

Study on Adsorption of Sr^{+2} and Co^{+2} Ions from Aqueous Solution by using Modified Bagasse

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Abstract: Radioactive wastes are produced from various sources such as production and application of radioisotopes in medicine, industry, research and agriculture. ^{90}Sr and ^{60}Co are considered as low level liquid waste which can effect on human health and environment. According to the fact of the chemical behavior of radioactive liquid waste that containing ^{90}Sr and ^{60}Co is chemically similar that the waste containing Sr^{+2} and Co^{+2} . So that the adsorption of Sr^{+2} and Co^{+2} ions from aqueous solution by bagasse as by-product solid waste was investigated in this study. The investigation was performed by using untreated bagasse and treated bagasse with 1 M KOH or 1 M HCl and studying the various effects of the preparation conditions on adsorption process such as: Initial pH, Contact Time, Initial Concentration of Adsorbate, Adsorbents Dose and Adsorption Temperature. The optimum adsorption of Sr^{+2} and Co^{+2} was founded at pH 6.5 and pH 5 respectively in equilibrium time 30 minutes. The maximum amount of adsorption of Sr^{+2} by using bagasse without treatment and with treated by HCl and KOH found to be 4.65, 4.58 and 4.77 respectively, while for Co^{+2} was 3.1, 1.6 and 3.86 respectively. The characterizations of adsorbent have done by Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM). The equilibrium data were applied on Langmuir and Freundlich isotherm models and the values of their corresponding constants were evaluated from the slopes and intercepts of their respective plots. The isotherm data can be best described by the Langmuir equation.

Keywords: Adsorption Isotherm, Bagasse, Cobalt, Strontium.

1 Introduction

Radioactive waste is defined by the International Atomic Energy Agency as “Any material that has been contaminated by or contains radionuclide at concentrations or radioactivity levels greater than the exempted quantities established by the competent authorities, and for which no use is foreseen.” A widely used qualitative classification system divides radioactive waste into six classes: high level waste (HLW), intermediate level waste (ILW), low level waste (LLW), Very low level waste (VLLW), Very short lived waste (VSLW) and Exempt waste (EW). The low level liquid waste is generated in large amounts during operation and maintenance of reactors and application of radioisotopes in medicine, industry, research and agriculture [1]. So the low level liquid waste is a major concern worldwide due to its effect on human health.

Treatment of liquid radioactive waste can involve several methods for removing heavy metals ions and radionuclide

from aqueous solution such as solvent extraction, ion exchange, reverse osmosis, membrane filtration, chemical oxidation and reduction, chemical precipitation, evaporation recovery and adsorption [2-9].

Among various treatment technologies, the adsorption to activated carbon has found to be the most effective technique due to its capability of adsorbing a broad range of different types of adsorbents [10,11]. However, commercially available activated carbons are still considered expensive [12]. As many researchers have studied cheaper substitutes, which are relatively inexpensive, and are at the same time endowed with reasonable adsorptive capacity. These studies include the use of coal, activated clay, palm-fruit bunch, Bagasse pith, cellulose-based waste, peat, bentonite, slag and fly ash, rice husk, activated sludge [13-15], etc.

But in this present study, we consider the removal of radioactive heavy metals such as Sr^{+2} and Co^{+2} ions from

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aqueous solutions have performed by using untreated and treated bagasse either with HCl or with KOH as a low-cost by-product adsorbent.

2 Materials and Methods

2.1 Preparation of Adsorbent

The bagasse was used as the adsorbent in this study; it was collected and dried at ambient air for week then dried in the oven at temperature 110 °C for three hours to remove the moisture content. Then the bagasse reduced into small particles size and sieved through 3 mm size.

The bagasse treated once by soaking in 1 M HCl with concentration of 30% for a week at room temperature and once by soaking in 1 M KOH with for a week at room temperature. And then each adsorbent filtered through filter paper and rinsed thoroughly with distilled water. Then each adsorbent dried in an oven type Gravity Convection Oven - Economy Model at 160 °C for six hours and finally stored in plastic containers. This study to make comparison between the efficiency of blank bagasse without treatment and the efficiency of treated bagasse which treated by 1 M HCl or treated by 1 M KOH.

