

Improvement of Manure Adsorption Capacity for Cobalt Removal by Chemical Treatment with Citric Acid

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ABSTRACT

This paper focuses on how the surface chemical groups of sheep manure affect the adsorption capacity of cobalt ions. Improvement in cobalt ions uptake onto sheep manure was achieved successfully by introducing more carboxylic functional groups into its surface due to citric acid treatment. According to Langmuir model, cobalt ions uptake was increased from 22.88 mg/g for dried sheep manure (**D-SM**) to 37.45 mg/g when **D-SM** was treated with 0.6 M citric acid (**C-SM**). Point of zero charge and cation exchange capacity were determined and found as 4.3 and 82 meq/100g for **D-SM** while it was found as 3.4 and 281 meq/100g for **C-SM**, respectively. The effects of process parameters such as solution pH, initial concentration of cobalt ions, contact time and concentration of citric acid on the uptake of cobalt ions were also investigated. Langmuir and Freundlich models were applied to the experimental data. Both models fitted quite well with the experimental data.

KEYWORDS: Surface modification, Sheep manure, Adsorption, Cobalt, Citric acid.

INTRODUCTION

Toxic heavy metals contamination exists in aqueous waste streams through a variety of sources, such as mining, refining and electroplating (Gardea-Torresdey et al., 1999). The most common heavy metals found in wastewater are copper, cadmium, nickel, cobalt, lead and zinc which are toxic at high concentrations. These heavy metals are not biodegradable and can be carcinogenic, if not fatal, in high concentrations (Wartelle and Marshall, 2000).

Adsorption has been extensively used in industrial processes for separation and purification. In wastewater treatment, activated carbon is the most popular adsorbent but its high cost motivates researchers to investigate and develop new adsorbent materials, which are inexpensive, and exhibit a high capacity for adsorbing heavy metals. In

general, the development of new cheap adsorbent materials has been focused on producing activated carbon from agricultural or industrial waste materials such as walnut (Kim et al., 2001) and rice husks (Yalcin and Sevinc, 2000). Since the pioneer work of Mattson et al. (1969) to others' works published more recently (Rodrigues-Reinoso, 1998; Li et al., 2002; Boehm, 1994; Franz et al., 2002; Leng and Pinto, 1997; Hydar et al., 2003), it is found that adsorption capacity is significantly affected by the activated carbon surface chemistry. Several published studies investigated the modification of different waste by-products in order to enhance their metal ion-adsorbing properties. Marshall et al. (1999) developed a process to enhance the metal ion binding properties of soybean hulls by modification with citric acid. Sessa and Wing (1998) studied the thermochemical reaction between corn fiber and citric acid and obtained a modified corncob, which had a larger cation exchange capacity than natural corncob (Wing, 1996). Marshall et

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al. (1999) used citric acid treatment for soybean hulls to produce a higher value product with potentially lower costs as compared to commercially available ion exchange resins.

Sheep manure is one of the solid wastes produced in Jordan and currently used as fertilizer. This under-utilized waste could be converted into a product of greater value, such as an adsorbent. Recently, Kandah (2001) used this product as an environmental friendly alternative adsorbent to remove zinc ions from aqueous solutions without any surface modification. After that, Abu Al-Rub et al. (2002) and Kandah et al. (2002) investigated its capability to remove other heavy metals such as nickel, copper and cadmium ions.

The objective of this work is to show how surface chemistry of sheep manure may affect the results of adsorption capacity of cobalt ions. In this work, an enhancement to the sheep manure adsorption capacity by modifying its surface chemistry using citric acid was investigated. Its cobalt ions uptake from aqueous solution was investigated as a function of citric acid concentration, contact time and solution pH. Adsorbent point of zero charge, cation exchange capacity, types and percentages of functional groups were determined for both dried and treated manure adsorbents. Langmuir and Freundlich models were applied to the experimental data.

Table (1): Characteristics of dried sheep manure (D-SM).

Parameter	D-SM
Apparent density, g/ml	0.588
Ash content, %	31.6
Moisture, %	4.7
Crude protein, %	15.4
NDF, %	36.92
Average particle size, mm	1

EXPERIMENTAL PROCEDURE

Adsorbent Preparation and Characteristics

The capacity of sheep manure depends on its chemical composition, which may have a very wide range of properties depending upon source and pretreatment.

