

Adsorptive Removal of Cobalt and Cadmium by Using Bagasse Pith

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ABSTRACT- The wastewater of industries flows which contain heavy metal ions are manufactured from different industries. The heavy metals ions are amongst the mainly dangerous of the elemental pollutants and are of particular concern as their increasing level in the environment represents a serious threat to human health, living resources and ecological systems. Adsorption is one of the most promising techniques for the removal of cobalt and cadmium from water and wastewaters. The sugarcane bagasse pith is developed from locally sugarcane industries to measure the suitability remediates cobalt and cadmium contaminated water. Bagasse pith was pre-treated with 0.1 N NaOH followed by 0.1 N H₂SO₄ for the present work before its use. Batch adsorption experiments were carried out to study the adsorption of cobalt and cadmium on sugarcane bagasse pith sorbent taking into account the effect of initial concentration, contact time, adsorbent dosage, pH and temperature. The experimental maximum adsorption removal of bagasse pith was found to be 99.8% and 93% for cobalt and cadmium at the higher adsorbent dosage of 10 g/100ml.

The removal of cobalt ions decreased with increasing in pH, thus pH of 2, which gives maximum removal of cobalt, was shown as 97.4 %. The maximum removal of cadmium (81.5%) was observed at optimum pH 6 for bagasse pith. The adsorbent material which shows a good adsorption capacity for both the metal ions. The processes of adsorption on bagasse pith were evaluated by using Langmuir and Freundlich isotherm models. The values of correlation coefficient of Langmuir and Freundlich models for cobalt and cadmium were found to be 0.999 and 0.9977 respectively. The Langmuir adsorption model exhibited excellent indication of adsorption data than the Freundlich isotherm model.

Keywords: Adsorption Isotherms, Bagasse Pith, Cobalt and Cadmium, Langmuir, Freundlich, Wastewater.

I. INTRODUCTION

The primary thing required in all the living organisms is the contact to clean water. Due to increase of population, not only the stress on the reserves raise but contaminations of these natural resources is increasing day by day. The different pollutants discharge from different industries is making the scenario poorer. A few water that has been unnatural by the use of public is called wastewater. Cobalt is a very contaminated element which affects the environment. It can be react with different particles or adsorb on particles of soil or water sediments. Soils which contain very less amounts of cobalt can grow plants that contain a deficiency of cobalt. While the regular level of cobalt in soils is 8 ppm, there are soils with as little as 0.1 ppm and others with as much as 70 ppm [4]. This metal ion which causes sterility, loss of hair, vomiting, bleeding, diarrhoea, coma and even death. Cadmium has been classified as a carcinogen of human and teratogen which affects the kidneys, lungs, liver and reproductive systems.

The heavy metal ions separated from inorganic waste matter can be achieved by using conventional treatment methods. Separations of heavy metal ions from industrial wastewaters can be consummate through different treatment methods which includes like unit operations as chemical precipitation, complexation, coagulation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, membrane operation and adsorption methods [5].The majority of them engage high capital costs with returning operating cost, which are not appropriate for small-scale industries.

Adsorption process to be the most efficient process for the reason that it is very much efficient, low-priced, and simple and eco-friendly technique among all physicochemical processes. Adsorption on bagasse pith is widely used for elimination of cobalt and cadmium metal ions at trace levels. Bagasse is one of the fibrous waste gone after the sugarcane juice has been extracted for crystallize into sugar. The analysis which shows that bagasse production is equivalent to 20-30 percentage of full cane volume

which is crushed in a sugar factory. Bagasse pith used as a low cost adsorbent for the removal of cobalt and cadmium from industrial wastewater [6].

II. MATERIALS & METHODS

Cobalt Nitrate, Cadmium Chloride, Sodium Hydroxide, Dimethyl glyoxime, Sulphuric acid, Distilled water and Bagasse pith available from sugar industries located at Pandyapuram in Karnataka. All chemicals were used of analytical reagent grade only.

ADSORBENT PREPARATION

The bagasse pith is obtainable from the sugar industries situated at Pandyapuram in Mandya district in Karnataka. Using a 200 Tyler mesh, the bagasse pith was sieved and the opening of mesh at 72 μm . Initially the adsorbent is washed with deionised water to keep away from the release of colour by using adsorbent into the aqueous solution [7,8]. The adsorbent activation was investigated out by treating with 0.1N Sulphuric acid and dried at room temperature. Once more the activated adsorbent washed with deionised water to remove the traces of acid.



Fig. 1 Bagasse pith

PREPARATION OF ADSORBATE SOLUTION

Cobalt Stock Solution

4.9379 g of cobalt Nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is dissolved in a 250 ml volumetric flask and then diluted with distilled water up to the level. The required concentration of the cobalt solution is 1000 mg/L. From the cobalt stock solution (1000 mg/L), various initial concentrations of 50, 100, 200, 300, 400 and 500 mg/L were made by diluting with required distilled water. For pH adjustment, the Solutions of 0.1 N Sodium Hydroxide and 0.1 N Sulphuric acid were used for the experimental work.