Characterization of the prepared materials was carried out using different analytical techniques such as: Scanning Electron Microscope (SEM) by using JSM-650 LA Analytical SEM, Fourier Transform Infrared Spectroscopy (FTIR) by using a JASCO FTIR 6100 FTIR spectrometer.

2.2 Preparation of the Metal Solutions

Chemicals and Reagents used in this study were all of Analar purity grade. The 1000 ppm of stock metal solutions was prepared by dissolving the appropriate amount of Cobalt Chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) with distilled water and also dissolving the appropriate amount of Strontium Chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) with distilled water. The experiments solutions in the desired concentrations were prepared by diluting the stock solution appropriate proportions. The pH of solutions was adjusted at a desired value by adding 0.1 M KOH or HCl and was measured by using pH meter produced by ULTRAMETER 6 P.

2.3 Metal Adsorption Experiments

The batch experiments of adsorption were studied by various effects such as; Initial pH, Contact Time, Initial Concentration of Adsorbate, Adsorbent Dose and Adsorption Temperature were investigated. In each adsorption experiments 0.2 gm of adsorbent which added to 20 ml of Sr^{+2} or Co^{+2} ions solution in several 100 ml conical flasks at room temperature within ± 2 °C, the mixture was shaken for certain contact time with stirring range from 0 to 150 rpm by using a Thermostatic mechanical shaker of the Biotech. Then the mixture was filtered through filter paper produced by CHMLAB Group. Inductively Coupled

Plasma – Optical Emission Spectrometer (ICP-OES) of the model Agilent5100Synchronous Vertical Dual View (SVDV) was used for determining the final concentration of Sr^{+2} and Co^{+2} aqueous solutions.

The amount of adsorption at time t , Q (mg/g), was calculated by using the following equation (1). While the amount of adsorption at equilibrium time, q_e (mg/g) can be calculated by using equation (2) as following:

$$Q = (C_o - C_t) \frac{V}{W} \quad (1)$$

$$q_e = (C_o - C_e) \frac{V}{W} \quad (2)$$

Where: V is the volume of solution W (L), W is the weight of dry adsorbent (g) and C_o (mg/L) is the initial concentrations of Sr^{+2} ions solution or Co^{+2} ions, C_t (mg/L) is the liquid phase concentration of Sr^{+2} or Co^{+2} ions solutions at any time and C_e (mg/L) is the concentration of Sr^{+2} ions solution or Co^{+2} ions at equilibrium

3 Results and Discussions

3.1. Characterization: Scanning Electron Microscope

The SEM was used to study the surface morphology of the adsorbent and to characterize the different in surface of the bagasse without treatment and bagasse treated with KOH or with HCl with magnification of 100 X as in Figure (1). It was observed that the surface contains high roughness and hollow cavities with porous structures which the metal ions can enter through the adsorption process adsorption.

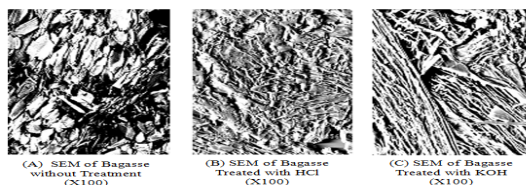


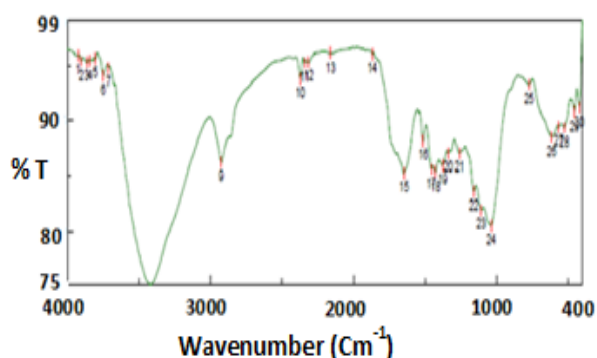
Fig. 1: SEM of Bagasse before adsorption.