Therefore, the adsorbent used in this work was collected from a village called Shatana in the north of Jordan. The sheep manure (SM) was washed, dried, ground and sieved to the minimum particle size that can be achieved using the available grinding machine (i.e. 1 mm in diameter), and referred to as dried sheep manure (D-SM).

The characteristics of the dried sheep manure (such as apparent density and ash content) were determined according to the ASTM methods and are shown in Table 1. The Neutral Detergent Fiber (NDF) includes insoluble protein, cellulose, lignin and bound nitrogen; the moisture content and crude protein were determined according to the AOAC methods (Cunniff, 1995). Adsorbent pH was measured by making a suspension of 1 g of the sample in 20 cm³ of CO₂-free distilled water, after a contact time of 48 h at 298 K. It is usually determined to show whether the adsorbent is more basic (tend to attract cations), more acidic (tend to attract anions) or almost neutral as shown in our manure. Table 2 shows the chemical composition of the distilled water after a twenty four hour shaking of the dried sheep manure. Since the concentrations of the different heavy metals in the manure were very small, the competition with the adsorbed Co²⁺ will be negligible. The functional groups on the manure surface were determined according to Boehm method (Boehm, 1994).

Table (2): Chemical analysis for D-SM.

Fe ²⁺ , ppm	0.29
Zn ²⁺ , ppm	0.05
Mn ²⁺ , ppm	0.02
Cu ²⁺ , ppm	0.04
Ni ²⁺ , ppm	0.0
Co ²⁺ , ppm	0.0

Point of Zero Charge Determination

A batch equilibrium technique was applied to determine the pH at the point of zero charge. A portion of the manure powder (0.5 g) was introduced into a known volume (20 cm³) of 0.1 M KNO₃ solution. Potassium Nitrate (KNO₃) was selected as an inert electrolyte. Initial

pH values ($\text{pH}_{\text{initial}}$) of KNO_3 solutions were adjusted to cover the range from 2 to 8 by adding 0.1 M HNO_3 or KOH . The solutions were allowed to equilibrate for 24 h in an isothermal shaker at 25 ± 1 °C. Then, the suspensions were filtered through filter paper and the pH values (pH_{final}) were measured again using ion-pH meter (Smiciklas et al., 2000).

Table (3): Cation exchange capacity measurements.

Adsorbent	Cation exchange capacity, meq/100-g
D-SM	82
C-SM	281

Cation Exchange Capacity Determination

Cation exchange capacity was obtained according to ASTM method (9081). A sample of 4 g of the manure was mixed and saturated with an excess of sodium acetate solution (33 ml of 1 M), resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample was washed with 33 ml of isopropyl alcohol. This procedure was repeated three times to make sure that the manure was completely saturated with sodium. A volume of 33 ml ammonium acetate solution (1 M) was then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium was then determined by atomic absorption spectrophotometer.

Manure Surface Enhancement

Thirty grams of D-SM was mixed with 200 ml of 0.1-0.6 M citric acid and shaken for two hours at 50 °C under continuous air injection from a small compressor. The solids were separated from the liquid by centrifugal process. It was then washed with deionized water until no pH change could be detected, filtered and dried at 50°C for 24 h, then at 105 °C for 2 h. This modified manure was referred to as C-SM.

Functional Groups Determination

The surface functional groups formed on the D-SM and C-SM surfaces due to citric acid oxidation were

quantified by Boehm method (Boehm, 1994) and presented in Table 4. This method is based on sodium hydrogen carbonate neutralizing only carboxyl groups, sodium bicarbonate neutralizing carboxylic and lactonic groups, and sodium hydroxide neutralizing carboxylic, lactonic and phenolic groups. By subtracting any base from the next more exclusive base, it is possible to estimate surface charge residing in a variety of functional groups as mmol H^+ equivalent/g manure. So the different kinds of functional groups can be calculated through the known volume of used acid and bases.

Table (4): Surface functional groups determination.

