

# STUDY OF COBALT ADSORPTION ONTO SALINE SOIL WITH AND WITHOUT BIOSURFACTANTS IN THE AREA OF DERA ALLAH YAR (JHATPAT), BALOCHISTAN

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**ABSTRACT:** *This research paper compares biosurfactant- and biosurfactant-free cobalt adsorption on saline soil and examined biosurfactants including rhamnolipid derivatives, lipids, trehalose, and surfactin. Co adsorption kinetics and isotherms on salty soil were first investigated and the outcomes of each biosurfactant's type/dose in relation to Co adsorption were evaluated. After looking into different adsorption kinetic models, the pseudo-second-order kinetic model was found to be the most in line with the experimental data. Each biosurfactant was tested with and without the addition of Co, and four isotherms were used to regulate the adsorption of Co. Co adsorption on salty soil was studied further to learn how different factors interact with one another. This work will contribute to our understanding of the mechanisms involved in Co adsorption in salty soil and the interactions between Co and cosurfactants throughout the adsorption procedure. The data might also be beneficial for evaluating a more effective strategy for soil remediation.*

**Keywords:** Advance Technology, Salinity, Cobalt Concentration, and Inductively Coupled Plasma.

## INTRODUCTION

Cobalt (Co) occurs naturally in carbonate and igneous rocks on Earth's surface [1-2]. It's used as a fertiliser, but it's also used to make refractory metals, permanent magnets, and even certain colours. Co may be introduced to the environment via both natural and anthropogenic processes, and it does so in a number of different chemical forms. Coal and oil combustion, incinerator use, automobile emissions, and industrial processes like mining and processing cobalt ores all contribute to its release into the environment. Alloys made from Co and other metals are produced by combining them. Alloys are used in the manufacturing of airplanes, grinding wheels, and cutting tools [3] because of their durability. Many research teams have investigated the ecotoxicity of Co using various safety metrics for the natural world. Co has been associated with a number of lung diseases [4], including asthma, hard metal sickness, and diffuse interstitial lung disease. Exposure to Co may lead to serious health problems, such as asthma and pneumonia [5]. Co is an essential trace element, but it may be toxic if Based on information on cobalt there is too much ecotoxicity, and protection requirements for ecosystems were created [6, 7]. Many animal investigations (including ones conducted on mice) demonstrated a significant correlation between the presence of cobalt contamination and radical activation and lung injury [8]. Human exposure to Co-induced carcinogens has been acknowledged as a possibility by the International Agency for Research on Cancer [9]. Companies that produce paints, varnishes, linoleum, and electroplate put their employees at risk of exposure to co [10]. Because of its ecotoxicity and the hazards it poses to the environment, the USEPA [11] has set recommended values for Co.

Adsorption controls soil Co mobility and fate [12]. Soil and acidity impact Co adsorption [13]. pH greatly impacted soil Co sorption in a pH-dependent experiment [14]. When pH neared 9, Co adsorption from an aqueous solution increased [15]. Co removal from clay is difficult because sand and silt enhance metal adsorption. Nonetheless, soil salinity may affect Co adsorption. Adsorption equilibrium data can only be obtained by the careful definition of a solid-liquid adsorption system,

which is why isotherm studies are so important. A high correlation coefficient was found between the equilibrium data for Co adsorption and the Langmuir model, as stated in [16]. The equilibrium relationship between the adsorbate concentration in the solid and liquid phases may be represented by an isotherm. It has been suggested by earlier [12] that the Langmuir and Freundlich models are a suitable fit for the Co sorption. Chon [15] found that the Freundlich equation fits experimental data for Co sorption in soil sorption isotherm. Chen and Lu [14] discovered that Co's adsorption isotherm on montmorillonite soil was linear. The Freundlich model anticipated the experimental results. Guerra and Airoidi [7] fit Co cation, clay, and divalent copper adsorption data using a nonlinear Langmuir isotherm model.

Soil washing is an affordable physiochemical method of thoroughly cleaning the soil, and it is a reliable option for removing metals [17]. For its many uses and low cost, soil washing has been widely implemented in the field. Co extraction can involve a variety of additives [18], including acid solutions, reducing agents, and oxidising agents [19]. In soil cleaning applications, biosurfactants have steadily taken the role of conventional surfactants in recent years. The low toxicity, reusability, and biodegradability of biosurfactants make them promising [20-21]. The elimination rate might be poor when employing it to treat Co in the ground, however. For instance, soil washing with the use of a biosurfactant (specifically, a lipopeptide biosurfactant made of fengycin and surfactin) only successfully removed 35.4% of Co from a polluted soil [22]. A biosurfactant's great potential for adsorption in soil may also make it inapplicable for cleaning the soil. The biosurfactant would add to the chemical load in the environment if it were to adsorb heavily onto soil particles [23-24].

