

Experimental study of the removal of cobalt ion from aqueous solution using chitosan

Augustine Odiba Aikoye , Ifiok D. Ufia and E. O. Udofia

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Abstract High concentration of heavy metals (such as cobalt) can create serious environmental problems through pollution of the aquatic environment and subsequent magnification, accumulation and transfer to other components of the environment. In attempt to search for ecofriendly approach aimed at reducing concentration of cobalt in contaminated water. The effectiveness of chitosan for the removal of cobalt ion from aqueous solution was investigated with reference to concentration, period of contact and through the measurement absorbance before and after adsorption. We observed that chitosan has good adsorption surface for cobalt ion and the adsorption was facilitated through the N-H and C-O functional groups in the chitosan.

Key Words Contamination of water, cobalt, remediation, adsorption, chitosan

Augustine Odiba Aikoye

Department of Pure and Industrial Chemistry
University of Nigeria, Nsukka, Enugu State,
Nigeria

Email: augustine.aikoye.pg00132@unn.edu.ng

Orcid id: 0000-0002-8640-4094

Ifiok D. Ufia

Department of Genetics and Biotechnology,
Akwa Ibom State University,
P. M. B. 1167, Uyo, Akwa Ibom State, Nigeria.

Email: ifiok.uffia@yahoo.com

Orcid id:

O. E. Udofia

Department of Genetics and Biotechnology,
Akwa Ibom State University,
P. M. B. 1167, Uyo, Akwa Ibom State, Nigeria.

Email:

Orcid id:

1.0 Introduction

Industrialization and increasing urbanization have contributed largely to the development of modern societies and increasing number of wastes that must be disposed. Waste management policies are hardly implemented by most domestic and industrial wastes generators. The consequence of

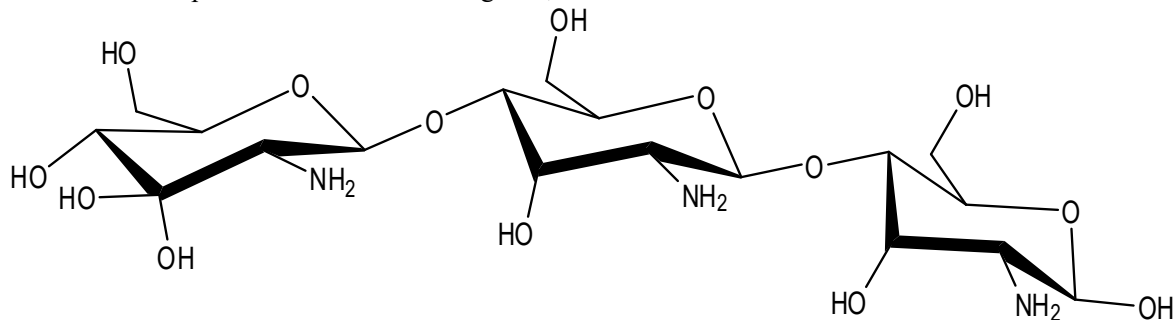
improper waste management is the pollution of the land, water and the air. Gradual increase in the volume of waste discharged to the environment is significantly imparting on the natural cycles. . Consequently, cycles that are meant to renew the quality of our environment have been overloaded with undesirable burdens through environmental pollution. The water system is one of the most affected ecosystems because many lives depend on the availability and quality of water. Water pollution is caused by the introduction of contaminants into water, at a level and concentration that affect its useful utilization. However, among all the water quality indices, heavy metals appear to gain significant attention because of its toxicity and non-biodegradability. They are metals, whose density is greater than 5 g/dm³ and are toxic above certain concentration (Eddy *et al.*, 2004; Odoemelam *et al.*, 2018). These metals are found in numerous industrial wastes, some find their way to water and water bodies through surface run off, direct discharge and other mechanism. However, industrial sources account significantly to the pollution of water by heavy metals (Li and Huang, 2013; Repo *et al.*, 2011).