3.2 FTIR Spectrum Analysis

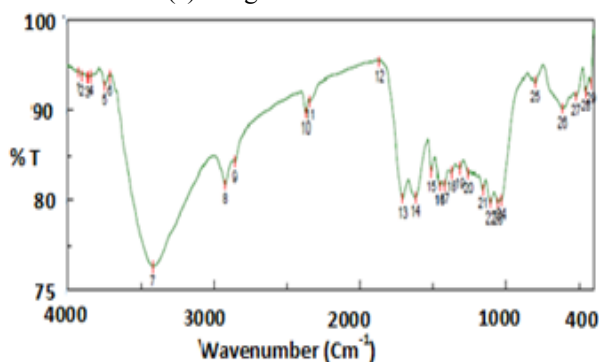
The FTIR spectra were studied to understand of the changes in the chemical structure of bagasse without treatment, bagasse treated with HCl and bagasse treated with KOH as shown in Figure (2). The spectra were recorded with 64 scans in the frequency range 400–4000 cm^{-1} . The description groups of bagasse without treatment showed up around 3421, 2924, 1648, 1512, 1428, 1376, 1339, 1261, 1037 and 773 cm^{-1} .

The retention of (O-H) extending happens at 3421 cm^{-1} seems to be normal for OH groups display in lignin and starches. The assimilation at 2934 cm^{-1} emerges from (C–H) extending. The little absorbance at 1648, 1512, 1428,

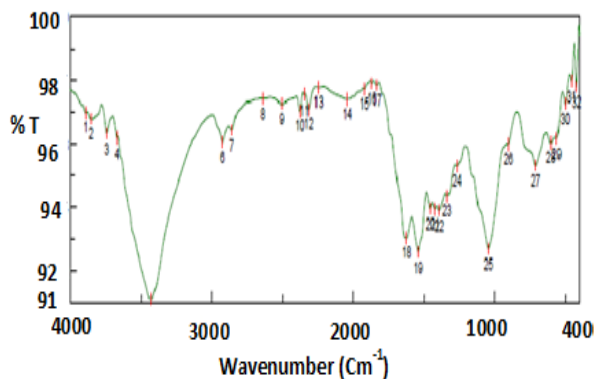
and 1339 cm^{-1} is associating to the stretching vibration with (C-O) extending in lignin. The groups at 1376 and 1261 cm^{-1} are credited to assimilation by (C-H) and (C-O) extending in acetyl gathers in hemicelluloses, individually. It was selected a solid band at 1037 cm^{-1} to (C-O) extending celluloses, hemicelluloses and lignin or (C-O-C) extend in celluloses and hemicelluloses extend in celluloses and hemicelluloses [62,63]. The Bagasse treated with either KOH or HCl showed absorption structures similar to Bagasse without treatment but with different intensities.



(a) Bagasse without treatment



(b) Bagasse treated with HCl



(c) Bagasse treated with KOH

Fig. 2: FTIR for Bagasse.

3.3 Effect of Initial pH

The experiments of adsorption were carried out in pH range from 3 to 7 with 50 mg/L initial concentration, 0.2 g adsorbent dose and 20 mL volume of metal solution at room temperature. The results of the amount of adsorption for Sr^{+2} and Co^{+2} are shown in Figure (3) and it was observed that the increasing in pH of solution occur increasing in the amount of adsorption for Sr^{+2} and Co^{+2} . The effect of increasing of pH was more pronounced in case of bagasse treated with KOH than in case of bagasse without treatment or for the bagasse treated with HCl. Also, it was detected that the effect of pH for adsorption of Sr^{+2} was greater than the adsorption of Co^{+2} . The optimal pH for adsorption of Sr^{+2} at pH 6.5 while the optimal pH for adsorption of Co^{+2} at pH 5.

The minimum amount of adsorption observed at low pH (pH 3) may be due to the fact of the presence of higher concentration and higher mobility of H^+ ions favored the preferential adsorption of hydrogen ions compared to Sr^{+2} or Co^{+2} ions. It would be acceptable to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H^+), thereby preventing the metal ions (Sr^{+2} or Co^{+2} ions) from approaching the binding sites of the adsorbent.