Biosurfactants have been created to speed up the cleaning process of dirt [25, 26]. The advantages of these natural

surfactants include low toxicity, biodegradability, and reusability [27]. A biosurfactant's ability to function as a "bridge" between the liquid and the air contact reduces surface tension. It is easier to recover heavy metals by washing, pumping, or flushing [28] because of greater soil heavy metal mobilisation and increased availability [29]. Aşç *et al.* [29] looked at how much Cd might be recovered by rhamnolipid from kaolin at different biosurfactant concentrations. (0-100 mM). When rhamnolipid concentrations increased, so did Cd recovery rates. According to Wang and Mulligan [30], the recovery of precious metals from mine tailing is improved by adding 0.1 percent rhamnolipid solution [27]).

Interactions between soil particle size, biosurfactant concentration, biosurfactant type, and the initial heavy metal content in the soil are possible. Having to consider the effects of each interaction would complicate our ability to understand the effects of any one of them. Soil with a small particle size (like clay), for example, has a complicated influence on the sorption/desorption of heavy metals in soil [28-29], although this has not been well studied. The four aforementioned characteristics influence soil heavy metal sorption, and the majority of the study done on the topic has focused on their separate effects. As no studies have systematically analysed the factors and their interactions using a mathematically and statistically acceptable method[30]. Modeling and optimization have employed the statistical design for experimental (DOE) method to probe causal connections between operational factors[31]. Adjusting business processes and the functionality of a product is common practise. This mathematical and statistical method expedites experiments when compared to OFAT [32]. One kind of response surface approach [33] is the tried-and-true factorial design, which allows one to investigate interactions between variables using a smaller number of runs. This statistical design trials allow for efficient data retrieval with less experiment runs since components are simultaneously adjusted at their levels. Full factorial experiments investigate not only the impact of numerous variables on outcomes but also the relevance of each variable, as well as the possibility for several factors to interact with one another to generate additional effects [34]. The four factors that impact cobalt adsorption in soil are the particle size of the soil, the concentration of the biosurfactant, the kind of biosurfactant, and the initial concentration of Co, however, no previous study has utilised the DOE method to investigate these relationships.

Soil salinity is only one of several environmental conditions that might affect sorption [35, 36]. It has been proven that higher soil salinity increases heavy metal mobility [37, 38], albeit the extent to which this occurs varies per metal.

## MATERIALS AND METHOD

### 2.1 Soil Characterization

Both natural clay and sand (in equal parts) were used for each trial run. The samples were taken using a clean bucket, a trowel, and a soil sampling tube. Several sites in Dera Alayar have soil borings, or thin slices, collected (Jhatpat) by December 2022. A composite sample of the obtained soil was made, spread out on paper, and left to air dry overnight in a warm setting. In order to conduct the experiment, a single cup was used as a typical sample. Overnight, an oven was set at 105 degrees Celsius, where the dirt was maintained. After this, the dirt was passed through a 1.18-mm-mesh stainless steel sieve (No. 16). The soil was altered by adding NaCl to make it 3 percent saltier. Soil's chemical and physical properties, such its pH, [39]), bulk density [40], and moisture content, were all characterised using industry-standard methods. To evaluate the soil's ability to exchange cations, we used the procedure established by [41]. The results are shown in Table 1.

**Table 1 Nature of the soil's physical makeup**

Clay (~ 0.002 mm)	50
Particle size distribution (%)	50
Sand (~ 1.18 mm)	
Salt (%)	3
Water content (%)	13.79
Bulk density (g/cm <sup>3</sup> )	1.97
pH (soil materials suspended in water)	7.91
pH (soil materials suspended in a 0.01 M calcium chloride solution)	7.68
pH (saline soil (3%) suspended in water)	7.59
pH (saline soil (3%) suspended in a 0.01 M calcium chloride solution)	7.35
CEC (cmol (+) / kg)	135

X-ray fluorescence (XRF) spectrometry was used to conduct a soil analysis and determine which oxides of the principal elements were present. In each experiment, 20 mg of the mixture was employed.

Soil trace element concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer Elan DRC II ICP-MS). Each sand and clay mixture was digested thoroughly before the examination. The data show that the soil used in the study did not contain any detectable levels of Co.

**2.2 Production of Bio-surfactant**

Different biosurfactants created in the lab were used. Each biosurfactant's effect on Co adsorption in soil was assessed. Biosurfactant used in this study, as shown in Table -2.