Cadmium Stock Solution

The stock solution of cadmium 1000 mg/L was made by dissolving 2.0360 g of cadmium chloride in 100 ml deionised water. All the different working solutions were made by diluting stock solution with deionised water for the present experimental work. The test solutions of pH were adjusted by using 0.1 N Sodium Hydroxide and 0.1 N Sulphuric acid solutions.

Characterization of the Adsorbent

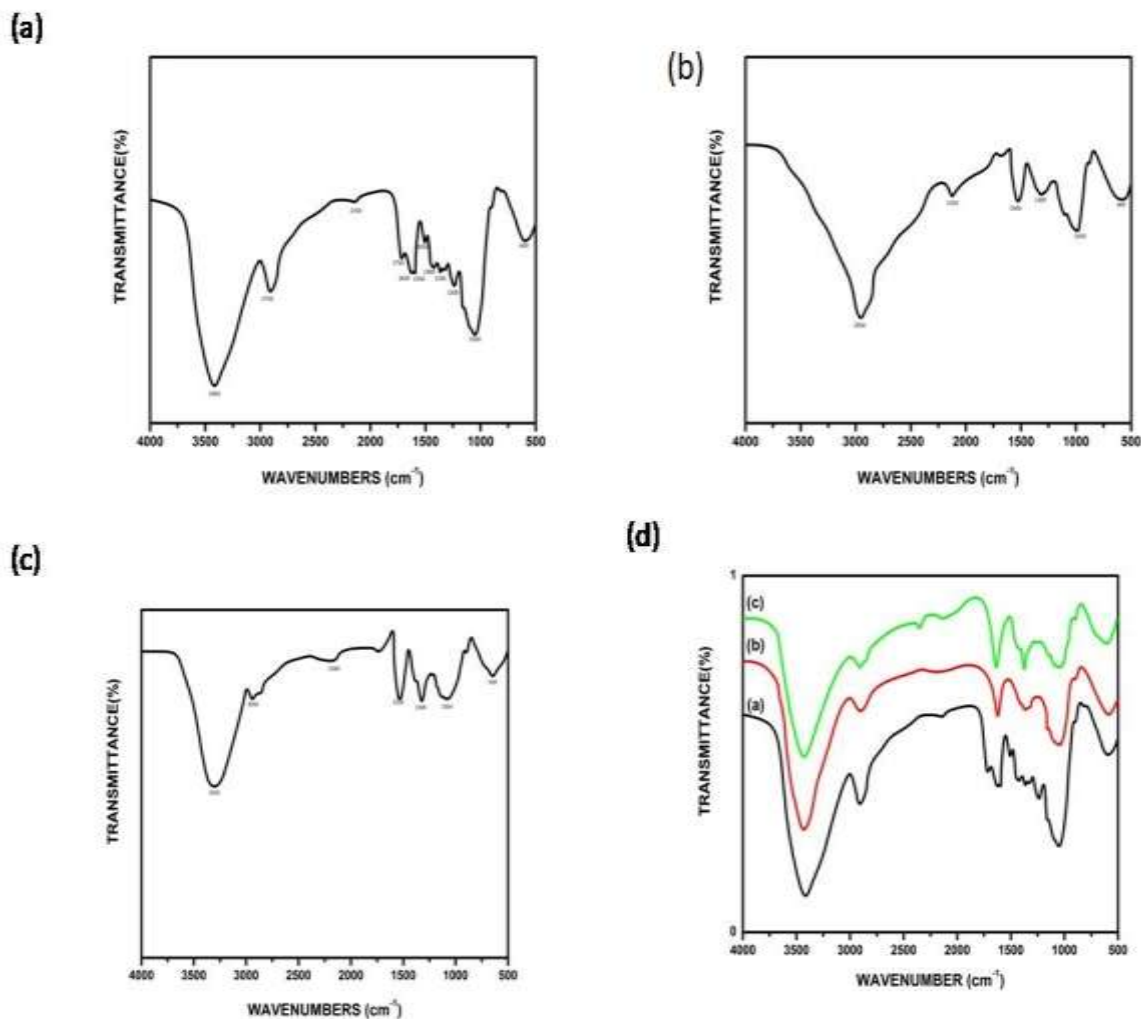


Fig. 2 FTIR spectra for samples of Bagasse pith (a) Untreated (b) Treated with NaOH (c) Treated with H2SO4

The functional groups of the bagasse pith adsorbents, visualization of their morphology and the amount of their surface loads and of the metal ions in their construction were performed to characterize the adsorbents. The organized adsorbent was characterized by Fourier-transform infrared (FT-IR) technique. Consequently, the spectrum which fits to covers clear peaks at 3450 (N-H/C-H/O-H group), 2750 (C-H group), 2250 (Carboxylic acid), 1650 (N-H), and 1550 cm^{-1} (C=C), 1450 ($=\text{CH}_3$), 1050 (Alkyl amine) and 600 (C-I) that are present in the Untreated condition of bagasse pith in the figure (a). Some of the functional groups like N-H/C-H/O-H, Ketones, Alkanes and Alkyl amines are disappeared in the figure b. Presence of these peaks is decent indication on adsorption of bagasse pith in the figure c.

SEM images for Bagasse pith:

The SEM images were obtained and found that the treated bagasse pith was showing that the adsorbent surface is clearly visible in the below figure.

