

Case Study

Removal of Chromium (VI) as a heavy metal from aqueous solution using Chitin obtained from Bargi fish (*Heterotis Miloticus*) scale.

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ABSTRACT

The extraction of chitin from Bargi fish (*Heterotis Miloticus*) scale used in removing Cr (VI) have been evaluated using chemical and physical methods. The physical parameters investigated include: Equilibrium Contact Time (ECT), pH Adsorption Isotherm (AI) Langmuir isotherm (LI), Freundlich Isotherm (FI) and Thermodynamic Studies (TS). The chemical parameter used is Initial Metal Concentration (IMC). The physical parameters show the following: increasing the contact time increased the adsorption of the Cr (VI) ion and remained constant after an equilibration time of 60 min. The uptake of Cr (VI) ion by chitin was due to the presence of crystalline network, acetamide groups instead of hydroxyl groups and little amino groups which prevent further adsorption of Cr (VI). The adsorption of Cr (VI) increased with increase in pH from 2 to 6. The adsorption isotherm showed a sort of plateau, hence there is a formation of a complete monolayer of the metal ion covering the adsorbent surface. The thermodynamic study revealed that increasing the temperature decreases the adsorption capacity. The chemical parameter showed that when the concentration of the initial metal ion was increased, there was an increase in the amount of metal ion removed from the solution. Therefore the process is temperature dependent, pH dependent and maximum adsorption capacity was found at pH 6-8.

Keywords: Bargi fish scale, Chitin, Chromium (VI), Adsorption isotherm, Thermodynamics studies.

INTRODUCTION

Many substances pollute the marine environment, but non-biodegradable compounds are the most dangerous due to their innate ability to constantly remain in the ecosystem ^[1]. Heavy metals are notable for their high toxicity as are organochlorine compounds such as pesticides and polyvinyl chloride, amongst others ^[1].

Metal pollutants are currently considered to be some of the most toxic contaminants present world-wide ^[2]. Furthermore, Carvalho et al., (1999) stated that heavy metals are some of the most toxic, persistent and widespread contaminants in estuarine systems in the sense that dissolved or suspended metals become available to plankton, nekton, and benthic fatter and deposit feeders. The release of metal ions into a river system poses a serious threat to aquatic life and causes secondary effects upon the water quality. The two factors which contributed principally to the damaging effect of metals as environmental pollutants are their inadequate biological degradation to inert metals (as in the case of most organic pollutants) and the trend of metals to accumulate and largely remain in the aquatic environment ^[1,2,3].

Some heavy metals in their trace concentrations are normal constituents of marine organisms, but are potentially toxic at elevated concentrations. Therefore, metal pollution has become a major international issue since 1960s when thousands of people were poisoned in Minamata, Japan after consuming mercury fish ^[4]. Pollution by heavy metals is a world-wide problem and the main sources of metal pollution are domestic/industrial sewage, industrial effluents, and chemical spills, combustion emission, mining operation, metallurgical activities and non-hazardous landfill sites.

According to Hernandez, et al., (1990), the presence of metals in the marine environment is partly due to natural processes such as volcanic activity and erosion, but mostly results from industrial processes, with metals mainly entering the sea suspended in both liquid solid industrial wastes, and in solid particles carried by winds and deposit in the sea. It has been stated that with regard to metal accumulation in marine organisms, several authors have proved their high accumulation ability in crustaceans, molluscs and fish, which generally depends on their exposure time and

the concentration of metals in the water. Chromium is one of the most studied heavy metals because of its relative high toxicity. It is commonly present as Cr (VI) and Cr (III) of which the former is the most hazardous species^[5]. It is usually introduced into water bodies from industrial processes such as electroplating, metal processing, paint manufacturing, steel fabrication and agricultural activities. But tanneries are one of the most representative industries causing chromium pollution^[2, 5]. Chitin is the second most abundant organic compound in nature after cellulose^[5]. Chitin is widely distributed in marine invertebrates, insects, fungi and yeast. However, chitin is not present in higher plants and animals^[4, 5, and 7]. Knorr in 1984 reported that the shell of a selected crustacean contained 30-40% protein, 30-50% calcium carbonate and calcium phosphate and 20-30% chitin. Structurally, chitin is associated with protein and its fibrils are embedded in a matrix of calcium carbonate and calcium phosphate^[7].