Adsorbent	Carboxylic (mmol/g)	Lactonic (mmol/g)	Phenolic (mmol/g)
D-SM	1.52	0.56	0.97
C-SM	2.93	1.48	1.55

Adsorption Procedure

The adsorption was performed by batch experiments. Solid (0.4 g) in 50 ml of cobalt solution prepared from cobalt (II) acetate tetrahydrate, extra pure ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$) of varying concentrations (10-150 ppm Co^{2+}) was shaken for a predetermined period at constant temperature (25 ± 1 °C). Solution pH was adjusted by adding 0.1 M phosphoric acid or 0.1 M sodium hydroxide. The solid was separated using a centrifuge and the supernatant solution was analyzed for cobalt ions spectrophotometrically on an atomic absorption spectrophotometer. Cobalt solutions without adsorbent were analyzed before and after filtration. Neither precipitate nor cobalt ions adsorbed to the wall of the flasks were observed under the experimental conditions. All the experiments were duplicated to confirm the reproducibility of the experimental effects.

RESULTS AND DISCUSSIONS

Effect of Citric Acid Concentration

Figure 1 illustrates the effect of increasing the concentrations of citric acid during the modification of sheep manure at pH=6, particle size =1 mm, adsorbent

concentration = 8 mg/ml and cobalt ions concentration from 10 to 150 ppm. Figure 1 indicates that the maximum cobalt ions uptake was achieved at 0.6 M or more regardless of the initial cobalt ions concentration. However, the increase in citric acid concentration beyond 0.6 M did not affect the cobalt ions uptake significantly. Similar results were reported in the case of adsorbing cadmium ions by Leyva-Ramos et al. (2005) on oxidized corncob and Marshall et al. (2001) on oxidized soybean hull. One possible explanation is that the concentration of carboxylic sites in the manure that is modified with citric acid reached its maximum concentration at 0.6 M citric acid.

Table (5): Langmuir and Freundlich parameters for D-SM and C-SM.

Adsorbent	Langmuir	Freundlich
D-SM	$q_{mon} = 26.315 \text{ mg/g}$ $K_L = 0.015 \text{ L/mg}$ $R^2 = 0.9055$	$K_F = 0.5759$ $N = 1.196$ $R^2 = 0.9981$
C-SM	$q_{mon} = 77.519 \text{ mg/g}$ $K_L = 0.013 \text{ L/mg}$ $R^2 = 0.9452$	$K_F = 1.085$ $N = 1.2978$ $R^2 = 0.9975$

Functional Groups Formation

Table 4 shows that different functional groups such as carboxylic, lactonic and phenolic groups were formed by citric acid treatment. These acidic nature functional groups can dissociate at different pH values and are expected to enhance the attractive forces between Co^{2+} and OH^- which increases the adsorption capacity. It is known that the surface oxides provide hydrophilic sites on a hydrophobic surface and the adsorption properties of the oxidized carbons are greatly affected (Adams et al., 1988). When modified sheep manure is placed in an aqueous solution, the acidic surface groups, present on the surface, undergo ionization producing H^+ ions which are directed towards the liquid phase leaving the manure surface with negatively charged sites. Larger the number of acidic groups on the manure surface, greater will be the negative charge on the manure surface. This enhances

the electrostatic attractive interactions between the negative charged manure surface and the positively charged cobalt cations, thereby increasing the adsorption capacity.

Table (6): Characteristics of adsorption Langmuir isotherms.

Separation factor, R_L	Characteristics of adsorption Langmuir isotherms
$R_L > 1$	unfavorable
$R_L = 1$	linear
$0 < R_L < 1$	favorable
$R_L = 0$	irreversible

Effects of Contact Time and Initial Cobalt Ions Concentration on Cobalt Ions Uptake

The capability of dried sheep manure (**D-SM**) and sheep manure modified with 0.6 M citric acid (**C-SM**) on cobalt ions uptake was investigated for different initial cobalt ions concentration (10, 30, 60, 90, 120 and 150 ppm Co^{2+}). It is clear from Figs. 2 and 3 that the chemical treatment of sheep manure improved its cobalt ions uptake significantly. The maximum cobalt ions uptake was increased, for example, from 7.75 mg Co^{2+} /g manure for **D-SM** to 9.5 mg Co^{2+} /g manure for **C-SM** when 90 ppm of Co^{2+} were used. It is obvious from Figs. 2 and 3, that increasing the contact time increases the cobalt uptake onto the manure significantly during the first 5 minutes regardless of the initial nickel ions concentration, and then slows down gradually from 5 to 10 minutes until finally attained equilibrium. This is due to the availability of more vacant sites onto the adsorbent surface at the beginning of the adsorption which results in an increase in the concentration gradient between the cobalt ions in the solution and that onto the manure surface. As the contact time increased, this concentration gradient is decreased because of the accumulation of Co^{2+} on the vacant sites which leads to a decrease in the adsorption rate after the first 5 minutes. The maximum cobalt ions uptake was achieved after about 10 minutes of reacting for both adsorbents regardless of the initial cobalt ions concentration.