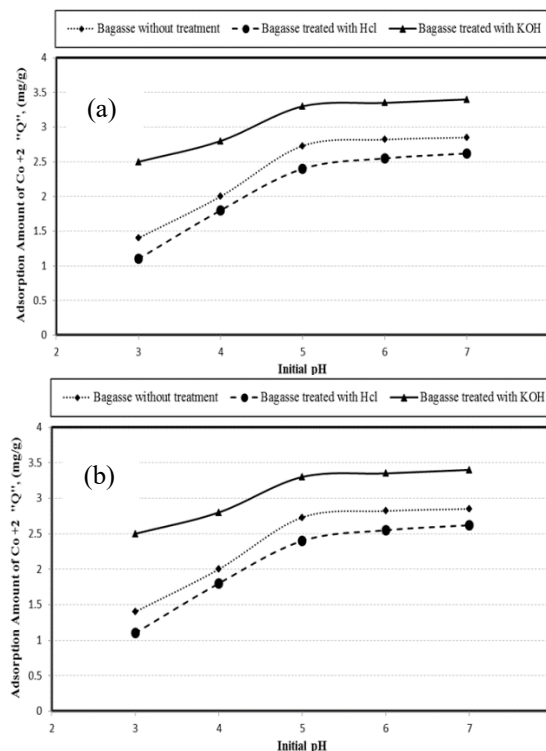


Fig. 3: Effect of Initial pH on Adsorption Amount by Bagasse on (a) Sr^{+2} ions, (b) Co^{+2} ions. With Initial Concentration = 50 mg/L , Room Temperature, Time = 30 Minute, Weight of Sample = 0.2 g and Volume = 0.02 L .

This means that at higher H^+ concentration, the adsorbent surface becomes more positively charged such that the attraction between an adsorbent and metal cations was reduced. In contrast, as the pH increases, the surface charge density decreases and more negatively charged surface becomes available thus facilitating greater Sr^{+2} or Co^{+2} ions removal so that the electrostatic repulsions between the adsorbent and the positively charged ions is less. It is commonly agreed that the adsorption of metal cations increases with increasing pH as the metal ionic species become less stable in the solution [20-23].

3.4 Effect of Contact Time

The influence of contact time on adsorption of Sr^{+2} and Co^{+2} was studied at pH 6.5 and 5 respectively, initial concentration of metal solution of 50 mg/L at room

temperature for various times from 5 to 60 minutes. The results of the amount of adsorption for Sr^{+2} and Co^{+2} are shown in Figure (4). It was detected that the amount of adsorption of Sr^{+2} or the amount of adsorption of Co^{+2} increased rapidly for the first 5 min, and then proceeded at a slow rate and finally attained equilibrium in 30 min.

This difference of adsorption of metal ions through various contact time may be due to at the initial of adsorption process there are a large number of vacant surface sites on the adsorbent surface for adsorption [19, 24]. While the slowing in the rate of adsorption occurred according to decrease the number of vacant surface sites of adsorbent and the remaining vacant surface sites are difficult to be occupied due to repulsive force between adsorbent and bulk fluid [25].