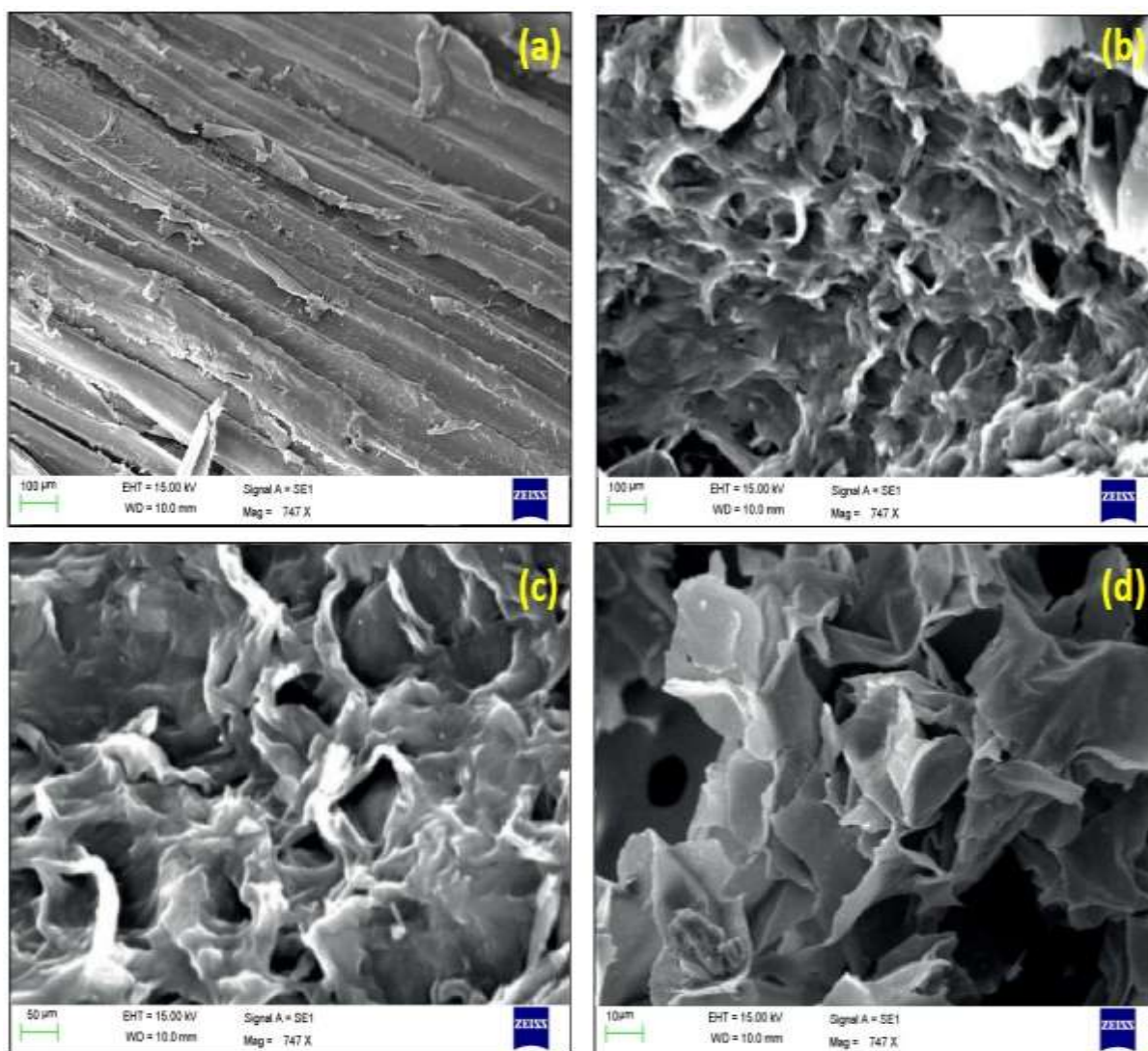


Fig. 3 SEM images of Bagasse Pith :a Untreated , b Treated with NaOH, cTreated with H₂So₄ (50 μm), d Treated with H₂So₄ (10 μm)

BATCH ADSORPTION EXPERIMENT

The present experimentation is carried out in batch wise operation on adsorption of cobalt and cadmium from aqueous solutions onto Bagasse pith [9,10]. Batch adsorption experiments were carried out to find out the adsorption isotherms of Cobalt and Cadmium metal ions onto the various adsorbents in 250 ml glass flask. The glass flasks were shaken at a stable rate, which allowing adequate time for the stability of adsorption. The effect of contact time and pH was studied with a cobalt and cadmium concentrations of 100 mg/l and an adsorbent dosage of 2 g/100ml, the aqueous solution pH was adjusted in the range of 2 to10 by using dilute Sulphuric acid and Sodium hydroxide solutions. Experiments were carried out by changing the amount of adsorbent from 2 to10 g/100 ml with cobalt and cadmium concentration of 100 mg/l. Eventually, cobalt and cadmium concentrations were analyzed by using spectrophotometrically.