**Table-2 Oxides elements in soil**

Element oxides	Na <sub>2</sub> O Wt%	MgO Wt%	Al <sub>2</sub> O <sub>3</sub> Wt%	SiO <sub>2</sub> Wt%	P <sub>2</sub> O <sub>5</sub> Wt%	K <sub>2</sub> O Wt%	CaO Wt%
Clay / Sand Mixture	1.42	2.52	12.74	47.98	0.1	2.99	3.04

**2.3 Adsorption of Co in Soil**

Co adsorption onto salty soil was studied under different pH, starting Co content, and time conditions. The number of runs where one component was studied at a time is shown in Table 3.

**2.4 pH effect on adsorption of Co**

The soil was mixed together, dried by air, and then heated for one day at 105°C. In a polypropylene centrifuge tube, each 2.9 g sample of 3 percent salty soil was mixed with a 50 ml solution that had 300 mg/L of Co.

**Table 3 Design of experimental Parameters**

Effect of factor	Number of		Number of		Total number of runs
	levels	Replication	blanks	Replication	
pH	8	3	1	3	27
Time	12	3	12	3	72
Initial Co concentration	6	3	1	3	21

Prior to conducting adsorption studies, samples were adjusted with NaOH solution to a pH range of 3 to 9. FAAS was used. The quantity of Co that was adsorbed by the soil was determined by differences between each Co concentration at the beginning of the experiment and the Co concentration that remained after sorption in the supernatant.

**2.5 Adsorption effect on time and initial Co level**

The reaction time impact and initial Co level on adsorption of Co was examined at room temperature by performing initial content (300mg/l) of Co and saline soil (2.9g) using solution of Co (50ml).equilibration status of different time length was examined. No pH adjustments or soil Co additions were made in any of the blank runs.

**2.6 Biosurfactant-Soil Adsorption**

Co at various level range from 50 to 400 ppm were created in solutions. At two concentrations (1 and 2 CMC), three distinct kinds of biosurfactant products were used. Using

**Table 4**

**Table 4 Number of runs for Co adsorption with biosurfactant**

Biosurfactant	Concentration	Number of		Total number of runs
		levels	Replication	
Surfactin	1 CMC	5	3	15
Surfactin	2 CMC	5	3	15
Trehalose lipids	1 CMC	5	3	15
Trehalose lipids	2 CMC	5	3	15
Rhamnolipid	1 CMC	5	3	15
Rhamnolipid	2 CMC	5	3	15

the runs shown in Table 4 was investigated.

A 50 mL centrifuge tube was filled with 2.9 g of saline soil for each experiment. A biosurfactant product was then added to the tube after the Co solution. A prior pH assessment experiment was used to guide the pH adjustment of the suspensions to the required level. At room temperature, each tube was shaken 200 times per minute in a shaker. According to section 2.3, the adsorption time was chosen based on past research. The adsorption of Co and biosurfactant in the soil were both investigated. The pH was adjusted and no biosurfactant was introduced to the soil in each blank run. Runs were done in three copies in each experimental condition.

**2.7 Biosurfactant Adsorption onto Soil without Existence of Co**

50 mL centrifuge tubes were filled with 2.9 g of salty soil to measure the amount of biosurfactant adsorption. Three distinct kinds of biosurfactants were used (1 and 2CMC level) to suspend the soil (Table 5). Without any biosurfactant, blank solutions included the soil solution.

**Table 5 Number of runs for biosurfactant adsorption without Co**

Biosurfactant	Concentration	Replication	Total number of runs
Surfactin	1 CMC	3	3
Surfactin	2 CMC	3	3
Trehalose lipids	1 CMC	3	3
Trehalose lipids	2 CMC	3	3
Rhamnolipid	1 CMC	3	3
Rhamnolipid	2 CMC	3	3

### 3 RESULTS AND DISCUSSION

Prior research has been done to determine the ideal pH of an aqueous solution to achieve the highest metal ion adsorption onto the adsorbent, including Cu, Cd, and Zn [44–45]. To evaluate the effect of pH on Co adsorption, the pH value of Co solutions was changed in this research from 3 to 9. The results showed that at a constant starting concentration of Co (300 mg/L) in all solutions, soil adsorption of Co increased with increasing pH. (Fig.1). When the pH was lowered to 3.0, 77 mg/L more Co was adsorbed. In further tests, a pH of 9 was used because it aided in achieving the greatest outcome.

