The Study of Typical Conditions to Remove Co from Water by Adsorption Using Activated Carbon

Shaymaa H. Khazaal *
Received on: 2/3/2011
Accepted on: 2/6/2011

Abstract
The effective removal of heavy metal ions from water is among the most important issues for many industrialized countries. The present work has been carried out to study the adsorption of cobalt [II] ion using activated carbon.
The removal of cobalt ions was investigated in batch conditions. The influence of initial cobalt ion concentration, pH, adsorbent dose, adsorbent practical size; contact time and shaking rate were studied at room temperature. The analysis of residual Co [II] ions was determined using Atomic Absorption Spectrophotometer GBC 933 plus. The results showed that the percentage adsorption of activated carbon increases with time and that maximum adsorption was obtained within the first 60 minutes of the process, and 300 rpm shaking rate.
The experiments showed that the maximum % adsorption of 100% was obtained at adsorbent dose=0.4 gm, pH=13, particle size= (0-75) μm and 10 mg/L of initial concentration of cobalt. These results indicate that activated carbon has potential for removing cobalt ions from water.

Keywords: adsorption, cobalt removal, activated carbon, batch process

Nomenclature
C₀: Initial Co (II) ion concentration of test solution, mg/L.
C: Final Co (II) ion concentration of test solution, mg/L.

*Applied Science Department, University of Technology/Baghdad

https://doi.org/10.30684/etj.29.9.6
2412-0758/University of Technology-Iraq, Baghdad, Iraq
This is an open access article under the CC BY 4.0 license http://creativecommons.org/licenses/by/4.0
1. Introduction

Development of modern industry causes increasingly serious pollution in the environment where human lives, constituting a catastrophic health risk including cancer\(^1\). Treatment of water and wastewater needs serious attention all over the world especially in countries with dry climate. The most important pollutants in water and wastewater are heavy metals\(^2\).

Rapid industrialization and urbanization has resulted in the deterioration of water, air, and land quality. Natural waters are contaminated with various heavy metals arising from mining wastes and industrial discharges. The tremendous increase in the use of heavy metals over the past few decades has resulted in an increased flux of metallic substances into the environment. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) etc. These metals are toxic both in their chemically combined forms and in the elemental form. Exposure to these contaminants, even in low concentrations in the environment, can prove to be harmful to human health. In order to solve heavy metal pollution in the environment, it is important to bring applicable solutions. Some in-place treatment techniques available for the removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, coagulation, and bioremediation and sorption/adsorption. Of all these techniques adsorption at solid substrate is preferred because of its high efficiency, easy handling, and cost effectiveness as well as the availability of different adsorbents\(^3\).

Cobalt [II] is one of the priority pollutants in waste discharge. Its introduced in the aqueous system through new clear power plants and industrial waste discharges including mining, metallurgical electroplating paints, pigments and electronic product. Strong exposure to Co [II] may cause, paralysis, severe diarrhea, low blood pressure, bone defects and lung irritation. In most of the countries level of Co [II] in water is limited to the value of 0.05 mg/L\(^4\).

Hence, the removal of cobalt from wastewater is considered necessary and vital to protect the public in environmental health. A number of technologies have been developed over the years to remove toxic metal ions from water. Such methods include chemical precipitation, electro deposition, ultra filtration, ion exchange, reverse osmosis, activated carbon adsorption and biological processes\(^5\). Adsorption has been recognized as an effective method for the removal of pollutants from water\(^6\). The adsorption of cobalt ions onto a solid phase has long been investigated using inorganic adsorbents such as peat moss\(^7\), magnetite\(^8\), kaolinite\(^9\), fly ash\(^10\), tea waste\(^11\), calcite\(^12\), cement kiln dust\(^13\), wood ash\(^14\), and tree waste\(^15\) are also used. The use of activated carbon for the adsorption of heavy metal was first reported in 1929 by Watonabe and Ogawa\(^16\). This adsorption by activated carbon appears to be
particularly competitive and effective in the removal of heavy metals at trace quantities \(^{(17)}\). It has been reported to have high and fast adsorption capacities \(^{(18)}\) due to its well-developed porous structure and tremendous surface area.

Gaikwad\(^{(19)}\) studied the removal of Cd\([\text{II}]\) from aqueous solution by activated charcoal derived from coconut shell. Cadmium ion removal efficiency was enhanced by decreasing the concentration. \(\text{pH}=6\) and control time of 80 minutes were found to be optimum.

Taha et al.\(^{(13)}\) studied the adsorption of Cd\([\text{II}]\), Al\([\text{III}]\), Co\([\text{II}]\), and Zn\([\text{II}]\), by using cement kiln dust (CKD). Batch adsorption experiments were conducted to evaluate the removal of Cd\([\text{II}]\), Al\([\text{III}]\), Co\([\text{II}]\), and Zn\([\text{II}]\)onto (CKD) waste over a wide range of operation condition of sorbent concentration, \(\text{pH}\), contact time, sorbent dose. The batch experiments showed that most effective \(\text{pH}\) range was found to be 5.5 to 8. Time-dependent experiments for the removal efficiency of heavy metal ions showed that Al [\text{III}] required a shortest contact time, for Zn[\text{II}] and Cd[\text{II}], binding to the CKD was rapid and occurred within 20 to 40 min and completed for Co[\text{II}] within 4 hours. The binding capacity experiments revealed the following amounts of heavy metal ions bound per gram of CKD: 165.994 mg/g, 75.389 mg/g, 64.296 mg/g, 108.875 mg/g for Zn [\text{II}], Al [\text{III}], Co [\text{II}] and Cd[\text{II}], respectively.