III. RESULTS AND DISCUSSIONS

Effect of contact time

The effect of contact time on percentage removal of cobalt and cadmium was studied at initial concentration 100 mg/L and adsorbent dose 2g/100ml. The contact time changes from 0 to 180 minutes. From the figure, it shows that the removal of cobalt ion increases with increasing in effect of contact time, attaining equilibrium at 160 to 180 minutes. The percentage removal of cobalt (39% to 92%) and cadmium (34% to 88%) metal ions increases for bagasse pith at 0 to 180 minutes. Finally we concluded from the below graph, that the percentage removal of cobalt (92%) was more than the cadmium ion

(88%). It has been observed from this figure that the curves are smooth for the adsorbent of bagasse pith [11]. The time required for contact is 160 to 180 minutes in both the metal ions.

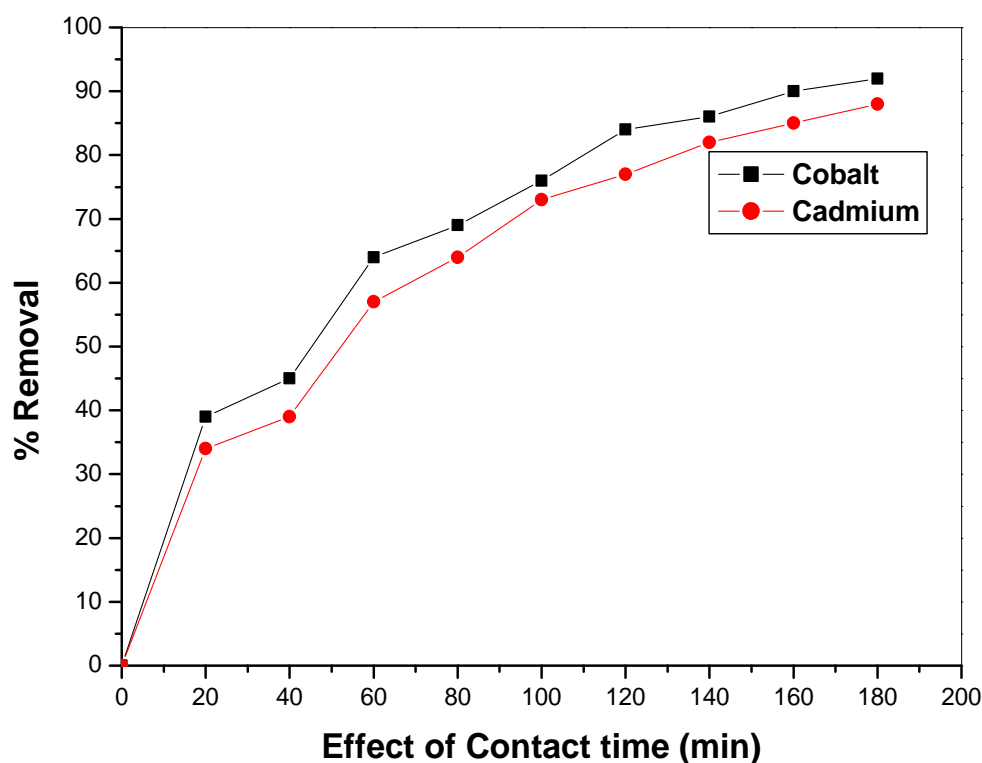


Fig. 4 Effect of contact time on cobalt and cadmium at initial concentration 100 mg/L, adsorbent dose 2g/100ml, temperature 320 C by bagasse pith.

Effect of initial concentration

The effect of initial concentration on percentage removal of cobalt and cadmium was studied at adsorbent dosage of 2 g/100ml. The initial cobalt and cadmium concentrations were changes from 50 mg/l to 500 mg/l. From the figure, it is noticed that the percentage removal of cobalt decreased (88% to 42%). For cadmium, percentage removal decreased and then slowly declines from (89% to 57%) with increasing initial concentrations 50 mg/l to 500 mg/L for bagasse pith. At lower concentration of 50 mg/L, the cadmium percentage removal was maximum i.e 89% than the cobalt ion for bagasse pith. The decrease in percentage removal of cobalt and cadmium for the adsorbent of bagasse pith [12] are found to be 88% to 42% and 89% to 57% respectively. The declining in removal of percentage can be described by the fact that the bagasse pith adsorbents had a inadequate number of active sites, which would turn into saturated above a definite concentrations.