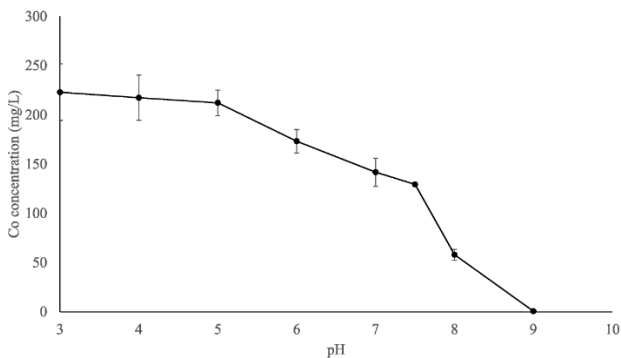


Figure 1 influence of pH on adsorption of Co

Within 120 minutes, the amount of CO absorbed by the soil dramatically increased (Fig.2). As a result of the metal ions occupying the available adsorption sites, the rate of Co absorption gradually decreased. The outcome is in line with previous research by [59]. The greatest amount of Co was adsorbed after 420 minutes, and the concentration of Co in the solid phase stabilised. Thus, the adsorption duration of 420 minutes was chosen for the further trials. Fig. 3 shows how the initial concentration of Co in the solution affects the ability of Co to adsorb onto soil. As the original Co concentration in the solution was raised, more Co ions were adsorbed onto the soil at equilibrium. Experiments were carried out without Co to gauge each kind of bio-surfactant's ability to adsorb substances upon application. One and two CMCs were Chosen of each kind of biosurfactant as the starting points prior to adsorption. Surface tension for Surfactin remained almost unaltered during adsorption treatment, indicating that Surfactin has a very low capability for adsorption in a soil-water system. Due to its limited adsorption capability, the discovery revealed that Surfactin would be an excellent option for soil cleaning treatment. Trehalose lipids' surface tension, however, dramatically rose following adsorption. A biosurfactant's strong capacity for sorption would result in a low level of availability for metal complexation [46].

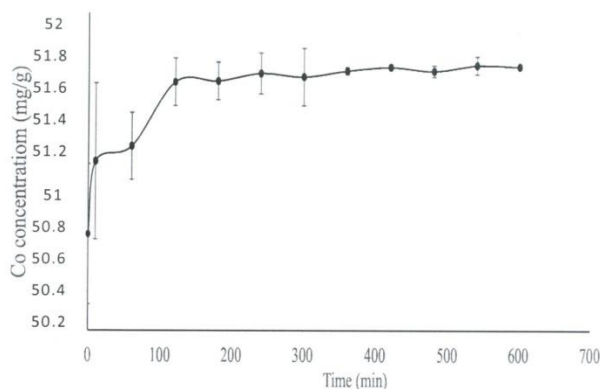


Figure 2 Adsorption of Co by contact time

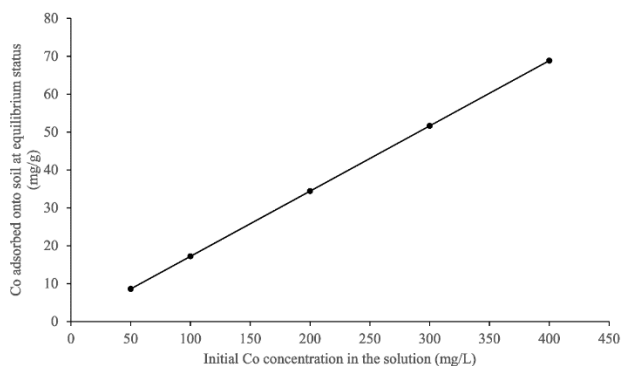
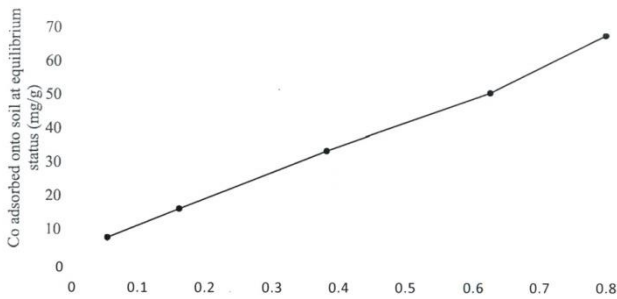


Figure 3 Influence of initial level on adsorption Co

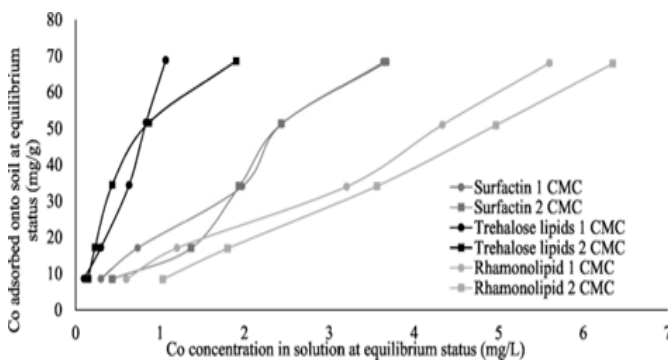
Table 6 Adsorption of bio-surfactant

Initial biosurfactant concentration	Surfactin ST	Trehalose lipid ST	Rhamnolipid ST
0 CMC (Blank)	72	72	72
1CMC	32.7	70	63.4
2CMC	32.5	69.5	57.6