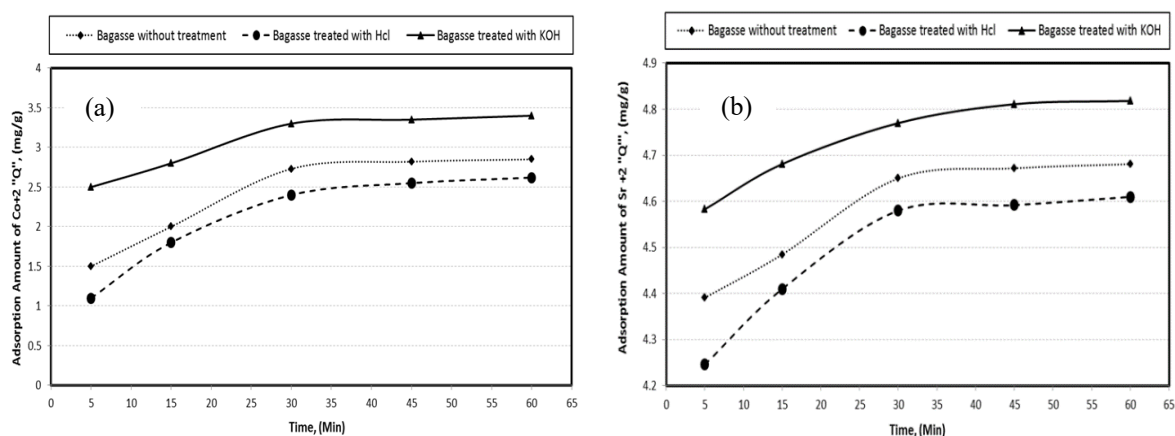


Fig. 4: Effect of Contact Time on Adsorption Amount by Bagasse on (a) Sr^{+2} ions, (b) Co^{+2} ions. With optimum pH, Initial Concentration = 50 mg/L, Room Temperature, Weight of Sample = 0.2 g and Volume = 0.02 L.

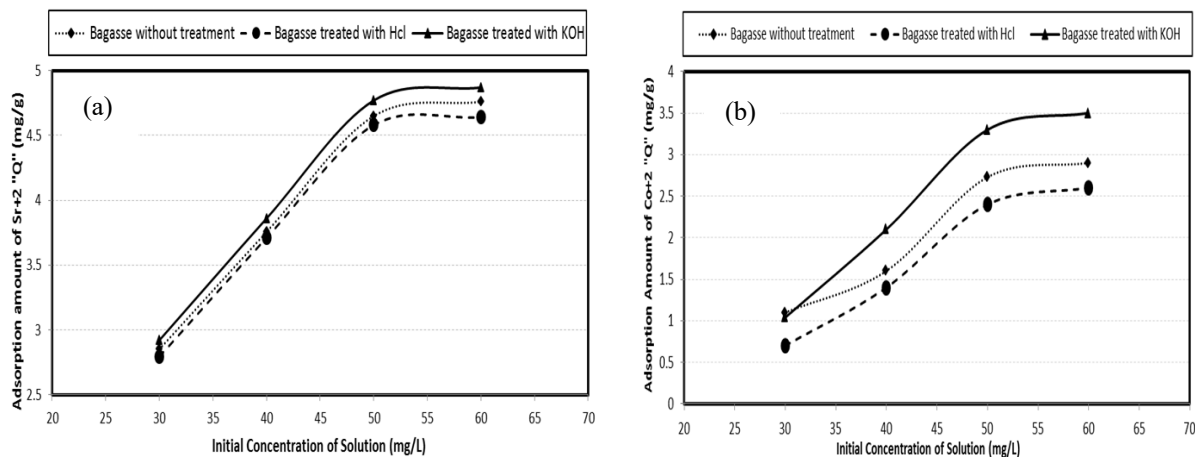


Fig. 5: Effect of initial concentration on adsorption amount by bagasse on (a) Sr^{+2} ions, (b) Co^{+2} ions. With weight of sample = 0.2 g, optimum pH, room temperature, time = 30 min., and volume = 0.02L.

3.5 Effect of Initial Concentration of Adsorbate

The adsorption of metals by any adsorbent was highly affected by the initial concentration of the metal ion. The influence of adsorption of Sr⁺² and Co⁺² was carried out at different initial concentrations of metal solution from 30 mg/L to 60 mg/L at pH 6.5 for Sr⁺² solution and pH 5 for Co⁺² and room temperature for 30 min contact time. The results of the amount of adsorption for Sr⁺² and Co⁺² are shown Figure (5). It was detected that the amount of adsorption of metal ions increased with increasing the initial concentration of metal ions according to the more adsorption sites were being covered as the metal ions concentration increases with increasing in the electrostatic interaction between the metal ions and the active sites [19, 26].

