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Soil Adsorption of Heavy Metals to Protect Groundwater Near Refinery Wastewater Discharge Points

Hamid A. Al-Falahi[1*], Ferdous A. Jabir[2], Muthanna H. Al-Dahhan[3]

[1] Department of Chemical and Petrochemical Engineering, University of Anbar, Ramadi 31001, Iraq
[2] Biochemistry Branch, College of Medicine, University of Al-Qadisiyah, Al-Qadisiyah 54004, Iraq
[3] Linda and Bipin Doshi Department of Chemical and Biochemical Engineering, College of Engineering, Missouri University of Science and Technology, Rolla 65401, USA

Corresponding Author Email: h.alfalahi@uoaanbar.edu.iq

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ABSTRACT

This study presents a strategy to manage the discharge of wastewater, which is either partially treated or untreated, to safeguard the groundwater reserves in the region. A case study involving Ad Diwaniyah refinery wastewater disposal into an adjacent desert was utilized to evaluate the influence of soil adsorption on the attenuation of Pb, Cu, and Cd ion concentrations. Investigation of competitive adsorption of heavy metal ions (Pb^{2+}, Cu^{2+}, and Cd^{2+}) in Dolomite-Limestone soil was conducted through batch and column methods. The adsorption behavior of the bivalent metal cations was observed to be pH-dependent. However, the competitive extraction of the three heavy metals exhibited low sensitivity to pH variations. Isotherms for Pb, Cu, and Cd ions on Dolomitic Limestone soil were determined and found to align satisfactorily with both Freundlich and Langmuir models. Competitive adsorption was recognized as a cost-effective and environmentally friendly method for the elimination of toxic heavy metals from wastewater, even at minimal concentrations. The column test method revealed the adsorption capacity of Dolomite-Limestone soil to be (Pb: 1.5, Cu: 1.18, Cd: 0.9) mg/g. The affinity of the metal ions to the Dolomite-Limestone soil was ordered as Pb > Cu > Cd. Breakthrough curves of the heavy metals, obtained from soil column tests, were used to estimate the retention time for the Dolomitic Limestone to reach saturation. The findings suggest a wastewater management strategy that involves changing the discharge point every 17 months to a new location 90 m from the previous discharge point. This paper offers a feasible solution for managing wastewater discharge and protecting groundwater reserves, especially in areas with heavy metal contamination.

1. INTRODUCTION

Globally, about 40% of refinery wastewater, a complex mixture containing organic and inorganic pollutants such as oils, phenols, dissolved solids, polyaromatic hydrocarbons, and heavy metals, is only partially treated before being discharged into the environment [1, 2]. It's a necessary work to treat such wastewater before release to alleviate soil and water pollution. Some research reported the use of Emulsion Liquid Membrane (ELM) in extracting Pb2+, Cu2+, and Cd2+ ions from saline refinery wastewater, and the efficiency reached 92%, 88%, and 76% respectively [3]. Although the ELM technique has been proved efficient, for refineries and oil fields in remote places often discharge wastewater in lagoons directly without any treatment.

For soil types with high permeability, such as rocks and gravel, a high seepage rate is allowed to promote migrating pollutant discharge points to groundwater reservoirs or other water reserves [4].

Common wastewater treatment methods usually produce large amounts of sludge and they require skilled workers, and this situation urges the oil industry to search for alternative methods [5]. Adsorption technology has advantages in simplicity, cost, and adaptability, so it is a good alternative scheme [6, 7].

Heavy metals, due to their non-degradable and persistent nature, pose a significant environmental risk, even at low concentrations [8]. The mobility of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions is impeded by reactions that cause these metals to be adsorbed or retained in the soil. However, upon reaching saturation, substantial amounts of metal compounds migrate into the groundwater [9, 10].