Additionally, when biosurfactants with high adsorption capacities were used as soil washing agents, resulted from their high adsorption capacity. Surfactant in the soil may have an impact on Co adsorption. The pattern of Co adsorption alters when different amounts of each biosurfactant are added to soil. The outcomes of the control trials are shown in Fig. 4. According to Fig. 5, Co was added to soil together with 1&2 CMC biosurfactant. Concentration of equilibrium in solution was increase by addition of 2CMS biosurfactant. There was inverse in trend when biosurfactant level at high level (2CMS) combined with lower Co level (50 and 100ppm).

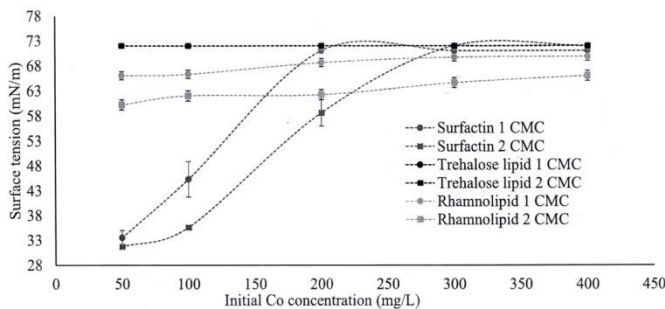


**Figure 4 Soil co-adsorption without the use of a biosurfactant**



**Figure- 5 Co-adsorption of biosurfactant by soil after application of 1 CMC and 2 CMC**

In Fig. 6, A correlation is seen between the initial concentration of Co and the final surface tension of each solution. With 1 CMC biosurfactant concentration, surface tensions are somewhat higher than at 2 CMC biosurfactant concentration. The surface tension varies between 60 and 70 (mN/m). The rhamnolipid has remarkable soil adsorption capacity (Table 6).

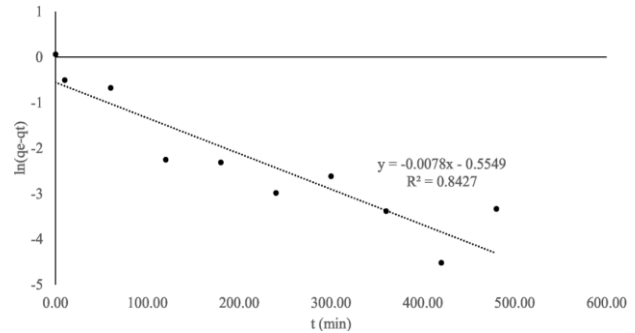


**Figure-6. Adsorption induced changes in the surface tension at 1CMC and 2CMC of Bio-surfactant**

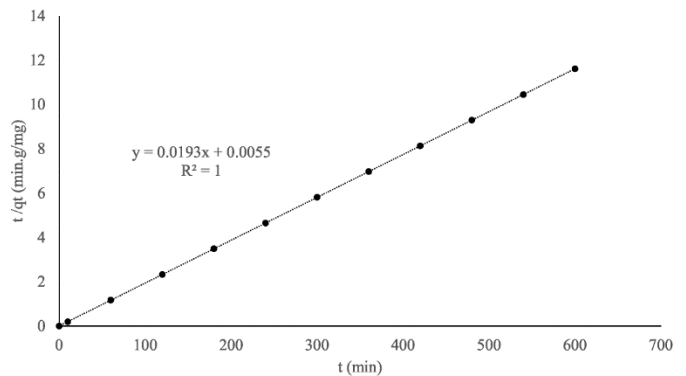
Adsorption kinetics describes the rate at which Co is taken up by the soil particles. Using the pseudo-first-order kinetic model, the experimental results are shown in Fig. 7. The values of  $k_1$  and  $q_e$  are found using the slope. The

computed slope of the model illustrates how well absorbed Co. The results showed that the  $R^2$  value was 0.8427 and the  $k_1$  value was 0.0078.

The values of  $q_e$  and  $k_2$  in the pseudo-second-order model were determined using the intercept and slope of the linear plot of  $t/q_t$  vs  $t$ . (Fig. 8). The calculated value of  $k_2$  is 0.0677. The coefficient of determination demonstrates the validity of the pseudo-second-order theory.



**Figure 7 Adsorption kinetics of Co onto soil at a pseudo-first-order surface**



**Figure 8 Adsorption kinetics of cobalt onto soil at a pseudo-second-order rate**

In Fig. 9, the terms  $1/\beta \ln(\alpha\beta)$  and  $1/\beta$  for Elovich kinetic model are calculated from the intercept and slope of the linear plot of  $qt$  versus  $\ln(t)$ . The value of the correlation coefficient ( $R^2$ ) of the Elovich model was 0.8741.