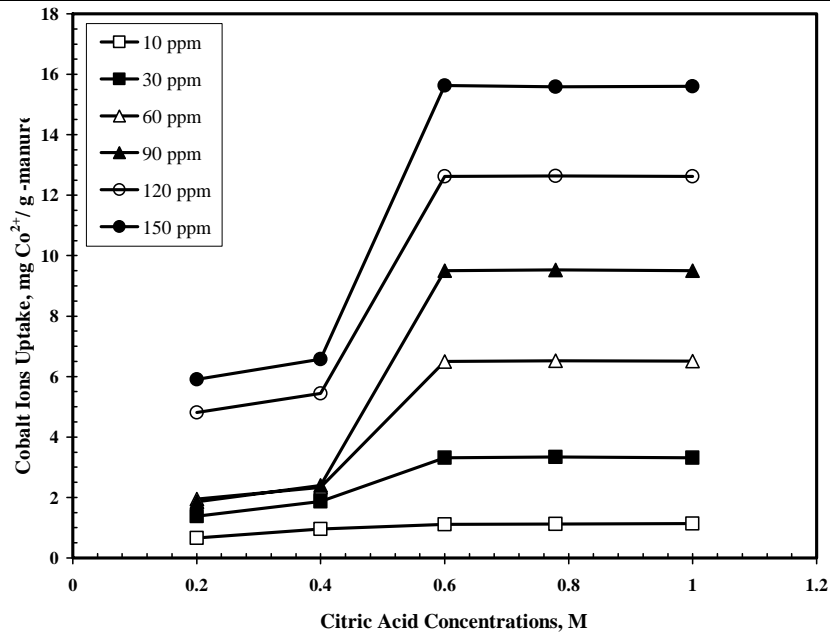


Figure (1): Effect of citric acid concentrations on cobalt ions uptake for C-SM when initial cobalt ions concentrations vary from 10 to 150 ppm, adsorbent concentration = 8 mg/ml, agitation time of 1 hr and solution pH = 6.

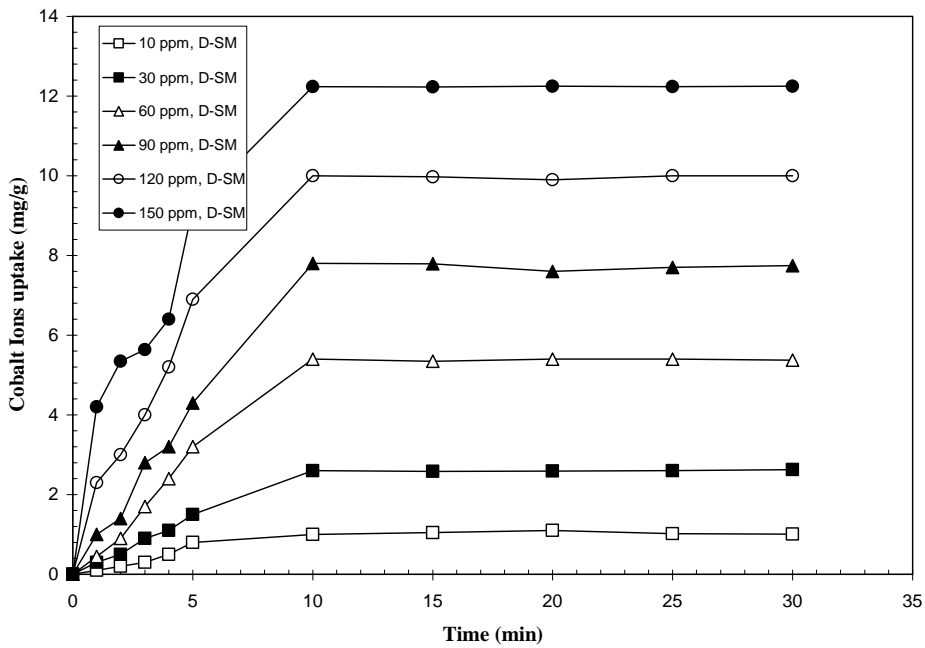


Figure (2): Effect of contact time and initial cobalt ions concentration on cobalt ions uptake for D-SM at solution pH=6 and adsorbent concentration =8 mg/ml.