Several methods such as filtration, ion-exchange, adsorption and others, have been found to be effective in reducing the concentration of heavy metals in aqueous media (Wan *et al.*, 2011, 2012; Wang *et al.*, 2010, 2013). However, adsorption is one of the best methods because it is less expensive and more efficient (Odoemelam *et al.*, 2018). Therefore, the present study is aimed at using chitosan to investigate its potential for the adsorption of cobalt from aqueous solution. Due to its known and confirm impact on the environment, several studies have been engaged towards finding measures to reduce the concentration of heavy metal ions in solution. Some plant wastes have been reportedly used as effective adsorbent for the removal of heavy metal ion from aqueous solution (Eddy, 2009; Okwunodulu and Eddy, 2014). Human hair is also excellent adsorbent for heavy metals (Ekop and Eddy). The use of microorganism has also been

reported as effective against the removal of heavy metals from aqueous solution (Adedirin *et al.*, 2011a-c). Chitosan has been reportedly synthesized from crustacean shells (ref). However, most of these shells have been reported as good adsorbent for the removal of heavy metal ions from aqueous solution (Eddy and Ekop, 2005, 2009; Odoemelam and Eddy, 2009). Chitosan composites and derivatives have gained wide attention as effective biosorbents due to their low costs and high contents of amino and hydroxyl functional groups, which are functional groups that can enhance adsorption (Wu *et al.*, 2001; Zuo, 2014). They have showed significant potentials of removing metal ions, dyes and proteins from various media. Chemical modifications that lead to the formation of the chitosan derivatives and chitosan composites have been extensively studied and widely reported in literatures (Liu *et al.*, 2013). Some of the reported works are hereby reviewed. Cr(VI) ion was removed through cross-linked chitosan CRCH which was synthesised by gamma irradiation in the presence of carbon tetrachloride. The adsorption efficiency and product formed CRCH was compared with simple chitosan at pH of 3. CRCH showed higher adsorption capacity of Cr(VI) ion and the results obtained was consistent with the adsorption models of Langmuir,

Freundlich and Dubinin-Radushkevich. Alginic acid and chitosan which are naturally occurring polysaccharides have been found to be effective for the removal of Co(II), Cu(II), and Cd(II) from waste water. According to Qinn *et al.* (2007) the polymers are efficient adsorbent for these metals because they are capable of forming a cross-linkage that can facilitate adsorption. The adsorption data best fitted the Langmuir, Temkin and Dubinin-Radushkevich isotherms. The mechanism of physical adsorption was confirmed because the calculated adsorption energy was less than the threshold value.

Dhanesh *et al.* (2013) synthesized chitosan-zeolite(CZ) using zeolite and chitosan and was used to the adsorption of Cu(II) ions the treated waste water. Polyethylene glycol cross-linked chitosan films has also been found to be effective for the removal of iron from aqueous solution (Peter *et al.*, 2013). Other works are those reported by Thilagen *et al.* (2013), Soundarrajarr *et al.*(2011, 2013), Reiad *et al.* (2013), Shanmugapriya *et al.* (2013), Hritcu *et al.* (2012), Chiou *et al.* (2001), and Crini and Badot (2008) for Cu²⁺, Pb²⁺ for Hg²⁺/Cu²⁺/Pb²⁺, Cr⁶⁺/Cu²⁺, Pb²⁺, and Cu²⁺ ions. The Chemical structure of chitosan is presented below



Chemical structure of chitosan

The present study is aimed at investigating the adsorption capacity of chitosan for cobalt ion

2.0 Materials and Methods

Chitosan sample was supplied by Prof. Lee Wills, a Professor in the Department of Chemistry, University of Saskatchewan, Canada. Batch adsorption experiments were carried out as reported elsewhere. The experiments investigated the effect of concentration, effect of contact time and temperature. The wavelength of maximum absorption of cobalt was determined using Pye Unicam atomic absorption spectrophotometer and this wavelength was used for subsequent analysis after the preparation of calibration curve.

Concentration of cobalt adsorbed was calculated using the following equation,

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (1)$$

where C_0 is the initial concentration of the dye, C_e is the equilibrium concentration of the dye, V is the volume of solution and m is the mass of the adsorbent.

FTIR analyses of the dye, adsorbent (before and after adsorption) were carried out using Scimadzu FTIR-8400S Fourier transform infra red spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 500 to 4500 cm^{-1} .