Constructed wetlands, comprising shallow ponds layered with sand, rocks, and soil and planted with aquatic flora, have emerged as a potential solution for wastewater treatment in oil fields and remote refinery industries [11-14]. However, not all facilities are equipped with such systems, leading to the discharge of untreated heavy metal compounds into the environment.

Taking the Ad Diwaniyah refinery in Ash Shinafiyah of Iraq as an example, the plant discharges 150 m3 primitively treated wastewater into the nearby desert every day, according to report, the heavy metal concentration is increasing year by year [15, 16].

Under the conditions of limited resources, inability to build zero-pollutant discharge treatment plants, and unsound or unenforced regulations, groundwater protection is a key issue. For refineries located in remote areas that have similar conditions, they can make use of the adsorption capacity of local soil to alleviate the migration of heavy metal pollution to groundwater. In order to set strategies and management plans for wastewater discharge, it's a necessary work to assess the adsorption capacity of the soil, so this paper attempts to solve these matters by evaluating the adsorption capability and capacity of the soil around the Ad Diwaniyah refinery.

For the purpose of deciding soil adsorption isotherms and capability, batch and column adsorption tests had been performed. Quantifying these parameters allows the formulation of a strategy and management plan for wastewater discharge, ensuring the protection of the regional groundwater. The case study of Ad Diwaniyah refinery is utilized to establish a strategy and protocol to safeguard the groundwater reservoir from heavy metal compounds present in the refinery's wastewater.

It is acknowledged that the transfer of heavy metal compounds from wastewater to soil is not an ideal long-term solution. The ultimate objective should always be comprehensive wastewater treatment to protect the environment. However, under current circumstances, the immediate priority is to protect the regional groundwater reservoir, a vital resource for human, agricultural, and industrial use in an area experiencing significant expansion.

2. AREA OF STUDY

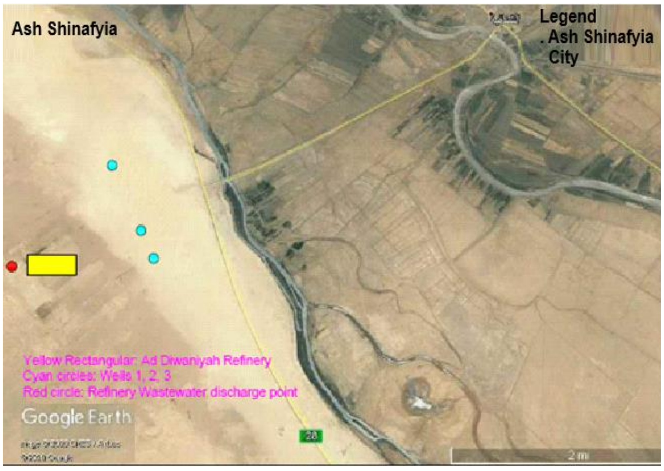

Figure 1. Area of study

As mentioned above, the area of the study is the area of the Ad Diwaniyah refinery, which is located 65 km to the southwest of Ad Diwaniyah city at the eastern border of the Ash Shinafiyah desert, Iraq. Its latitude is 31 32 35 N, and its longitude is 44 34 20 E. The area of study is a small part of the Euphrates formation, as shown in Figure 1. The geological structure of the area of study is mainly Dolomite and Limestone [17]. The aquifer near the Ad Diwaniyah refinery has a recharge zone located far west, while its discharge is located near the Euphrates riverbank to the east of the wells in the region where its groundwater was analyzed. The groundwater hydraulic gradient runs from west to east according to rainfall, which is considered one of the most important sources of groundwater recharge, which in turn varies in terms of its levels, depths, quality, and quality according to the sources of its recharge, its layer system, and its hydraulic characteristics. In order to evaluate the hydraulic gradient of groundwater aquifers in Iraq, the study relied on hydrogeological and hydrochemical data from the database, hydrogeological maps available at different scales, and geological and topographical maps of Iraq.