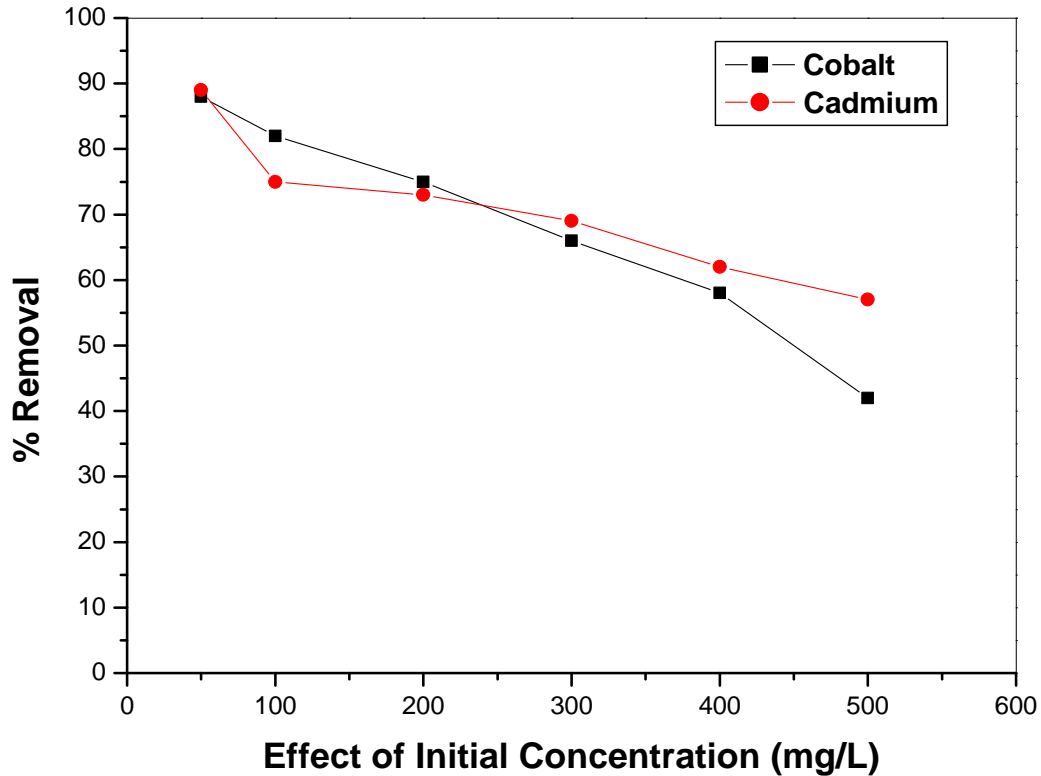


Fig. 5 Effect of initial concentration on percentage removal of cobalt and cadmium at adsorbent dose 2 g/100 ml, temperature 320 C by bagasse pith

Effect of adsorbent dosage

Effect of adsorbent dosage on removal of cobalt and cadmium was studied by varying the dose of adsorbents from 2 to 10 g/100ml at fixed adsorption conditions varying bagasse pith. The adsorbent dosage on percentage removal of cobalt and cadmium was investigated at the initial concentration of 100mg/L and temperature 32°C by using bagasse pith as adsorbent. The maximum removal of cobalt and cadmium were found to be 99.8% and 93% achieved at the higher adsorbent dosage of 10 g/100ml. The maximum removal of cobalt was achieved more than the cadmium on adsorption process with mounting in adsorbent dosage for Bagasse pith. The percentage removal of metal ions increased with increased in the dose of adsorbent and maximum adsorption was occurred at the dosage of 8 to 10 g/100ml solution, beyond which no further increase was noticed [13]. This is due to the increase in the surface area and adsorption sites available for adsorption. Especially at higher adsorbent dosage the account of active sites and surface area results from accumulation of the adsorbents

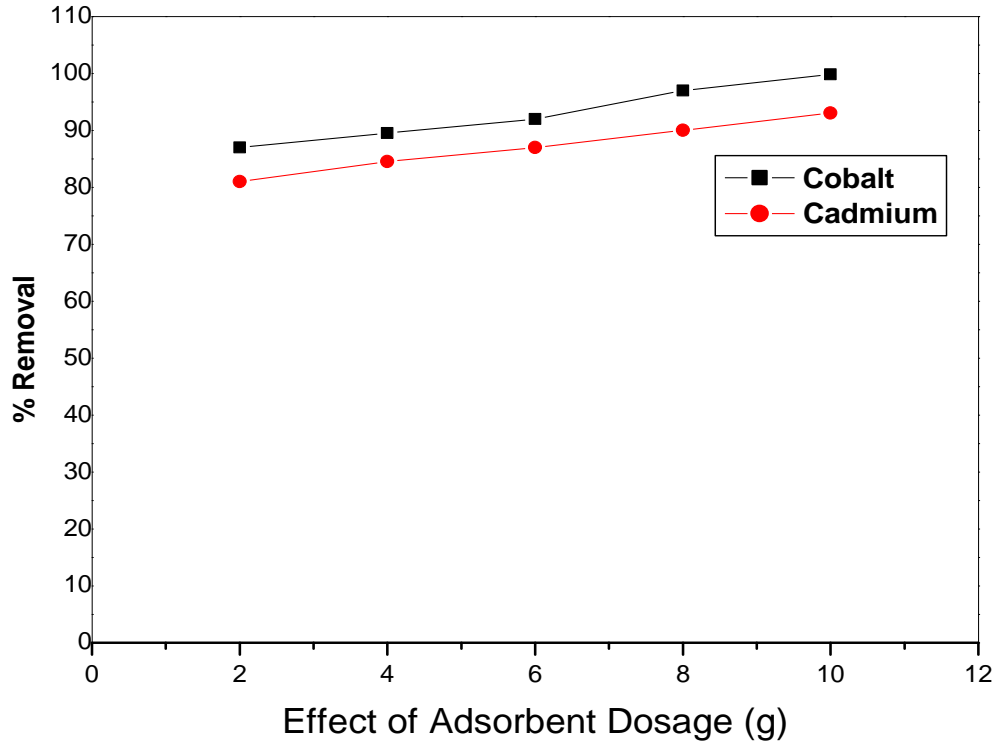


Fig. 5 Effect of adsorbent dose on percentage removal of cobalt and cadmium at initial concentration of 100 mg/L, temperature 320 C by bagasse Pith.