3.6 Effect of Adsorbent Dose

The study of adsorbent dose factor is very important in adsorption studies because it determines the capacity of adsorbent for a certain initial concentration of metal ions. The effect of adsorption of Sr⁺² and Co⁺² was carried out at different adsorbent dosage from 0.05 g to 0.2 g for 50 mg/L initial concentrations of metal solution and contact time 30 min at pH 6.5 for Sr⁺² solution and pH 5 for Co⁺² and room temperature. The results of the amount of adsorption for Sr⁺² and Co⁺² are shown in Figure (6). And it was detected that the amount of adsorption of metal ions decreased with increasing the bagasse adsorbent dosage according to the existence of adsorption active sites remaining unsaturated during the adsorption process and also due to excess amount of adsorbent would be required for the adsorption of metal ions which causes overlapping of adsorption sites due to overcrowding of adsorbent particles [27-29].

3.7 Effect of Adsorption Temperature

The effect of adsorption temperature was carried out with different temperatures in range from 303 K to 333 K. The results of the amount of adsorption for Sr⁺² and Co⁺² are shown in Figure (7). It was detected that the adsorption of metal ions increased with increasing in the temperature until 323 K and then the adsorption of metal decreased with rising in temperature at 323 K according to increasing in availability of active adsorption sites because of breaking of some internal bonds near the edges of active surface sites of the adsorbent. While at high rise of temperature the amount of adsorption decreased according to the desorption caused by an increase in existing thermal energy [30- 32].

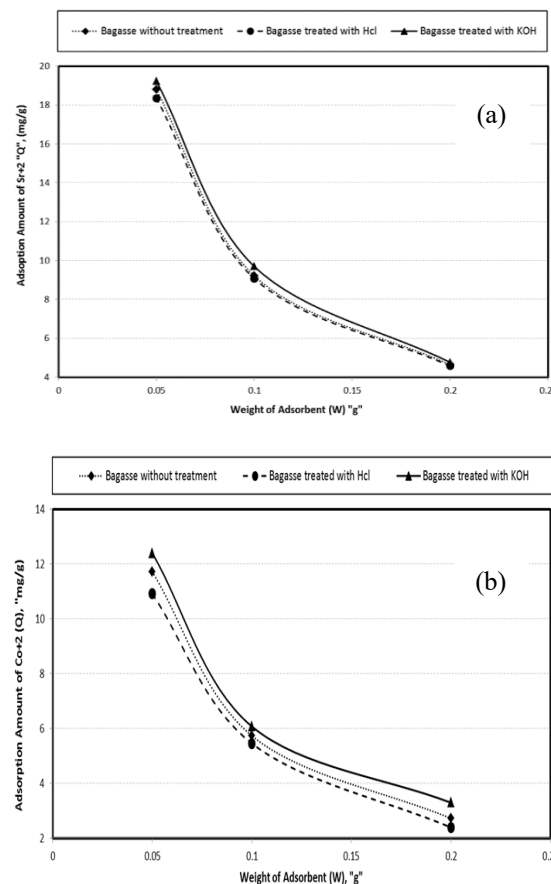


Fig. 6: Effect of Weight on Adsorption Amount by Bagasse on (a) Sr⁺² ions, (b) Co⁺² ions with Initial Concentration = 50 mg/L, optimum pH, Room Temperature, Time = 30 Minute and Volume= 0.02 L.

4 Adsorption Equilibrium

The adsorption isotherms model show the equilibrium relationship between metal concentration in solution and the amount of metal adsorbed on a specific adsorbent at a constant temperature [37]. The equilibrium adsorption isotherms for the Sr⁺² and Co⁺² ions removal were conducted using varied initial concentration at pH 6.5 for Sr⁺² solution and pH 5 for Co⁺² solution and at room temperature. The data were obtained then fitted to Langmuir adsorption isotherm as the following equation (3) [39] and Freundlich adsorption isotherm as the following equation (4) [42]. These isotherms are used to describe experimental adsorption data to develop suitable industrial adsorption system designs. These isotherms relate the amount of substance adsorbed per unit mass of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk liquid phase (C_e).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \tag{3}$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{4}$$

where: q_e is the amount of adsorption for ions per unit mass of adsorbent at equilibrium in (mg/g), C_e is the equilibrium concentration of the adsorbate in (mg/L), k_L is the Langmuir constant related to energy or net enthalpy of adsorption in (L/mg), q_{max} is the amount adsorbed to form a complete

monolayer on the surface and it is the Langmuir constant related to maximum adsorption capacity in (mg/g), k_f is the constant related to the adsorption capacity in (mg/g) and n is the constant related to intensity of the adsorbent.