The point of discharge of the Ad Diwaniyah refinery wastewater (shown as a red circle in Figure1) is located to the west of the refinery site (shown in yellow rectangular), making the issue of protecting the groundwater even more essential and critical. Three wells 60 m deep each (shown in cyan color circles in Figure 1) were considered in this study for groundwater characterization, which is located east of the refinery discharge point, as mentioned earlier. All rocks and soil used for the experimental investigations and groundwater samples were collected from this area during the dry and wet seasons of the year. Dry season in Iraq runs between June and October, while wet season in Iraq runs between December and March.

3. MATERIALS AND EXPERIMENTAL METHODS

3.1 Wastewater characterization

Table 1. Composition of the refinery wastewater

Parameter	Value
pH	7.8
TDS*	3778 mg/l
PO_4	1.3 mg/l
Cl^- mg/l	314 mg/l
SO_4^{-2} mg/l	280 mg/l
$N\text{-}NO_3$ mg/l	30 mg/l
$N\text{-}NO_2$ mg/l	2.1 mg/l
Turbidity	25.3 NTU
Oil	1.4 mg/l
BOD mg/l	60 mg/l
COD mg/l	62.4 mg/l
Phenol mg/l	0.05 mg/l
DO	4.1 mg/l
Pb^{2+}	8.7 mg/l
Cu^{2+}	17.7 mg/l
Cd^{2+}	15.9 mg/l

The refinery wastewater comes from two sources: cracking units' wastewater and Reverse Osmosis (RO) unit wastewater, and the composition of the refinery wastewater is shown in Table 1. Both wastewaters are mixed and decanted in three settling horizontal columns to separate oil from it. Then, mechanical and chemical treatments are carried out to separate floatable matter and adjust its pH before it is biologically treated. Aerobic biological treatment is carried out to digest oil and phenol, and then clarified water is pumped as wastewater outside the site of the daily samples of the refinery wastewater is brought to the refinery laboratory for pH, Total Dissolved Solids (TDS), PO_4^{3-}, SO_4^{2-}, NO_3^-, NO_2^{2-}, Cl^-, turbidity, Phenol, Oil, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Dissolved Oxygen (DO) tests. No heavy metals tests for measuring their concentration are carried out at the refinery laboratory. However, for the present study, samples were taken to the laboratory of the University of Al-Qadisiyah to determine Pb^{2+}, Cu^{2+}, and Cd^{2+} ions concentrations using Atomic Absorption Spectrophotometer (AAS). The reason for choosing lead, copper, and cadmium metal ions is because they are primarily present in Dolomite and Limestone soils, which requires evaluating the ability of that soil to adsorb those metals and their affinity.

3.2 Adsorbent

The soil samples were collected from the area of study near the discharge point of the Ad Diwaniyah refinery wastewater. The samples of the soil were air-dried, crushed, and sieved through mesh No. 16 (1.2 mm sieve). The soil is classified as Dolomitic Limestone, which is a mixture of Dolomite ($CaMg(CO_3)_2$) and Limestone ($Ca(CO_3)$).

3.3 Soil sorption isotherms

Five replicated batch experiments were carried out at pH 6.5 to 7.0 to obtain competitive sorption isotherms for Pb^{2+}, Cu^{2+}, and Cd^{2+} ions which will be used to quantify the adsorption equilibrium capacity and the amounts of heavy metals adsorbed by the soil needed to establish the proper strategy and protocol for protecting the groundwater from partially and no treated wastewater. Different initial concentrations of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions were mixed with 1 gm of soil for each polyethylene test tube and agitated in a rotary shaker at 150 rpm speed for 4, 8, 12, and 16 hours to determine equilibrium adsorption capacity and equilibrium time. Then soils were percolated from the heavy metals' solutions using a 0.45 µm filter. The concentrations of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions in the diluted solutions were determined using Atomic Absorption Spectrophotometer (AA-7000 Shimadzu) with the furnace method.