Adsorption is one of the most effective and widely adopted techniques used in removal of toxic heavy metals from waste water^[8]. Xing et. al., in 2006 reported that use of modified biopolymers is cheap and more effective owing to the fact that they contain functional groups for effective binding and are biodegradable, hence are environmentally friendly.

This research is aimed at exploring the techniques used in extracting chitin from the fish scales and also to study the influence of contact time, pH, temperature and initial metal concentration on the removal of metal ions by Bargi fish scales, chitin from aqueous solution. The thermodynamics of the adsorption process is also studied.

MATERIALS AND METHOD

Bargi scale was obtained from fish vendors and chitin was isolated from Bargi fish scale. The following chemicals were used in the study: Potassium hydroxide 50%, Acetone, Hydrochloric acid 5%, Sodium Hydroxide 50%, Acetic Acid, Ethanol 95%, Potassium dichromate ($K_2Cr_2O_7$) and Shimadzu UV-3100 recording spectrophotometer.

Treatment of sample: Dried Bargi (*Heterotis Niloticus*) scales were obtained as waste from women fish vendors at Lake Geriyo, Yola, Adamawa State Nigeria. The scales were soaked in doubled distilled water (dd- H_2O) for 2 hours. After separation on 40 μ m screen, the sample was washed thoroughly with warm double distilled water. The bargi scales were then dried in an air oven at 105°C to constant weight. After pulverization to pass through 100 μ m sieve, it was stored in plastic containers at room temperature until used. The second method involved demineralization by extracting 1g of the deproteinized scale with 20ml of 5% hydrochloric acid at room temperature with continuous mixing for 18 hours to dissolve calcium carbonate in the sample. The crude chitin was collected on a coarse sintered glass funnel and washed with dd- H_2O to pH 7.0 and then by three portions of 25ml acetone and dried to constant weight at 105°C.

Preparation and analysis of CR (VI) ions: A stock solution (1000 mg/L) of Cr (VI) ions was prepared in dd- H_2O , from potassium dichromate ($K_2Cr_2O_7$) salt. Working solutions were prepared by diluting the stock solutions with dd- H_2O . The concentrations of Cr (VI) in aqueous solutions were analysed using Shimadzu UV-3100 recording spectrophotometer at 540 nm.

Adsorption experiments: Batch mode adsorption experiments were conducted in 250ml Erlenmeyer flasks to determine the best operating conditions, which facilitate the adsorption of Cr (VI) onto Bargi scale (BS) and chitin.

Equilibrium contact time: Experiments were carried out to determine the contact time needed by the system to reach equilibrium. The procedure entailed preparing 50mg/L of metal solution from the stock solution. A portion of 50 ml of this solution was taken into the flask and 0.1g of the adsorbents added. The pH was adjusted to 6.0 using 1M HCl and then agitated at 150 rpm in a rotary mixer at various, times at room temperature. After each time of agitation the samples were filtered through 0.45 μ m cellulose filter paper. The concentration of the metal remaining in the aqueous solution was determined as described earlier. The amount of metal removed was calculated by mass balance i.e. the amount of metal adsorbed (adsorption capacity) by adsorbent.

$$q = (C_o - C_e) \frac{V}{m} \quad \text{-----} \quad \text{Equation (1)}$$

Where V is the volume of the solution in liters, m is the mass of the adsorbent (g), q_e is the amount adsorbed per unit mass of the adsorbent (mg/g), C_e is the metal concentration remaining in solution and C_o is the initial metal concentration.

Effect of pH: The effects of pH of solution (50mg/L) ranging from 3-8 was studied in this experiment at 30°C and equilibration time of 1hour. The solutions were adjusted to the required pH values using 1M HCl or 1M NaOH.