During a batch process, the adsorption of a solute from the bulk of the solution on the solid surface may be the slowest stage (rate-limiting step) due to the formation of a boundary layer (film) or intra-particle (pore) diffusion. Increasing the value of intercept ( $I$ ) increases the boundary layer's effect. If the plot of  $qt$  vs  $t^{0.5}$  becomes a straight line that originates at and ends at the origin, this may indicate that intra-particle diffusion is involved in the rate-limiting phase [47]. The rate-limiting step is determined by diffusion in the boundary layer, as shown by the non-linearity of the curve in Fig. 10. The two or more steps involved in the soil's adsorption of Co are shown by the nonlinearity of the plot.[48].

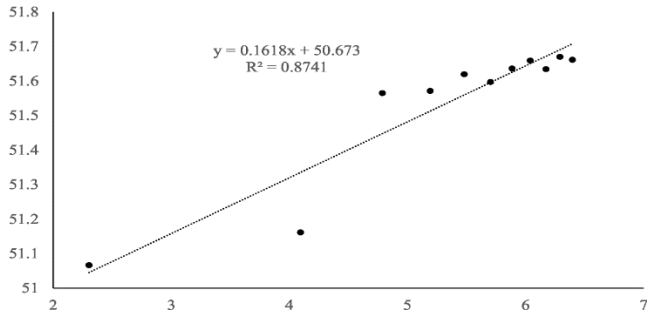


Figure 9 Kinetics of Co adsorption in the according to the Elovich equation

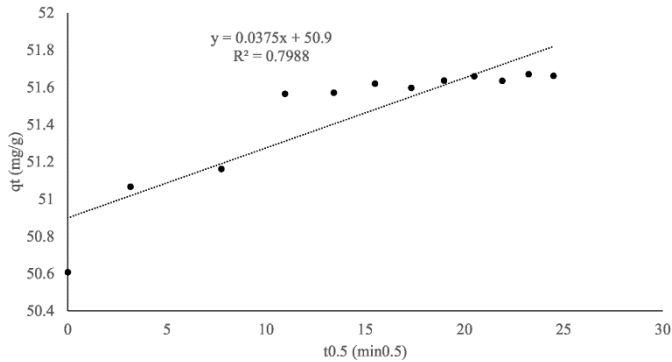


Figure 10 The kinetics of Co adsorption onto soil through intra-particle diffusion

Table 7. Estimating the rate of soil Co adsorption using kinetic models

Kinetic model	Equation	R <sub>s</sub>	RMSE
pseudo-first-order	$\ln(q_t - q_e) = -0.5549 - 0.0078t$	0.8427	0.6134
pseudo-second-order	$t/q = 0.0055 + 0.0193t$	1	0.0035
Elovich	$q_t = 50.673 + 0.1618 \ln(t)$	0.8741	0.0786
Intra-particle diffusion	$q_t = 0.0375 t^{0.5} + 50.9$	0.7988	0.1569

The Redlich-Peterson isotherm [49] is derived from the Langmuir and Freundlich equations. Monolayer adsorption occurs on a homogeneous adsorbent surface with a limited number of identical sites, as described by the Langmuir isotherm[50]. The strength of the sorbent's adsorption on the particles may be measured with the use of the Freundlich isotherm. The Temkin isotherm, one of the earliest, is similar to the Freundlich model. A concentration-dependent increase in electrostatic contact between the dipoles at the interface may be responsible for the Temkin isotherm [51]. Adsorption sites with inherently dispersed adsorption energies are another possible explanation. Several isotherm models are shown in Figures 11–17. Using the adsorption method pays off if n is bigger than 1 [52]. The Freundlich model's n value (1.169) depicted a successful adsorption process in the absence of biosurfactant.

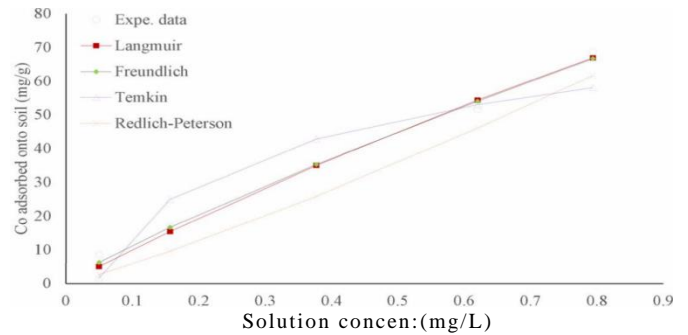


Figure 11 Sorption isotherm comparison of cobalt (Co) onto soil in the absence of biosurfactant.

