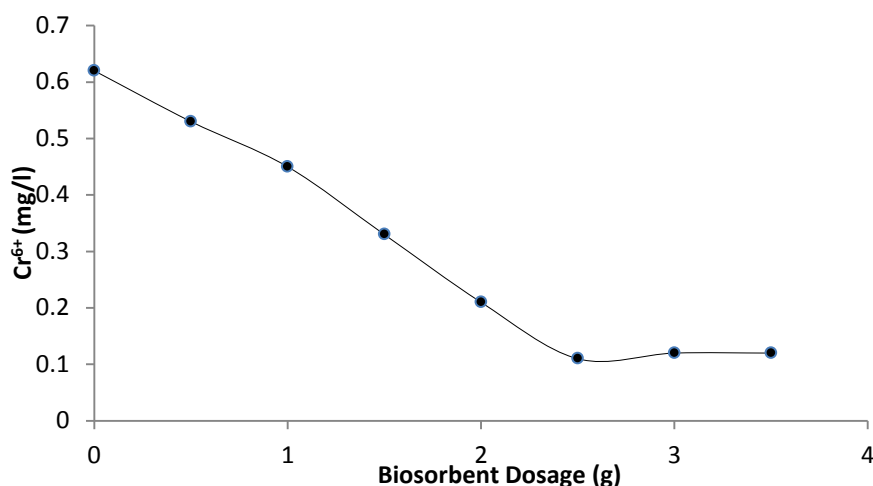


Figure 1: Effect of Chitosan Dosage on Cr⁶⁺ removal

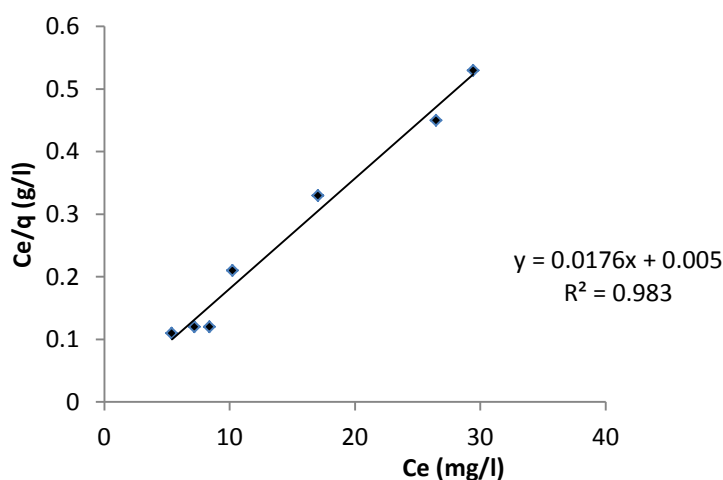


Figure 2: Langmuir plot for Cr⁶⁺ adsorption by Chitosan

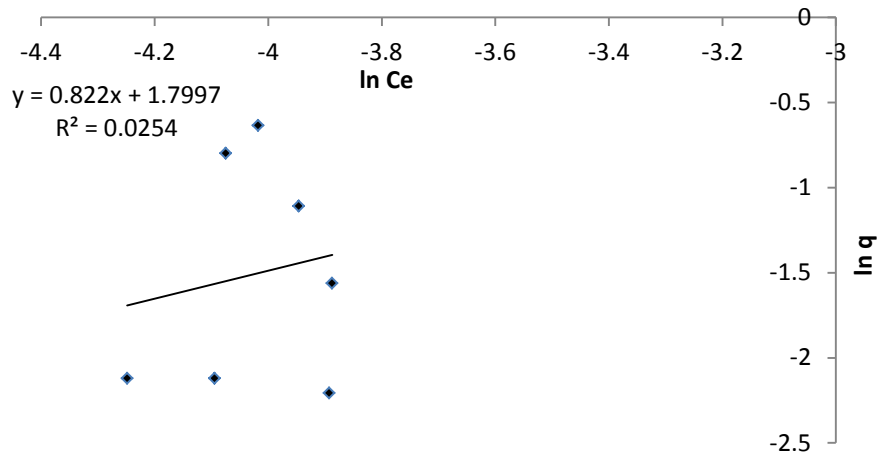


Figure 3: Freundlich plot for Cr⁶⁺ adsorption by Chitosan