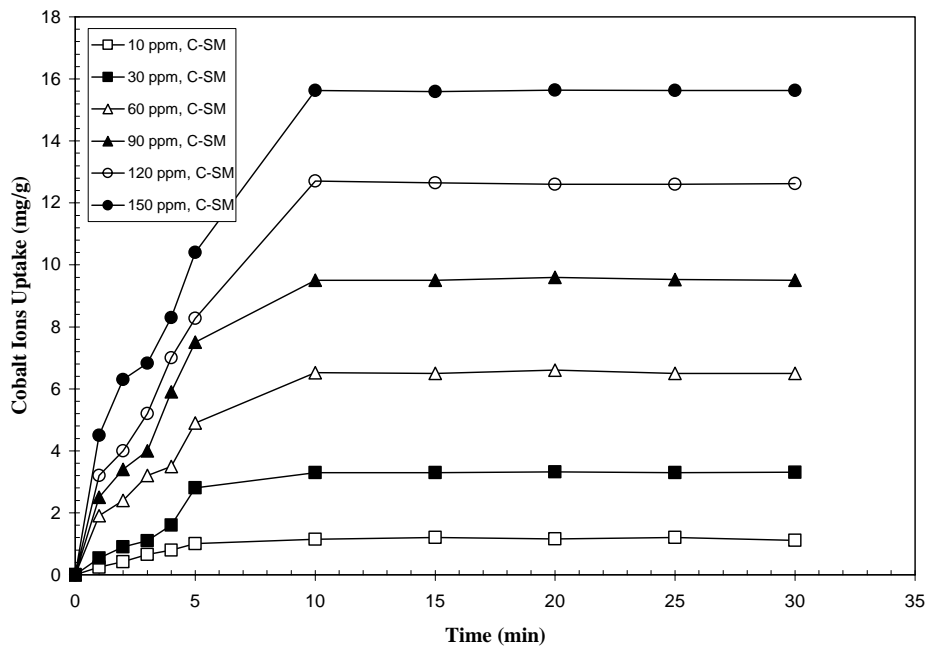


Figure (3): Effect of contact time and initial cobalt ions concentration on cobalt ions uptake for C-SM at solution pH = 6 and adsorbent concentration = 8 mg/ml.

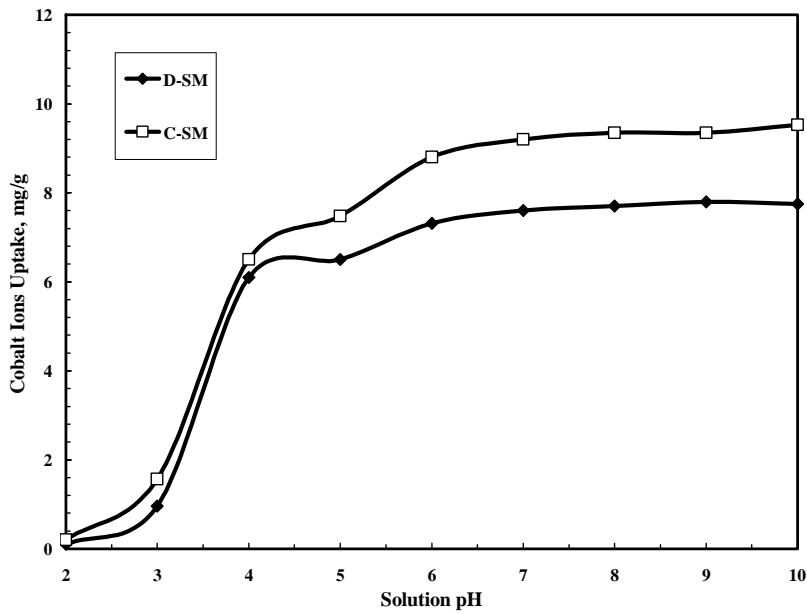


Figure (4): Effect of solution pH on cobalt ions uptake for D-SM and C-SM adsorbent concentration = 8 mg/ml, agitation time of 1 hr and initial cobalt ions concentration of 80 ppm.