3.0 Results and discussions

3.1 Adsorption study

Fig. 1 shows a plot for the variation of adsorbance with concentration of cobalt ion in solution. The plot reveals that there is a direct relationship between the absorbance of cobalt ion (at 550 nm) and concentration. The adsorbance increases with increase in concentration which is in obedient to the Beer-Lambert law, adsorbance is directly related to concentration of a chemical specie according to the following equation,

$$A = \epsilon Cl \quad (2)$$

where A is the adsorbance, ϵ is the molar adsorptivity, C is the concentration and l is the path length. This indicates that adsorption is directly proportional to concentration since the path length and adsorptivity are constant. The amount of cobalt ion adsorbed by chitosan for cobalt will therefore increase if the measured adsorbance of the solution decreases. In order to determine the maximum wavelength for the adsorption of cobalt in solution, adsorbance measurements of 100 ppm solution of the cobalt ion at different wavelengths were carried out and the data obtained are presented in Fig. 1. From the plots, the maximum wavelength of adsorption is 570 nm. Therefore, all measurement was carried out using 570 nm as the reference wavelength.

Fig. 2 shows a plot of variation of absorbance with concentration of cobalt ions in solution. The plot reveals that the adsorbance of the solution decreases as the initial concentration of cobalt ion in the solution increases from 100 ppm to 500 ppm. The trend can be explained as follows.

The adsorption of cobalt ion decreases the concentration of cobalt ion in the solution. Therefore, the more the amount of cobalt ion adsorbed, the less will be the concentration of the solution, which is the solution the absorbance measurement carried out.

Since adsorbance corresponds to concentration, then decrease in adsorbance implies a corresponding decrease in concentration indicating increase in the amount of cobalt ion adsorbed. Therefore, the adsorption of cobalt ion by chitosan increases with increase in concentration of cobalt ion.

Fig. 3 reveals the plot of adsorbance against time for the adsorption of cobalt ion unto chitosan. From the plot, it is evidence that relationship between the adsorption of cobalt ion by chitosan and time follows an irregular pattern. Generally, the adsorbance increase at first to a maximum and then fall to a minimum before rising again. This type of relationship has been reported for the adsorbance of some heavy metals (Eddy, 2009).

Fig. 4 also shows the variation of absorbance with temperature with respect to the adsorption of cobalt ion onto chitosan. The adsorbance first fall and then begins to rise after 50 °C. This implies the amount of cobalt ion adsorbed by chitosan increases at first but decreases with temperature after 50 °C. Therefore, the adsorption of cobalt ion on chitosan generally decreases with increase in temperature. This suggests the mechanism of physical adsorption because for a physiosorption mechanism, the extent of adsorption decrease with increase in temperature

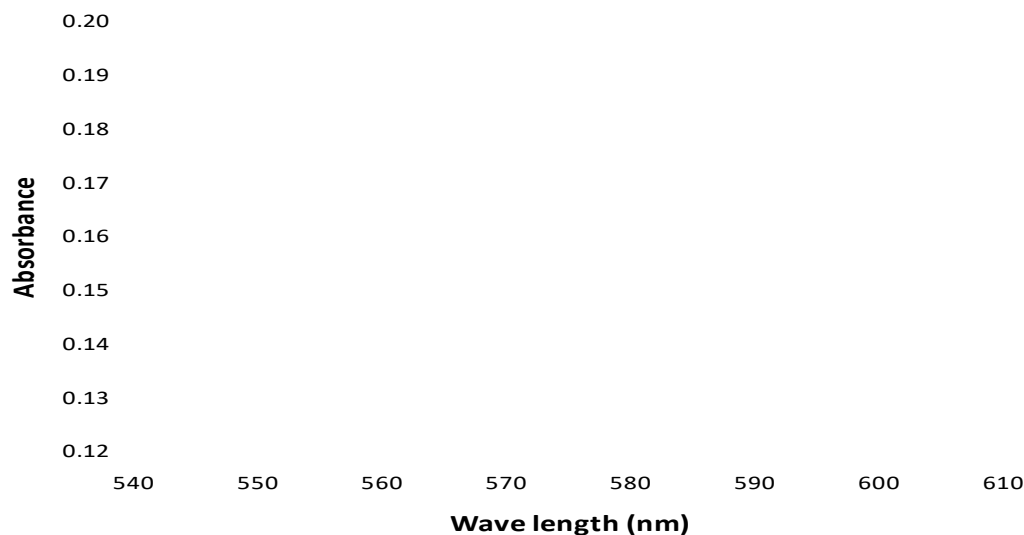


Fig. 1: Variation of adsorbance of 1000 ppm solution of cobalt ion with wavelength