To determine the soil adsorption Isotherms, Langmuir and Freundlich models were assessed to describe the competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on the Dolomite-Limestone soil excavated from the area of study. The parameters of both Langmuir and Freundlich models were calculated from the respective curves fitted to the experimental data. The Langmuir method assumes that adsorption of the metal ions occurs uniformly on homogeneous surfaces with no interactions between adsorbed molecules. The Langmuir Isotherm may be represented by the following equation.

$$q_e = q_m \frac{k_L Ce}{1 + k_L C_e} \qquad (1)$$

where, q_e: Equilibrium adsorption capacity; is the number of heavy metal ions adsorbed per unit mass of adsorbent (mg/g), q_m: Maximum adsorption capacity (mg/g), k_L: Langmuir model constant (L/mg), C_e: Equilibrium metal ions concentration (mg/L).

The separation factor (R_L), which indicates the favorability of the sorption process, is defined by the following equation.

$$R_L = \frac{1}{1 + k_L C_o} \qquad (2)$$

where, C_o: initial concentration of metal ions (mg/L).

For $R_L > 1$, unfavorable sorption, $0 < R_L < 1$, favorable sorption, $R_L = 0$, irreversible sorption.

The amounts of heavy metals adsorbed by the soil (q) can be calculated from the following equation.

$$q = \frac{(C_o - C_e)V_{sol}}{M_s.1000} \qquad (3)$$

where, V_{sol}: Volume of solution (cm^3), M_s: Mass of soil (g), C_e: Equilibrium concentration.

For reversible and non-ideal sorption processes, Freundlich isotherm is applied and represented by the following equation:

$$q_e = k_F C_e^{(-nF)} \qquad (4)$$

where, k_F: Freundlich constant (mg/g), $1/n_F$: Adsorption intensity (dimensionless).

For $n_F > 1$, favorable adsorption, $n_F < 1$, unfavorable adsorption, $n_F = 1$, linear adsorption.

The removal efficiencies of the metal's ions (Pb, Cu, and Cd) were calculated as per Eq. (5).

$$Re = \frac{c_o - c_i}{c_o} \times 100 \qquad (5)$$

where, C_o: initial concentration, C_i: the concentration at any time.

3.4 Soil column test

In order to represent the conditions of the soil sorption for assessing the soil capacity, column tests were performed to determine the adsorption and equilibrium adsorption capacity. The column was a Plexiglas tube of 6 cm inner diameter and 170 cm height, as shown in Figure 2. It was equipped with a perforated disc at the bottom of the column to retain soil particles (soil bed of 35 cm height) and allows the solution to flow out from the bottom. The arrangement consists of a peristaltic pump, rotameter, adsorption column, solution supply tank 1, outlet solution reservoir tank 2, and pipes and connections. The column is filled with the polluted groundwater by pumping it from supply tank 1 by the peristaltic pump. The infiltrated solutions out of the perforated disc at the bottom of the adsorption column were collected in predefined intervals in the outlet solution reservoir tank 2. Then, the collected solutions were taken for Atomic Absorption Spectroscopy (AAS) analysis to determine the concentrations of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions that remained in the seeped solutions. As the wastewater seeps downward, adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions take place as a function of adsorbent-adsorbate interaction, the solution flow rate, contact time, packed bed permeability, heavy metal ions concentrations, and temperature.

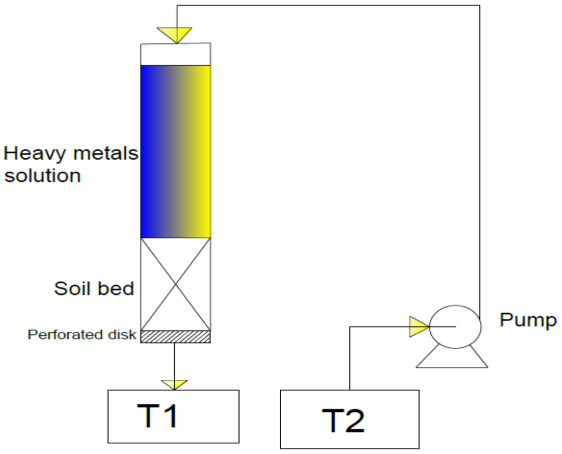

Figure 2. Schematic diagram of the column test arrangement
T1: solution supply tank, T2: outlet solution reservoir