Effect of initial metal concentration: At the equilibrium time of 1hour, pH 6 and temperature of 30°C, the batch experiment was repeated with various concentration of metal ion (50 to 100mg/L), the amount of metal removed in terms of mg/g and percentage (%) were calculated. The percent removal is defined as:

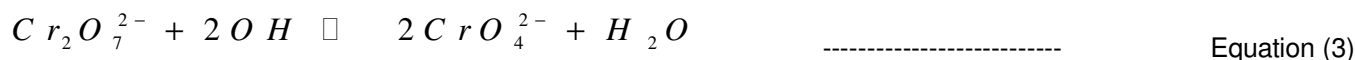
$$\% \text{ Removal} = \left\{ \frac{(C_o - C_e)}{C_o} \right\} \times 100 \quad \text{-----} \quad \text{Equation (2)}$$

Effects of temperature: At pH 6, the experiment was carried out in an environmental incubator shaker at 30°C, 40°C, 50°C and 60°C at 1h. After attainment of equilibrium at these different temperatures, the amount of metal ion adsorbed was determined as described earlier.

RESULTS AND DISCUSSION

Experiments were performed to determine the time needed by the systems to reach equilibrium. The results show that increasing the contact time increased the adsorption of this ion, and it remained constant after an equilibration time of 60min. Therefore, based on these results, the contact time, 1h was set for all the adsorption experiments. The result also shows that chitin removed Cr (VI) in solution more than the ordinary scale (BS). Chitin has a crystalline network [7], acetamide groups instead of hydroxyl groups and little amino groups [7, 8] that might prevent further absorption of Cr (VI).

Effect of pH: The adsorption of Cr (VI) on the adsorbents was influenced by the initial pH of the solution. The amount of this ion increases with increase in pH from 2 to 6. All the biomaterials display maximum adsorption capacities between pH 6 and 8. The optimal pH for the adsorption of Cr (VI) is 6. In solutions the equilibrium reaction that occurs is:



When the pH of solution increased, the amount of CrO_4^{2-} groups in the aqueous solution tended to increase. Between pH 6 and 8, CrO_4^{2-} may be the only species that may exist in solution. Hence, in acidic media, the adsorbent surfaces might be highly protonated and favor the uptake of Cr (VI) in the ionic form, CrO_4^{2-} . A similar result was observed by Xing et al., 2006. The adsorption of this ion depends on the solution pH, which influences electrostatic binding to the functional groups. The maximum adsorption observed at these pH values could be explained thus: according to the Pearson theory [9], during an acid-base reaction, hard acid prefers to coordinate with hard base and soft acid with soft base. Positively charged metallic species are soft and may interact with active groups on the adsorbents.

Effect of initial metal concentration: The removal of Cr (VI) ion by the adsorbent according to its initial concentration in solution is presented in Table 1. The amount of metal removed, from the solution increased with increase in the concentration of the solution. However, the percentage adsorption decreased after an initial concentration of 50mg/L. This shows that the removal of this metal ion is highly concentration dependent. At lower concentrations of the metal ions, the number of metal ions available in the solution is less as compared to the available sites on the adsorbent. But at higher concentrations the available sites for the adsorption becomes fewer and the percentage removal of the metal ions depends on the initial concentration.

Table 1: Effect of Initial Metal Concentration on the Adsorption of Cr (VI) on the Adsorbents.

Initial concentration (mg/L)	BS, q (mg/g)	% Removal	Chitin, q (mg/g)	% Removal
5	1.26	50.40	1.93	77.20
10	2.57	51.40	3.93	78.64
20	5.54	55.40	8.48	84.76
30	7.59	50.60	11.61	77.42
40	10.51	52.55	16.08	80.40
50	14.86	59.44	22.74	90.94
70	16.19	46.26	24.77	70.77
80	16.87	42.18	64.53	26.99
90	17.12	38.04	26.19	58.21
100	17.17	34.34	26.27	52.54

Adsorption isotherms: The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems. According to the slope of the initial portion of the curves, the isotherms may be classified as the H-type of the Giles classification [9, 10]. The H-type isotherms are the most common and correspond to high affinity of the adsorbate for the adsorbent and because of that, there is no completion from the solvent for the adsorption sites. The isotherm is characterized by a plateau. Hence, is possible that there could be a formation of a complete monolayer of the metal ion covering the adsorbent surface. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms of metal ions [10].

Langmuir isotherm: The main assumption of Langmuir model is that adsorption occurs uniformly on the active sites of the adsorbent, and when a molecule is adsorbed on the site, the latter does not have any effect upon other incident molecules. The Cr (VI) adsorption isotherms were fitted by this non-competitive model which can be expressed [10, 11, 12].