Effect of pH

Batch adsorption studies were carried out at different pH range of 2 to 10 and keeping all other adsorption conditions are constant. The pH of the solution is one of the most important critical parameters in the adsorption of metal ions such as cobalt and cadmium from aqueous solutions. Almost in cobalt and cadmium ions at bagasse pith, a significant enhancement and decrease in adsorption was noticed as pH increased with optimum pH of 6. The pH on percentage removal of cobalt and cadmium was studied at initial concentration of 100 mg/l, adsorbent dosage of 2g/100ml using bagasse pith as adsorbent. The processing parameter like pH increase from 2 to 10 with decreasing in percentage of cobalt and cadmium ions. From the graph, it is concluded that the removal of cobalt ions decreased with increasing in pH, thus pH of 2, which gives maximum removal of cobalt was shown as 97.4 %. The maximum removal of cadmium (81.5%) was observed at optimum pH 6 for bagasse pith. A remarkable jump in the removal of cadmium ions with growing pH could be accepted to negative charge density on the surface of adsorbent.

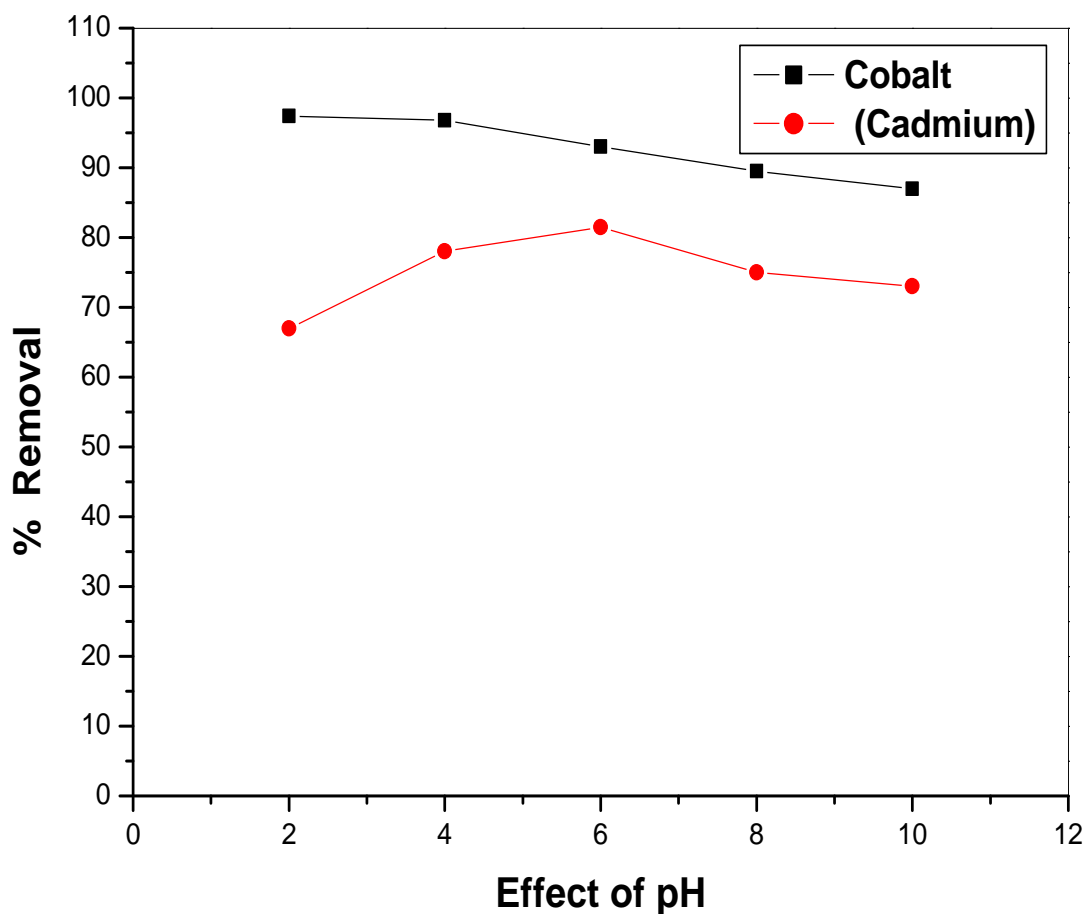


Fig. 6 Effect of pH on percentage removal of cobalt and cadmium at initial concentration 100 mg/L, adsorbent dose 2 g/100 ml and temperature 320 C by bagasse pith.