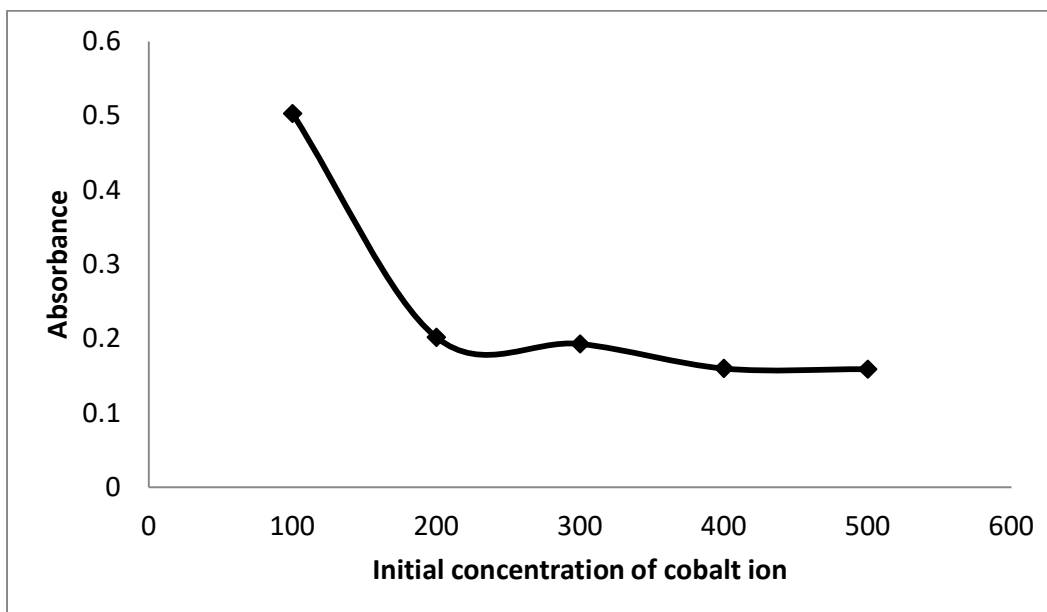


Fig. 2: Variation of adsorbance with initial concentration of cobalt ion in solution

3.2 FTIR study

Fig. 5 shows the FTIR of pure chitosan while peaks and frequency of adsorption are shown in Table 1. From the results obtained, the main functional groups or vibrations associated with chitosan are the C-N stretch at 1082 cm^{-1} , N-H bending vibration at 1587 cm^{-1} , C=C stretch at 1649 cm^{-1} , C-H stretch at 2890 cm^{-1} and oh stretch at 3385 cm^{-1} . After adsorption of cobalt by chitosan, the spectrum obtained is shown in Fig. 6 while the peaks and frequencies of adsorption are recorded in Table 2. C-N stretch shifted from 1082 to 1076 cm^{-1} with reduces intensity but increasing area. C-O stretch shifted from 1397 to 1388 cm^{-1} ,

C-H stretch shifted from 1649 to 1547 cm^{-1} , C-H stretch at 2890 shifted to 2891 cm^{-1} and OH stretch at 3385 shifted to 3410 cm^{-1} . New bonds were formed at 2391 cm^{-1} while N-H and C-O bond at 1587 and 1320 cm^{-1} respectively, were missing. Interestingly, the shift between 1082 and 1649 cm^{-1} occurred with decrease in frequency values while others occur with increasing frequency. Generally, shift in frequency after adsorption agrees with the existent of interaction between the adsorbent (chitosan) and the adsorbate (cobalt ion) while the appearing of new bond suggest the point of adsorption facilitated by the missing bond.