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{C_e Q_{\max} b} \quad \text{-----} \quad \text{(Equation 4)}$$

Where the values of Q_{\max} (maximum adsorption capacity (mg/g)) and b (L/mg) (Langmuir Isotherm constant, related to the energy of adsorption), obtained from the isotherms as well as the correlation coefficients are listed in Table 2. The values of the constant were calculated using a linear regression fitting analysis. From the correlation coefficients there is a good fit of the experimental data that conforms to a monolayer adsorption mechanism.

Table 2: Langmuir and Freundlich constants for the adsorption of Cr (VI) onto the adsorbents.

Langmuir Parameters				Freundlich Parameters		
Adsorbent	Qmax (mg/g)	B (L/mg)	r^2	K_F	1/n	r^2
BS	25.00	0.02	0.9992	0.68	0.921	0.9704
Chitin	37.04	0.04	0.9883	2.78	0.749	0.9297

Freundlich isotherm: The Freundlich isotherm is empirical and used for heterogeneous surface energies in which the energy term, b , in the Langmuir equation varies as the surface coverage, q , due to variation in the heat of adsorption. Equation is given by ^[12].

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad \text{-----} \quad \text{(Equation 5)}$$

Where K_F and $1/n$ are the Freundlich constants related to adsorptive capacity and intensity of adsorption respectively. These values calculated from regression analysis as well as their linear regression coefficients are also given in Table 2. The value of $0.1 < 1/n < 1$ shows favorable adsorption of Cr (VI) on the adsorbents. The higher fractional values of $1/n$ (0.631 – 0.921) show that strong adsorptive forces are in operation on the surface of the biomaterials. The correlation coefficient values (0.9698-0.9704) are lower than the Langmuir values (0.9700-0.9992). Hence, the Langmuir model agrees well with experimental results and could be used to describe the mechanism of the adsorption of Cr (VI) than the Freundlich model.

Thermodynamics studies: The effect of temperature on the adsorption process is shown in figure 4.4. The data show that the adsorption capacity decreases with increase in temperature, which shows that the process is exothermic. Therefore, the feasibility of the removal of Cr (VI) could be evaluated from thermodynamic considerations. This was deduced from an equation developed by Xing et al., 2006 as written below:

$$\log \left(\frac{q}{C_e} \right) = \frac{\Delta H^\pm}{2.303RT} + \frac{\Delta S^\pm}{R} \quad \text{-----} \quad \text{(Equation 6)}$$

The values of G can be determined from the thermodynamic equation:

$$\Delta G^\pm = \Delta H^\pm - T \Delta S^\pm \quad \text{-----} \quad \text{(Equation 7)}$$

The values of ΔH^\pm and ΔS^\pm are shown in Table 3. The negative value of ΔG^\pm suggests that the adsorption process is spontaneous and thermodynamically favorable. The ΔG^\pm value also determines the rate of the adsorption, i.e. rate increases as ΔG^\pm decreases and the reaction proceeds only when the energy requirement is fulfilled ^{[12] [13]}. The ΔG for chitosan is the lowest showing that the rate of adsorption of Cr (VI) is highest in this system and might lead to strong binding than the others. The ΔH^\pm values equally indicate that the process is exothermic and low temperature is appropriate and makes it easy and feasible, as it does not consume energy. The magnitude and sign of ΔS^\pm give an indication of whether the adsorption process is associative or dissociative mechanism ^[12]. Hence, the large negative values of ΔS^\pm obtained in this study suggest an associative mechanism.

Table 3: Thermodynamic value for the adsorption of Cr (VI) on the various adsorbents

Adsorbent	ΔH^\pm (KJ/mol)	ΔS^\pm (J/mol)	ΔG^\pm at 30°C (KJ/mol)
BS	-119.35	-171.85	-67.28
Chitin	-132.59	-184.99	-76.54

CONCLUSION

In this work, chitin was obtained from a fish scale waste. This biopolymer was used for the removal of Cr (VI) from aqueous solutions. Both Langmuir and Freundlich isotherms were used to successfully describe the adsorption process. The adsorption is exothermic, pH-dependent and maximum adsorption capacity was found at pH 6-8. The negative values of DG and DS implies a decrease in adsorption energy and an increase in the feasibility of the adsorption process at lower temperature. Finally, this work revealed the applicability of a waste material as a potential industrial biomaterial for wastewater treatment.

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