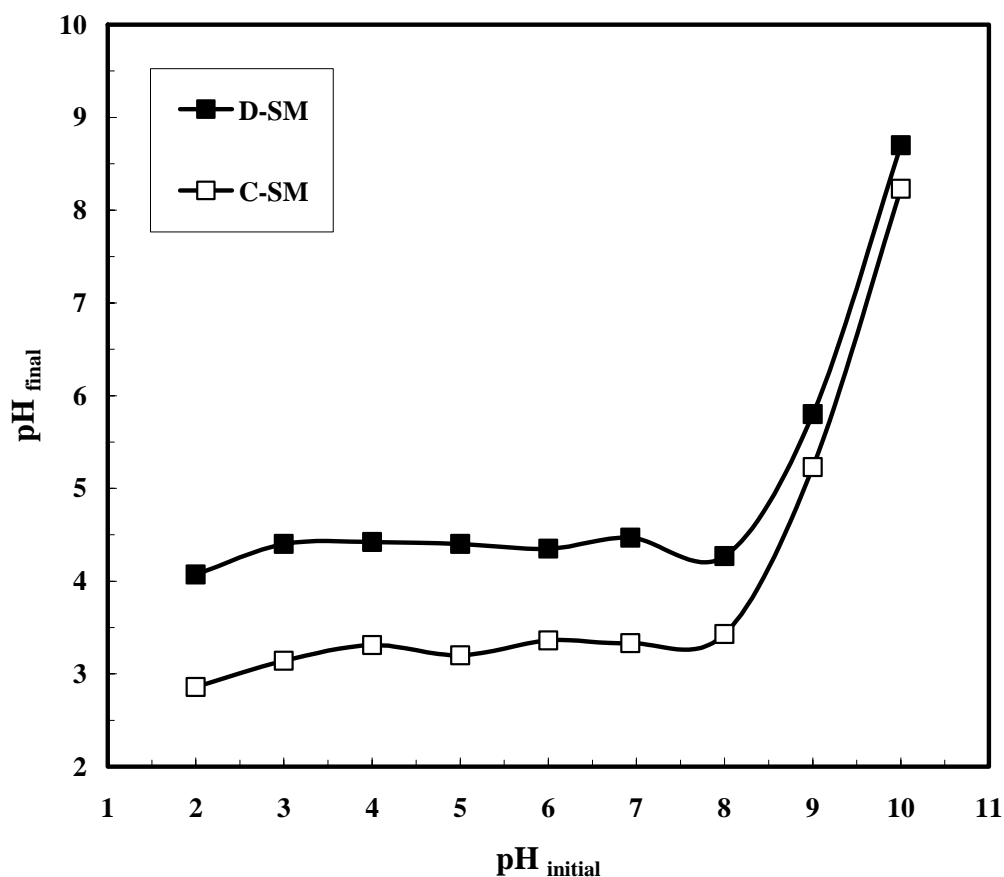


Figure (5): Point of zero charge for D-SM and C-SM.

As shown in Table 1, dried sheep manure (**D-SM**) contains NDF (lignin, cellulose and protein) as major constituents. These constituents, especially lignin, contain polar functional groups, such as alcohols, aldehydes, ketons, acids, phenolic hydroxides and ethers that can involve in chemical bonding and make it an effective adsorbent for divalent metal cations. It is clear from Table 3 that reacting the manure with citric acid improved the adsorption capacity of cobalt ions by increasing the cation exchange capacity for the adsorbent. Citric acid has a chemical formula of **HOOC-CH₂-COH(COOH)-CH₂-COOH**. It is a small biodegradable organic compound rich in carboxylic groups, which produces negative charges on the manure surface when it dissociates and increases the attractive ionic forces

between the adsorbent and the cationic heavy metals such as cobalt. The modification of manure surface with citric acid oxidation introduced more surface adsorptive sites (mainly carboxylic functional groups) which provided additional cobalt ion binding capacity.