4. RESULTS AND DISCUSSION

4.1 Adsorption isotherms

Table 2 summarizes the parameters of the Langmuir and Freundlich models. The Table 2 clearly shows that both Langmuir and Freundlich models fit the experimental data ($R^2 > 0.95$) except the Freundlich representation of Cd^{2+} ions sorption ($R^2 = 0.88$). Therefore, the Langmuir model represents the competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions despite the heterogeneity of the surfaces of Dolomite-Limestone soil due to the many ionic species of the system. Table 1 also shows the values of the favorability factor (R_L) obtained from Eq. (3) using the Langmuir model constant range between zero and one. Hence, the adsorbent favors all the metal ions that exist in the solution. The selectivity sequence of the metal ions of the system takes the order Pb > Cu > Cd. The adsorption capacities of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions expressed as q (mg/g) were highly dependent on initial concentrations of the metal ions (Pb^{2+}: 8.7 mg/L, Cu^{2+}: 17.7 mg/L, Cd^{2+}: 15.9 mg/L). The obtained results agree with other researchers' observations indicating that Pb^{2+} strongly competes with Cu^{2+} and Cd^{2+} ions. This can be attributed to the affinity of Pb^{2+} ions to form $PbCO_3$ in alkaline solutions (pH > 7.8).

Table 2. Fitting parameters of Dolomite-Limestone soil sorption isotherm models to Pb^{2+}, Cu^{2+}, and Cd^{2+} ions

Metal Ions	Langmuir Model			Freundlich Model			R_L (Dimensionless)	q (mg/g)
	q_m (mg/gm)	k_L (L/mg)	R^2	k_F (mg/gm)	n_F (Dimensionless)	R^2		
Pb^{2+}	0.128	0.299	0.995	0.034	2.08	0.996	0.277	0.375
Cu^{2+}	0.317	0.038	0.998	0.037	2.26	0.991	0.594	0.74
Cd^{+}	0.384	0.024	0.988	0.077	3.652	0.881	0.72	0.64

4.2 Effect of the contact time

The removal efficiencies of the Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from the groundwater were plotted as a function of time, as shown in Figure 3. Every 5 minutes, a sample from the outlet collecting reservoir was taken to measure the remaining concentrations of the metal ions using the AAS.

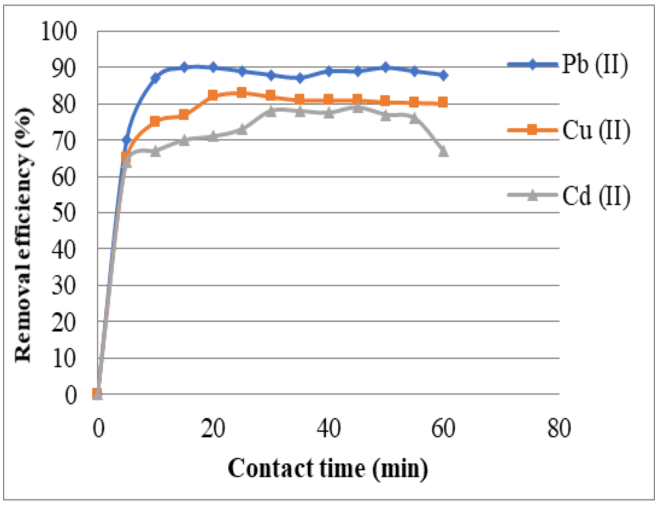

Figure 3. Effect of contact time on the competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on dolomitic limestone soil (Pb^{2+}: 8.7 mg/L, Cu^{2+}: 17.7 mg/L, Cd^{2+}: 15.9 mg/L)