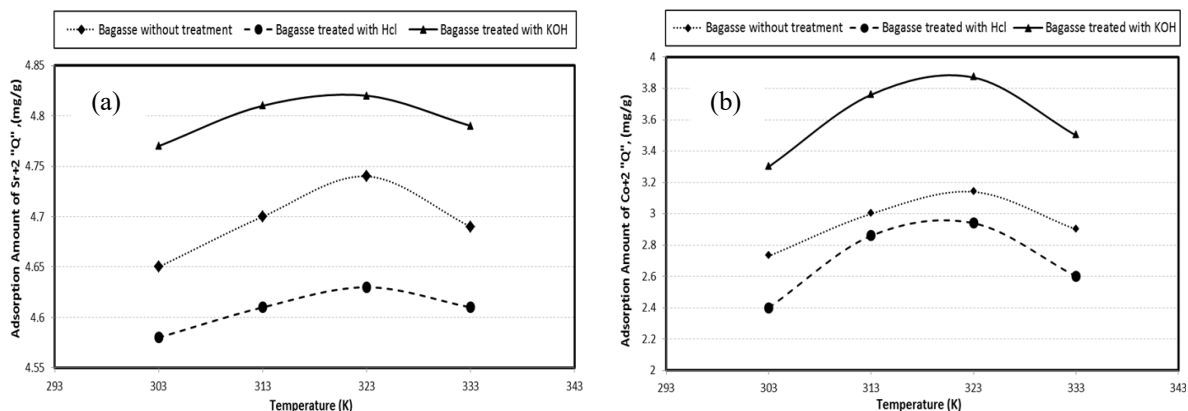


Fig. 7: Effect of initial temperature on adsorption amount by bagasse on (a) Sr+2 ions, (b) Co+2 ions. With initial concentration= 50 mg/l, optimum pH, time = 30 min., weight of sample = 0.2 g and volume = 0.02L.

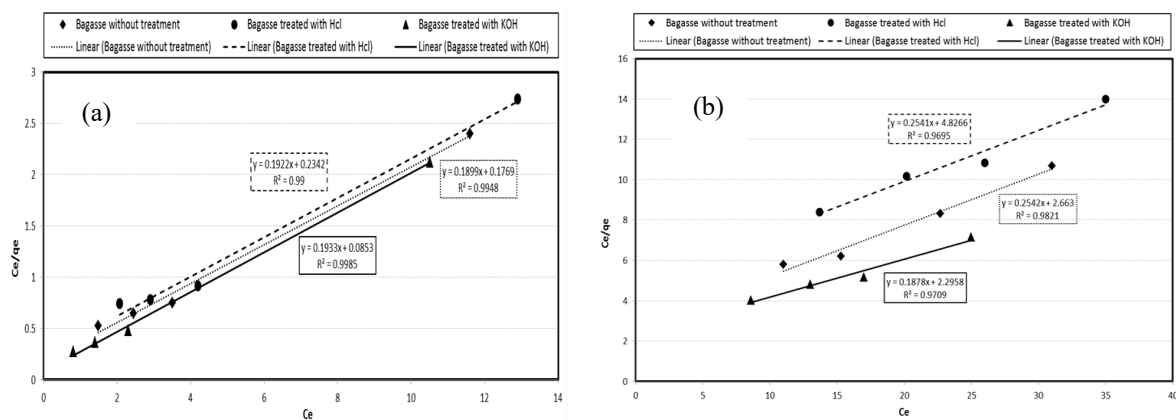


Fig. 8: Langmuir Isotherm for adsorption by bagasse (a) Sr+2 ions, (b) Co+2 ions.