Caramelau et al.\(^{(20)}\) studied the adsorption of cobalt [\text{II}] from aqueous solutions on un-treated and treated peat moss. The influence of initial solution pH, peat moss dose, initial cobalt [\text{II}] concentration and contact time, was studied in batch experiments. The optimum results were obtained at \(\text{pH}=6.0\) (acetate buffer), an adsorbent dose of 5 gm/L and an initial concentration of 240 mg Co [\text{II}]/L. The experimental results have show that in case of peat moss treated with NaOH, the adsorption capacity increase with 15 % and the contact time necessary to attain the equilibrium. The adsorption process of cobalt [\text{II}] on un-treated and treated peat moss was tested with Langmuir isotherm model and the isotherm constants were deduced from this.

This work concerns the uptake of cobalt ions in wastewater by activated carbon. In order to give complete description of batch adsorption phenomena, experimental runs have been carried out at different cobalt concentration, \(\text{pH}\), adsorbent dosage, adsorbent particle size, contact time and shaking rate.

2. Materials:

2.1 Adsorbent

The adsorbent used was powdered activated carbon it was dried at 200°C then grinded and sieved into three different particle sizes with range (0-75\(\mu\)m), (75-100\(\mu\)m), and (100-125\(\mu\)m).

2.2 Adsorbate

Metal ion used as nitrate salt is cobalt nitrate [Co (NO\(_3\)\(_2\))\(_6\)H\(_2\)O] from BDH. Distilled water was used for dilution.

3. Experimental

Experiments were carried out using activated carbon in batch adsorption at room temperature under various initial adsorbate concentrations, \(\text{pH}\), adsorbent dose, adsorbent particle
size, contact time and shaking rate. Stock solution of cobalt (1000 mg/L) was prepared by dissolving 4.940gm of cobalt nitrate in 1L of distilled water .The concentration range of cobalt ions prepared from stock solution varied between (10-100) mg/L.  
In order to determine the effects of different pH on adsorption rate, each prepared sample was divided into six samples of 100ml and the pH was adjusted by using standard HCl or NaOH solution (13).Before the adsorption process the final pH was recorded by pH meter. 
In order to estimate the Co [II] ions % adsorption a known weight of adsorbent (0.05-0.4) gm was equilibrated with 100 ml of the cobalt nitrate of known concentration in 250 ml glass conical flask at room temperature and shaked using GEMMY Orbital Shaker Model: VRN-480, at (50-400) rpm for (15-150) min. After shaking, the conical flasks were removed slowly from the shaker platform and the contents of the conical flasks were allowed to settle for 5min .After settlement, the adsorbent was removed by filtration through 15cm filter papers .The concentration of Co [II] ions remaining in solution was measured by Atomic Absorption Spectrophotometer. 

4. Removal and Adsorption of cobalt (II) 
The percent of cobalt adsorption % was calculated using the following equation: 

\[
\% \text{ Adsorption} = \left( \frac{C_o - C}{C_o} \right) \times 100
\]

5. Results and discussions 
Studies on the effect of initial cobalt ions concentration were conducted by varying it from 10 to 100 mg/L, keeping pH of 7, adsorbent dose of 0.2 gm/100 mL, adsorbent particle size (0-75) µm, contact time 30 min., and shaking rate 150 rpm. The experimental results for adsorptions of cobalt ion on the activated carbon at various concentrations are shown in Figure 1. The percent adsorption decreased from 40.65 to 4.57 % as the initial cobalt ion concentration increase from 10 to 100 mg/L. This means that the adsorption is highly dependent on the initial concentration of cobalt ion. This is because at lower concentration, the ratio of the initial number of cobalt ion to the available surface area is low; subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer, and hence the percentage removal of cobalt ion is dependent upon initial concentration. This agrees with the results of Taha et al. (13). Therefore 10mg/L of initial concentration was used in all further experiments. 
The initial solution pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions (20). The adsorption efficiency of cobalt [II] on activated carbon as a function of initial solution pH .Was varied in the range of (3, 5, 7, 9, 11, and 13) keeping the other parameters constant. Figure 2 was observed that
with the increase in the pH of the solution, the percentage removal of cobalt [II] ions increased. This agrees with Caramalău (20), Tumin et al. (21), and Egila et al. (22). This behavior is mainly determined by the ionic state of functional groups from adsorbent surface involved in adsorption process. The minimum adsorption observed at low pH 3 may be due to the fact that the higher mobility of H+ ions present favored the preferential adsorption of hydrogen ions compared to the metal. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydroxonium ions (H3O+), thereby preventing the metal ions from approaching the binding sites of the sorbent. As the pH increases, more negatively charged surface becomes available, thus facilitating greater metal ions removal. It is commonly agreed that the adsorption of metal cation increases with increasing pH as the metal ionic species become less stable in the solution. At pH 13, maximum adsorption percentage was obtained for the element in question. For the above reasons, the pH=13.0, this was considered as optimum value, and was used in all further experiments.