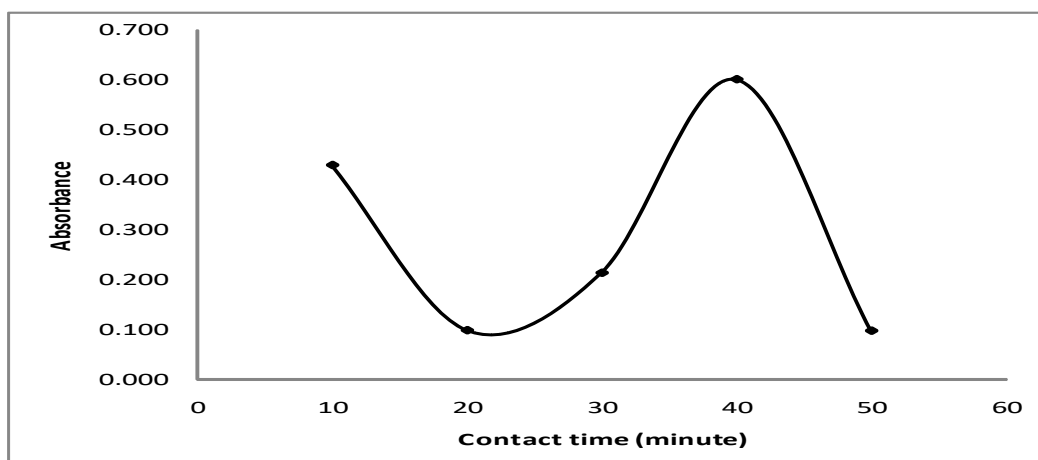


Fig. 3: Variation of adsorbance of solution containing various concentrations of cobalt ion with time



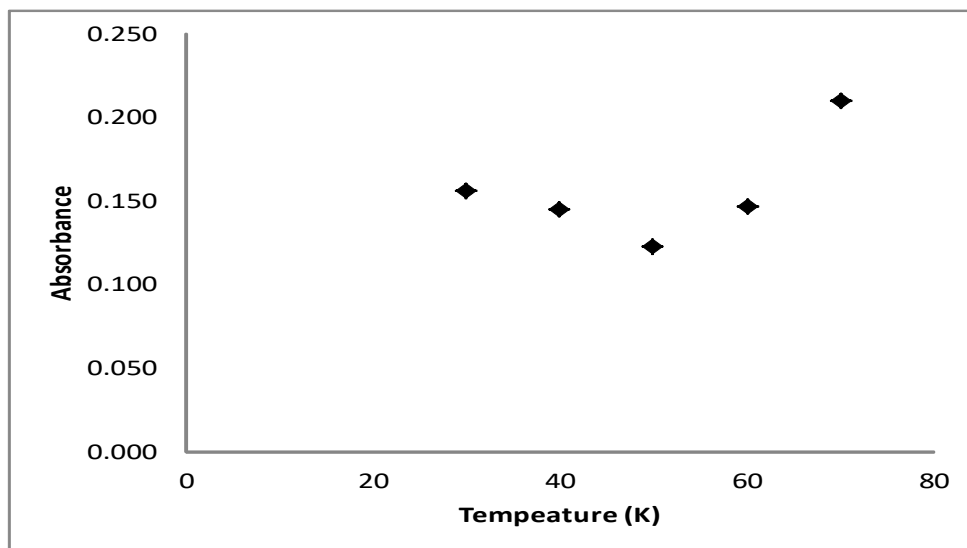


Fig. 4: Variation of adsorbance of solution containing various concentrations of cobalt ion with temperature