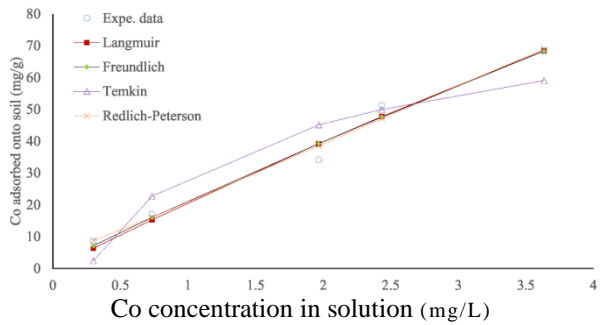


Figure 12 Sorption isotherms for Co onto soil using 1 CMC surfactin: a comparison

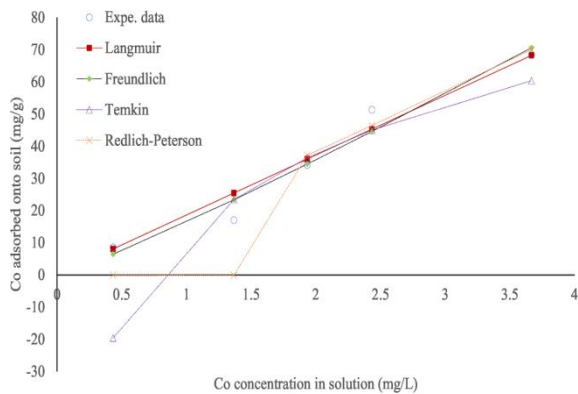
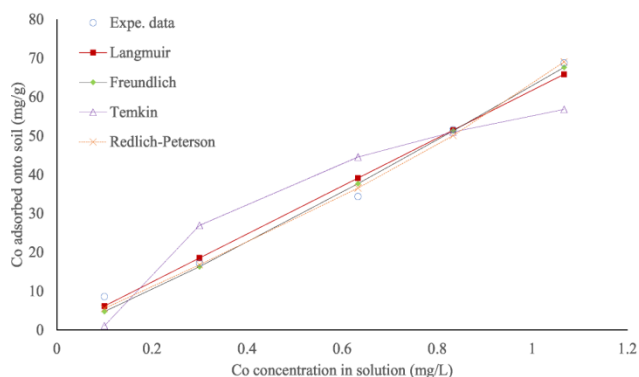
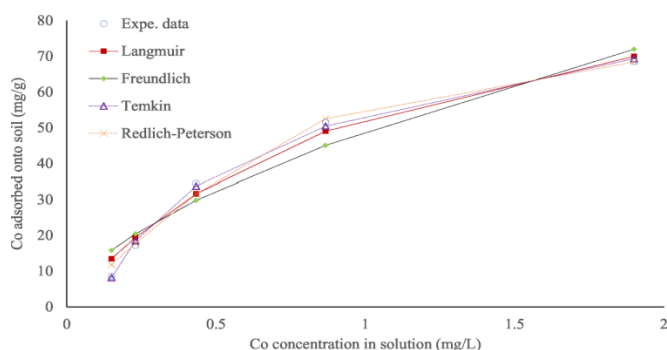


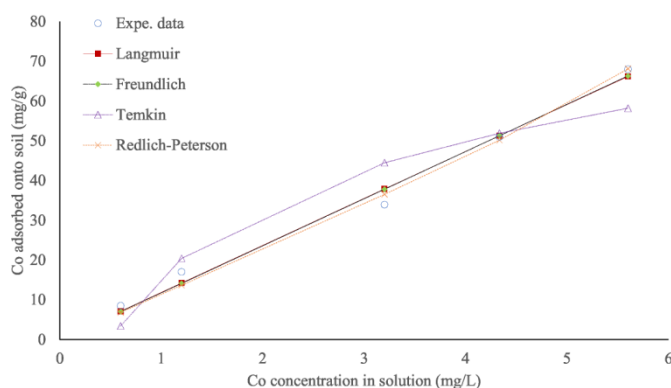
Figure 13 The effect of 2 CMC surfactin on the sorption isotherms of cobalt onto soil was compared.



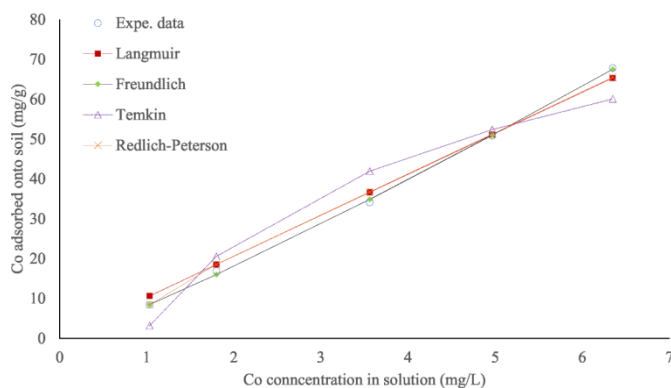
**Figure 14** Trehalose lipids sorb cobalt onto soil at 1 molar concentration: a comparison.