Effect of temperature

Batch adsorption studies were carried out at four different temperatures 32 °C, 42 °C, 52 °C and 62 °C and keeping all other adsorption conditions are constant. The temperature on percentage removal of cobalt and cadmium was carried out at initial concentration of 100 mg/l and adsorbent dosage of 2 g/100ml. With an increase in temperature, adsorbent capacity increased there by indicating the adsorption as an endothermic process. Maximum adsorption was observed at the temperature of 52 °C in both the metal ions for bagasse pith. The maximum percentage removal of cobalt and cadmium were found to be 97.4% and 91% at 52 °C. Further increase in temperature (beyond 52 °C) though activate the adsorption sites but at the same time decreases the physical forces responsible for the adsorption as well as increases the kinetic energy of the adsorbate molecules resulting there by in a net decrease in the adsorption [14]. The rise in temperature which favours the adsorbate transport within pores of adsorbent.

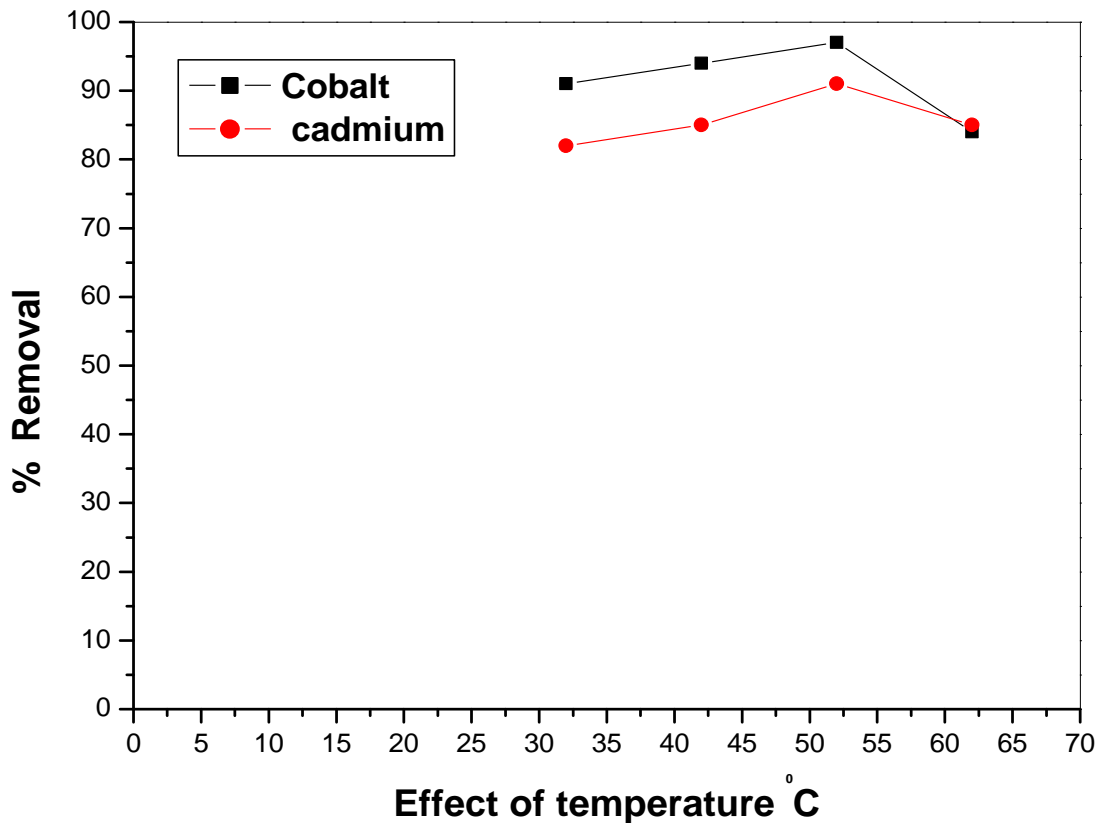


Fig. 7 Effect of temperature on percentage removal of cobalt and cadmium at initial concentration 100 mg/L and adsorbent dose 2 g/100ml by bagasse pith

ADSORPTION ISOTHERMS

Langmuir Isotherm

The adsorption isotherms models are numerical methods which explains the adsorbate sharing species between the liquid and adsorbent which is based on a set of prospect that are primarily connected to the homogeneity or heterogeneity of adsorbents, the type of coverage, and interaction opportunity between the adsorbate species. A series of solutions which containing various initial concentrations of cobalt and cadmium ions was prepared and batch adsorption experiments were undertaken at the temperature of 32 °C engaging these solutions to check the applicability of the Langmuir and Freundlich isotherms below the specified conditions, i.e. initial solution pH of 4, adsorbent dose of 2g/100 ml and an initial cobalt and cadmium ion concentrations 100 mg/L. In the present investigation the performance of bagasse pith in cobalt and cadmium adsorption from aqueous solutions was studied. Langmuir and Freundlich isotherms were applied to fit the experimental data [15]. The Langmuir and Freundlich adsorption isotherms are the plot between C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ respectively. The following Langmuir and Freundlich adsorption equations are written as