Figure 3 shows that Pb^{2+} ions exhibit the highest removal efficiency among Cu^{2+} and Cd^{2+} ions reflecting the higher selectivity of the three metal ions by the adsorbent. However, Cd^{2+} adsorbed on the dolomitic limestone soil started to desorb at a time of 45 minutes, indicating its weakness in binding to the adsorbent in comparison to other metal ions. The metal ions tend to be adsorbed very fast at the beginning period of adsorption (10-15 minutes) due to the large number of active sites of the soil particles. After 20 minutes, the curves of the removal efficiencies tend to flatten to indicate that the soil has become saturated. The relatively high removal efficiencies indicate that dolomitic limestone soil can be used to remove the metal ions in the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The single metal ions show higher adsorption than multi-metal ions. Therefore, the removal efficiencies of the Pb^{2+}, Cu^{2+}, and Cd^{2+} ions shown in Figure 3 represent the multi-metal adsorption, and higher values of removal efficiencies are expected if single metal ions were individually adsorbed on the dolomitic limestone soil.

4.3 Soil column test and breakthrough curves

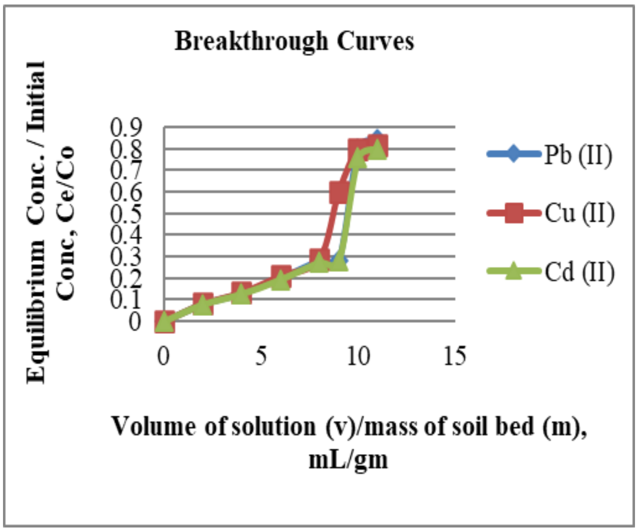

Figure 4. Breakthrough curves of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions adsorbed on a Dolomitic Limestone soil (C_{Pb}: 8.7 mg/L, C_{Cu}: 17.7 mg/L, C_{Cd}: 15.9 mg/L, column L/D = 28.33, pH: 7.8)

The breakthrough curve for each studied heavy metal (Pb, Cu, and Cd) is important to quantify how long it takes to get the soil saturated in order to estimate the equivalent height of the soil to reach saturation at the discharged wastewater point of the studied Ad Diwaniyah refinery surrounding area. This can be demonstrated in Figure 4 by plotting Ce/Co against the ratio of the collected solution volume (v) at specific intervals of time to the soil mass (m) expressed in (mL/g). The collected solution volume depends on the values of the main parameters that affect the residence time, which is the height of the soil bed in the column, the porosity of the soil, and the solution height above the soil bed. The soil column experiments are usually carried out under controlled conditions.

Figure 4 shows the variation of the heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) concentrations ratios (C_e/C_o) with respect to the collected volume of the solution (v) divided by the mass of the soil bed (m). The breakthrough curves of the Pb^{2+}, Cu^{2+}, and Cd^{2+} for the Dolomitic Limestone soil are depicted in Figure 4. The Cu^{2+} ions breakthrough curve shows an earlier response (breakthrough point) than the Pb^{2+} and Cd^{2+} ions. The initial phase of the breakthrough curves indicates the relatively long time needed to get the soil saturated. This may be attributed to the highly active sites available for heavy metals adsorption and the specific adsorption (less reversible adsorption type) of the Dolomitic Limestone soil. The breakthrough points of the Pb^{2+}, Cu^{2+}, and Cd^{2+} solution on the Dolomitic Limestone soil were found to be at v/m of 9 mL/g. The obtained ratio was utilized to find the equivalent height of the discharged wastewater at the point of discharge of the Ad Diwaniyah refinery that causes the soil to be saturated, as discussed below.