**Figure 15** Sorption isotherm comparisons of cobalt onto soil using two different concentrations of trehalose lipids from 2 CMC



**Figure 16** Comparing soil Co sorption isotherms with 1 CMC rhamnolipid.



**Figure 17** Comparing soil Co sorption isotherms with 2 CMC rhamnolipid

**Table 8** Isotherm parameters for various adsorption isotherms for the adsorption of Co onto the soil

Isotherms	Parameters	No	1 CMC	2 CMC	1 CMC	2 CMC	1 CMC	2 CMC
		Biosurfactant	Surfactin	Surfactin	Trehalose lipids	Trehalose	Rhamnolipid	Rhamnolipid
Langmuir	$Q_e$ (mg/g)	381.5	572.3	$3.7 \times 10^4$	$3.753 \times 10^4$	109.1	$1.939 \times 10^4$	39150
	$K_i$ (L/mg)	0.2683	0.03741	0.0005037	0.001648	0.9424	0.0006117	0.0002633
Freundlich	$K_x$ (L/g)	81.37	21.27	16.45	62.91	49.11	11.76	8.184
	$(mg/g)^{1/n}$	1.169	1.105	0.8922	0.8916	1.677	0.996	0.8759
Temkin	$b_T$	1.406	0.0639	0.01201	0.3852	0.1495	3.488	0.04999
	$A_T$ (L/g)	21.68	3.713	1.368	10.48	9.375	1.915	1.079
Redlich-Peterson	$K_s$ (L/g)	33.75	18.24	19.08	55.74	80	11.37	10.32
	$g$	-0.5852	-0.1262	$-3.101 \times 10^6$	-0.117	0.4081	$-9.283 \times 10^{-4}$	1.249

**Table 9** Isotherm error deviation data related to the adsorption of Co onto the soil

Isotherms	functions	No	1 CMC	2 CMC	1 CMC	2 CMC	1 CMC	2 CMC
		biosurfactant	Surfactin	Surfactin	Trehalose	Trehalose	Rhamnolipid	Rhamnolipid
Langmuir	R2	0.9886	0.9806	0.9536	0.9839	0.9811	0.9879	0.9914
	Adjusted	0.9848	0.9742	0.9382	0.9785	0.9749	0.9838	0.9885
	RMSE	3.039	3.93	6.086	3.609	3.893	3.096	2.605
Freundlich	R2	0.9931	0.9822	0.9603	0.9884	0.9427	0.9879	0.9993
	Adjusted	0.9908	0.9763	0.9471	0.9845	0.9236	0.9839	0.9991
	RMSE	2.368	3.767	5.63	3.064	6.786	3.085	0.7281
Temkin	R2	0.8774	0.8839	0.6079	0.8353	0.9983	0.8964	0.9301
	Adjusted	0.5095	0.5358	-0.5686	0.3414	0.9931	0.5857	0.7202
	RMSE	17.25	16.66	30.66	19.98	2.038	15.66	12.85
Redlich-Peterson	R2	0.9931	0.984	0.8326	0.9931	0.9918	0.9908	0.9936
	Adjusted	0.9861	0.9679	0.6653	0.9863	0.9835	0.9817	0.9871
	RMSE	2.9	4.379	14.16	2.886	3.149	3.293	2.756

## CONCLUSION

Co adsorption in salty soil was investigated, both with and without the use of a biosurfactant. Surfactin, lipids derived from trehalose, and rhamnolipid derivatives were all utilised as biosurfactants. Yet, at high Co concentrations, the residual Co is unaffected by the concentration of the biosurfactant. The soil was found to have weakly sorbed Surfactin.

The adsorption rate is affected by the boundary layer diffusion, as predicted by the intraparticle diffusion model.

The isotherm study employed the Langmuir, Freundlich, Temkin, and Redlich-Peterson adsorption models. It was discovered that the adsorption isotherm may be well described by the Freundlich model even in the absence of a biosurfactant. Surfactin's ability to increase adsorption in a system may be best shown by using the Redlich-Peterson or Freundlich model with either 1 or 2 critical micelle concentrations.

In saline soil with little permeability, Co adsorbs well. Co adsorption kinetics and isotherms may be used to study related processes and biosurfactant effects on soil Co destiny to assist pick effective soil remediation approaches.

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