$$C_e/q_e = (1/bQ) + (1/QC_e) \text{ ----- (1)}$$

$$\ln q_e = \ln K_f + 1/n \ln C_e \text{ ----- (2)}$$

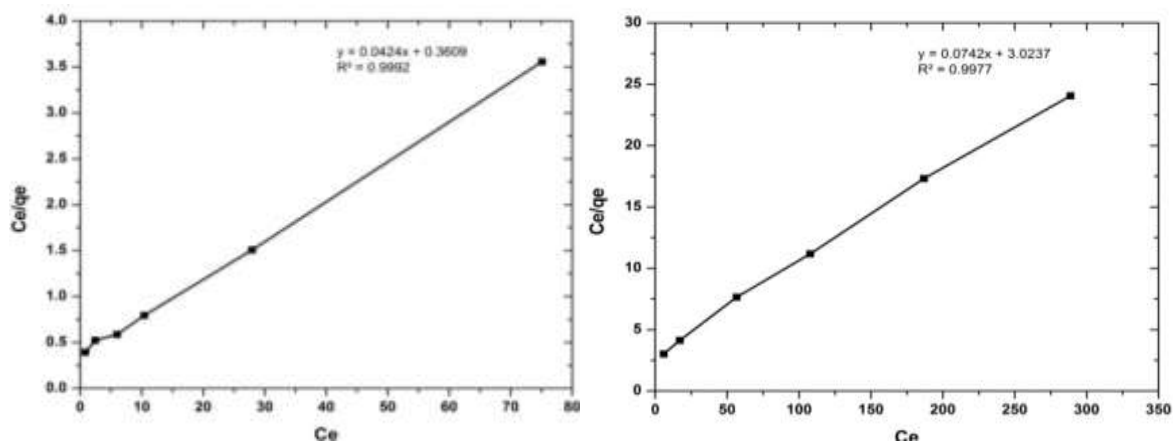


Fig. 8 Langmuir isotherms for cobalt and cadmium by bagasse pith at initial concentration 100 mg/L, temperature 320 C and adsorbent dose 2g/100 ml

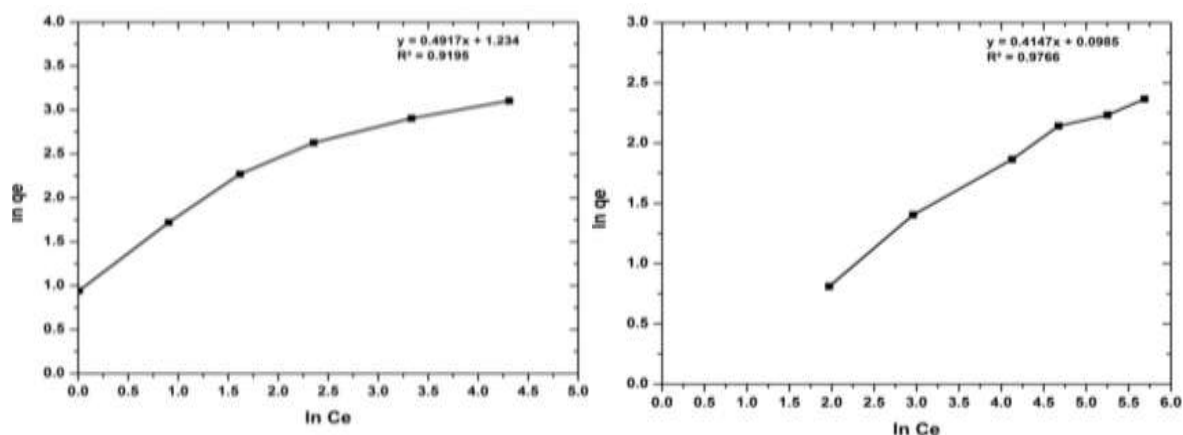


Fig. 8 Freundlich isotherms for cobalt and cadmium by bagasse pith at initial concentration 100 mg/L, temperature 320 C and adsorbent dose 2g/100 ml

IV. CONCLUSIONS

Use of sugar industries waste such as Bagasse pith for the removal of cobalt and cadmium from industrial waste water was conducted using batch adsorption techniques. Bagasse pith is found to be better adsorbent for the removal of cobalt and cadmium metal ions when compared to other low cost available adsorbents. The percentage removal of cobalt (39% to 92%) and cadmium (34% to 88%) metal ions increased with increasing in contact time for bagasse pith and the time required for contact is 160 to 180 minutes in both the metals. The decreased in percentage removal with increasing in initial concentrations of cobalt and cadmium for bagasse pith are found to be 88% to 42% and 89% to 57% respectively. At lower concentrations of 50 mg/L, the percentage removal of cadmium (89%) was more than the cobalt for bagasse pith. The maximum adsorption of cobalt and cadmium were found to be 99.8% and 93% at the adsorbent dosages of 8 to 10 g/100ml. It is concluded that the removal of cobalt ions decreased with increasing in pH, thus pH of 2, which gives maximum removal of cobalt was 97.4 %. The maximum percentage removal of cobalt and cadmium were found to be 97.4% and 91% at the temperature of 52 °C. With an increase in temperature from 32 to 52 °C, adsorbent capacity increased there by indicating the adsorption as an endothermic process. The rise in temperature which favours the adsorbate transport within pores of adsorbent. At higher temperatures a part of cobalt and cadmium leaves the solid phase and re-enters the liquid phase. Langmuir adsorption model better fits the experimental data for cobalt and cadmium since the values of correlation coefficient for Langmuir isotherm was higher than for Freundlich isotherms. The high correlation coefficient R^2 of cobalt and cadmium for Langmuir isotherm which gives an indication of favourable adsorption.

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