Effect of pH

The pH of the cobalt ions solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. According to the speciation diagram of Co, the precipitation of Co(OH)₂ occurs at pH 8 to 10 depending on the total concentration of Co. Therefore, to investigate the effect of pH on the adsorption, a series of cobalt solutions were prepared by adjusting pH over a range of 2 to 8 using 0.1 M

phosphoric acid or sodium hydroxide solution. Figure 4 indicates that at low pH values (less than 3), cobalt ions uptake onto the two adsorbents was relatively low. however, as the pH was raised (from 3 to 8), cobalt ions uptake increased significantly. This occurred due to the availability of the total net negative charge that increases at higher pH values. This negative charge was neutralized by the adsorption of positively charged cobalt ions, giving the sheep manure the ability to attract and hold cations such as cobalt ions. Increasing the pH causes more surface functional groups to dissociate and provides metal binding sites.

Considering the electrostatic interactions existing between the manure surface and the cobalt ions in the solution, it is necessary to make clear that the presence of ions in solution as well as on the manure surface depends on the solution pH. At pH values above that of the point of zero charge ($pH > pH_{pzc}$), the presence of an acid group on the surface of the activated manure will dissociate into negative ions and charge the activated manure negatively. Figure 5 shows the effect of surface modification on the point of zero charge for the two adsorbents used in this study (i.e., **D-SM** and **C-SM**). Citric acid modification clearly reduces the zero point of charge from 4.3 for **D-SM** to 3.4 for **C-SM**. This can be explained by the fact that more negative charges were introduced on the surface of the manure from the dissociation of the carboxylic functional groups. The stability of final pH of solution at this wide range of initial pH from 2 to 8 supports the use of this modified solid waste as good adsorbent.

Adsorption Isotherms

The equilibrium adsorption isotherms are of importance in the design of adsorption systems. Several isothermal models are available and the ones used in this study were the Langmuir and the Freundlich models. The Langmuir isotherm model, which is valid for monolayer sorption onto a surface with a finite number of identical sites and uniform adsorption energies, is given by the following equation:

$$q_e = \frac{q_{mon}K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_{mon} is the maximum adsorption capacity which is corresponding to monolayer coverage, K_L is the Langmuir constant which is related to the energy of adsorption and C_e is the equilibrium liquid-phase concentration. Equation 1 can be linearized to determine the Langmuir parameters; q_{mon} and K_L , by plotting C_e / q_e vs. C_e . The adsorption data of cobalt on **D-SM** and **C-SM** at pH 6, shown in Fig. 6, were fitted to Langmuir equation and the results are listed in Table 5. The fit of the Langmuir equation for the adsorption of cobalt on both **D-SM** and **C-SM** was good where the correlation coefficients of the linear regressions were found to be 0.9055 and 0.9452 for **D-SM** and **C-SM**, respectively.

The dimensionless constant separation factor or equilibrium parameter, R_L (McKay et al., 1982) is given by:

$$R_L \equiv 1 / (1 + K_L C_o) \quad (2)$$

where K_L is the Langmuir constant and C_o the initial concentration of cobalt ions. It is used to determine the type of isotherm according to the criteria shown in Table 6. The values of R_L for adsorption of cobalt on **D-SM** and **C-SM** were between 0 and 1, which indicates favorable adsorption of cobalt on all adsorbents.

The Freundlich equation, given by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F and n are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively, is based on sorption on heterogeneous surfaces and does not provide any information on the monolayer adsorption capacity. Eqn. 3 can be linearized to determine the Freundlich parameters; K_F and n , by plotting $\ln q_e$ vs. $\ln C_e$ (as seen in Fig. 7). The fits of the Freundlich equation were excellent and the correlation coefficients of the linear regressions (R^2) were found to be 0.9981 and 0.9975 for **D-SM** and **C-SM**, respectively. The values of the Freundlich parameters are listed in Table 5.