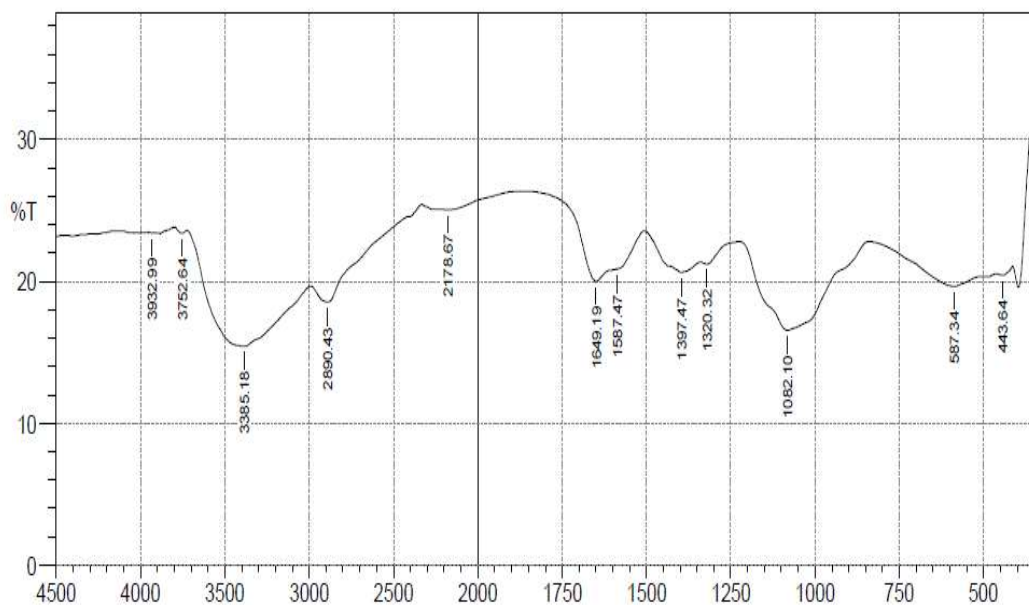


Fig. 4.5: FTIR of chitosan

Table 1: Frequencies and peaks of FTIR spectrum of chitosan

Frequency	Intensity	Area	Assignment	
1082	17	276	C-N stretch	Amine
1320	21	76	C-O stretch	Alcohol, carboxylic acid, ether, ester
1587	21	54	N-H bend	Amine
1649	20	133	C=C	Alkene
2890	19	387	C-H stretch	Alkane
3385	15	253	OH stretch	Alcohol, phenol



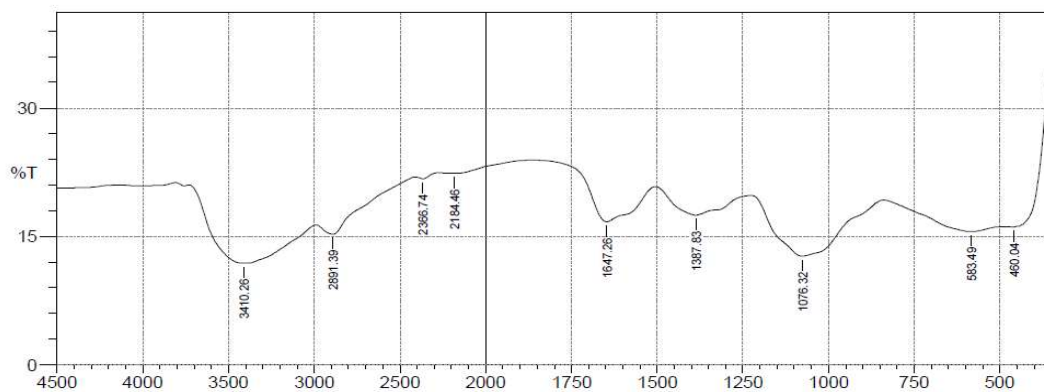


Fig. 6: FTIR of chitosan after adsorption of cobalt ions

Table 2: Frequencies and peaks of FTIR spectrum of chitosan after adsorption of cobalt ion

Frequency	Intensity	Area	Assignment
444	20	32	
587	20	225	C-X stretch Alkyl halide
1076	17	312	C-N stretch Amine
1388	17	203	
1647	17	249	C=C Alkene
2891	15	424	C-H stretch Alkane
3410	12	264	OH stretch Alcohol, phenol

4.0 Conclusion

From the results and findings of the study, the following conclusions were made

- Chitosan is a good adsorbent for cobalt ion from aqueous solution.
- The adsorption capacity of chitosan for cobalt ion increases with increase in the concentration of cobalt ion in the solution
- The adsorption capacity of chitosan for cobalt ion decreases with increase in temperature.
- The adsorption of cobalt ion onto chitosan follows the mechanism of physical adsorption.
- The adsorption of cobalt ion on chitosan can be optimised by taking advantage of time, concentration and temperature

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