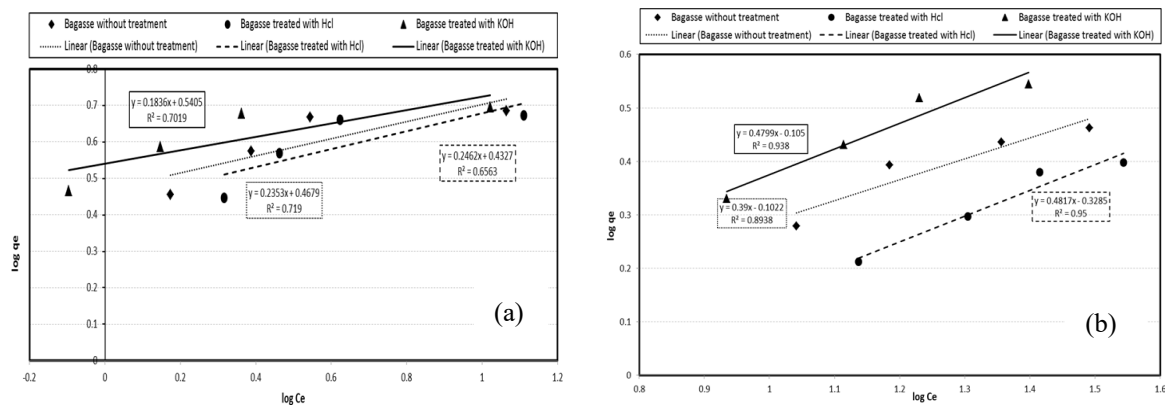


Fig. 9: Freundlich Isotherm for adsorption by bagasse (a) Sr+2 ions, (b) Co+2 ions.

Table 1: Adsorption Isotherm Parameters of Sr⁺² and Co⁺² ions onto Bagasse Adsorbent.

Adsorbate	Langmuir Isotherm			Freund		
	q _m (mg/g)	k _L (L/mg)	R ²	n	k _r (mg/g)	R ²
Sr ⁺²	5.2655	1.0736	0.9948	4.2499	2.937	0.719
Co ⁺²	3.934	0.0955	0.9821	2.5639	0.7903	0.8938
Sr ⁺²	5.2028	0.8207	0.99	4.0623	2.7085	0.6563
Co ⁺²	3.935	0.0527	0.9695	2.0761	0.4694	0.95
Sr ⁺²	5.1739	2.2646	0.9985	5.4466	3.4713	0.7019
Co ⁺²	5.3246	0.0818	0.9709	2.0838	0.7852	0.938

The plotting of $(1/q_e)$ against $(1/C_e)$ will obtained a straight line with a slope $(1/q_m k_L)$ and intercept $(1/q_m)$ as shown in Figure (8) while the plotting of $(\log q_e)$ against $(\log C_e)$ will obtained a straight line with a slope $(1/n)$ and intercept $(\log k_r)$ as shown in Figure (9).

The adsorption behavior of Sr⁺² and Co⁺² onto bagasse without treatment, bagasse treated with HCl and bagasse treated with KOH are modeled by Langmuir isotherm and Freundlich isotherm and the resulting isotherm constants illustrated in Table (1). And it was observed that the adsorption onto bagasse follow Langmuir Isotherm.

5 Conclusions

In this study, the investigation of adsorption of Sr⁺² and Co⁺² onto bagasse without treatment, bagasse treated with HCl and bagasse treated with KOH observed by studying characterization of adsorbents and several effects such as effect of time on adsorption, pH, adsorbent dose, initial concentration, adsorption of temperature. It was observed that the amount of adsorption had high values by using bagasse treated with KOH as adsorbent while the using of bagasse treated with HCl as adsorbent effected much lower than using bagasse without treatment. Also, the equilibrium adsorption of Sr⁺² and Co⁺² onto bagasse followed Langmuir isotherm.

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