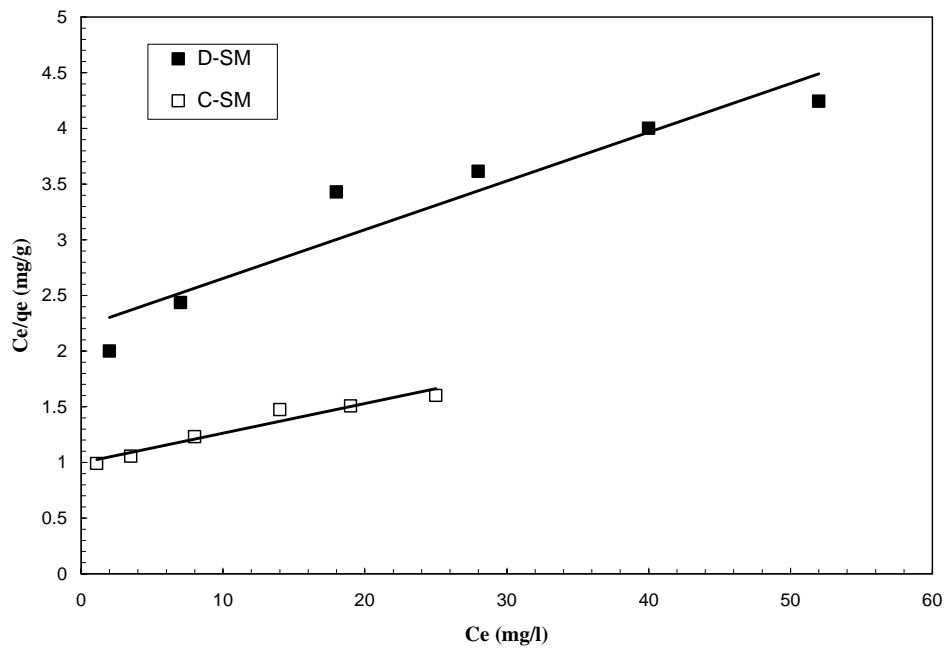


Figure (6): Langmuir isotherms for D-SM and C-SM.

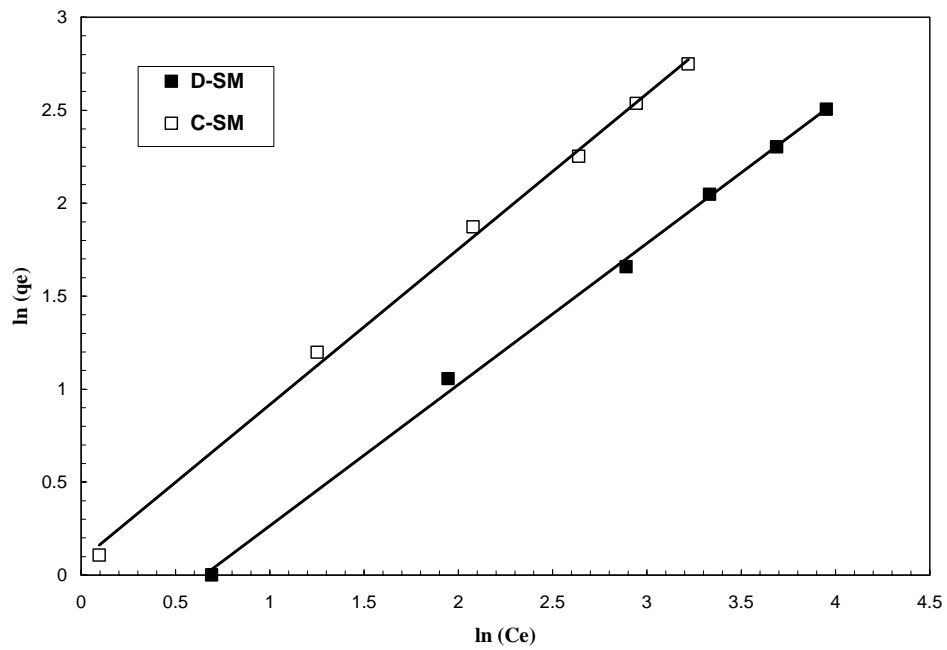


Figure (7): Freundlich isotherms for D-SM and C-SM.

CONCLUSIONS

Modification of sheep manure using citric acid reduced the point of zero charge and increased the cobalt ions uptake significantly due to the increase in the carboxylic functional groups on the surface. At any solution pH, contact time, citric acid concentration or initial cobalt ions concentration, the cobalt ions uptake was found to be higher for **C-SM** compared to that for

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D-SM. Freundlich model fitted the experimental data very well and much better than Langmuir model.

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