The influence of the amount of activated carbon on the adsorption of metal cations has been tested in the range (0.05-0.4) gm. The results are given in Figure 3. The plots of adsorption % vs. amount of activated carbon indicate that initially, the adsorption increases sharply with increasing the amounts of activated carbon. The increase in the removal efficiency is due to the greater availability of adsorption sites and more surface area with higher functional groups at higher activated carbon concentration. An identical trend was observed by other investigations. Rengaraj and Moon (23) obtained the same results for adsorption of Co [II] by ion exchange resins. Therefore 0.4 gm of adsorbent was used in all further experiments. Also Figure 3 shows the relation between the adsorption efficiency and adsorbent particle sizes of three different pore size of particle {(0-75), (75-100), and (100-125)µm}. The removal efficiency decreases with increasing adsorbent particle size and the best removal was obtained at (0-75)µm. In experiments performed under gravitational flow operation increases in adsorbent particle size ranges allow larger flows, but at the same time it significantly decreases for the removal of cobalt. Therefore (0-75) µm of adsorbent particle size was used in all further experiments. Figure 4 indicate that the removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as initial concentration, pH, dose of adsorbent, and adsorbent particle size were kept optimum. This is in agreement with Arivoli S. et al. (3), but after 60 min, it gradually gives a constant value, and reach equilibrium. Further increase in contact time does not increase % adsorption due to deposition of cobalt ions on the available adsorption sites on adsorbent material. This might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the cobalt % adsorption by
adsorbent decreased significantly, due to the decrease in the number of adsorption sites. Decreased extent of adsorption, particularly towards the end of experiment, indicates the possible monolayer of cobalt ions on the outer surface, pores of the adsorbent and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment. Therefore 60 min was used in all further experiments. Also studies on the effect of shaking rate were conducted by varying speeds of shaker from 50 to 400 rpm, at initial concentration of Co [II] 10 mg/L, pH of 13, adsorbent dose of 0.4 gm/100 mL, adsorbent particle size (0-75) µm, and contact time 60 min. The influence of shaking rate on the extent of adsorption is shown in Figure 5. It reveals that cobalt removal is a function of shaking rate, this is in agreement with Tembhurkar and Dongre (24). At a given time, cobalt removal increases with the increase in the rate of shaking. The removal is 83.5% at 50 rpm and attains 100 % at 300 rpm. The reason for the increase in efficiency is that at higher speeds better contact between the adsorbent and adsorbate is possible.

**Conclusions**

The objectives of this work were to study the effectiveness of activated carbon in removing Co [II] ions from water. The results indicate that the increase of initial metal concentration cause a decrease in removal of cobalt ion, the increase in the pH of solution showed an increase in quantity of Co [II] ion that adsorbed on activated carbon surface. Optimum pH for highest Co [II] adsorption% was 13. The particle size influences the adsorption removal. The increase in contact time increased the % adsorption of Co [II], and reach equilibrium at 60 min. The best shaking rate was 300 rpm.

**References**


The Study of Typical Conditions to Remove Co From Water by Adsorption by Using Activated Carbon

The Study of Typical Conditions to Remove Co From Water by Adsorption by Using Activated Carbon


Figure (1) Effect of Initial Co (II) Concentration of Efficiency Of Adsorption% of Cobalt

(Ph = 7, Adsorbent dose = 0.2 gm/100 mL, adsorbent particle size = (0-75) µm, contacttime = 30 min, and shaking rate = 150 rpm)
The Study of Typical Conditions to Remove Co From Water by Adsorption by Using Activated Carbon

Figure (2) Effect of pH on Efficiency of Adsorption% of Co
(Initial cobalt (II) concentration =10 mg/L, adsorbent dose= 0.2 gm/100 mL, adsorbent particle size = (0-75)μm, contact time =30 min, and shaking rate = 150 rpm)

Figure (3) Effect of Adsorbent Dosage and Adsorbent Particle Size Efficiency of Adsorption% of Co
(Initial cobalt (II) concentration = 10 mg/L, pH =13, contact time = 30 min, and shaking= 150rpm)
The Study of Typical Conditions to Remove Co From Water by Adsorption by Using Activated Carbon

Figure (4) Effect of Contact Time on Efficiency of Adsorption % of Co (Initial cobalt (II) concentration = 10 mg/L, pH = 13, Adsorbent dose = 0.4 gm/100 mL, adsorbent particle size = (0-75) µm, and shaking rate = 150 rpm)

Figure (5) Effect of Shaking Rate on Efficiency of Adsorption % of Co (Initial cobalt (II) concentration = 10 mg/L, pH = 13, adsorbent dose = 0.4 gm/100 mL, adsorbent particle size = (0-75) µm, and contact time = 60 min)