4.4 Estimation of the retention time that is needed for the dolomitic limestone soil to reach saturation

Assuming homogeneous field soil and water load distribution along the passageway of the seeped wastewater containing Pb^{2+}, Cu^{2+}, and Cd^{2+} ions, the mean retention time of the heavy metals can be estimated as:

We have a breakthrough point from Figure 3:

$$\frac{V}{m} = \frac{1}{1000} \times 9(kg/m^3) = \frac{Ah_l}{Ah_s\rho_s} = \frac{h_l}{h_s\rho_s}$$

Therefore; $h_l = 0.009 h_s \rho_s$.

where, h_l: equivalent liquid height (m), h_s: soil height from the top of the land to the aquifer = 94 m for the case of the Ad Diwaniyah refinery discharge point, ρ_s: bulk density of the soil = 2400 kg/m^3 for the Dolomitic Limestone soil, A: cross-sectional area (m^2).

If we substitute for h_s and ρ_s to calculate the equivalent liquid height, $h_l = 0.009 h_s \rho_s = 0.009 x 94 x 2400 = 2038.4$ m. And we also have the ratio ($\frac{h}{d} = 28.33$) from the soil column test (h=170 cm, d=6 cm), therefore; if we apply the same ratio for the field soil, we obtain 72 m diameter of the passage of the seeped wastewater towards the groundwater aquifer.

Then, the volume of the wastewater that wets the soil of the passage = $\varepsilon . \frac{\pi}{4} d_p^2 h_s$ (m^3).

where, ε: porosity of wet Dolomitic Limestone soil (0.15 – 0.25) [18].

Assuming ε: 0.2, then $V = 0.2 \times 3.14/4 \times 72^2 \times 94 = 76505$ m^3

Therefore, the time of retention:

$$(t) = \frac{V}{v} = \frac{76505.472}{150} = 510 \text{ days} = 17 \text{ months}$$

If we take a 10% safety factor, the time of retention becomes (15.3 months).

where, V: the volume of the wastewater within the soil of passage of the seeped wastewater, v: the daily volumetric flow rate of the Ad Diwaniyah refinery wastewater (150 m^3/day).

4.5 Suggested strategy or protocol to protect the groundwater of the Ad Diwaniyah refinery area

Having determined the retention time of the heavy metals in the soil (15.3 months) and the diameter of the seepage path of the wastewater downward the groundwater aquifer (72 m), a strategy to manage the wastewater discharge has been established by changing the point of discharge every 15.3 months to a new location of 90 m from the centre of the previous discharge point to the centre of the new discharge point for the area of study. The new location was estimated with a 25% safety factor.

5. CONCLUSIONS

The following remarks were concluded:

1. A strategy to manage wastewater discharge by changing the point of discharge has been established to protect the region's groundwater. For the case study of the Ad Diwaniyah refinery area, the discharge point of the effluent wastewater has to be moved every 17 months to a new location of 90 m from the previous discharge point.
2. The presented methodology, results, and calculations can be extended to any cases of wastewater discharges from any sources for any areas, regions, and locations where their wastewater is either partially treated or not treated.
3. As the rocky soil at the discharge point of the wastewater is permeable, it facilitates the seepage of the wastewater down to the aquifer and contributes to pollution of the groundwater of the formation near the refinery site. At the same time, the rocks and soil layers work as effective adsorbents to naturally attenuate heavy metal pollutants.
4. To utilize the soil's capability to adsorb heavy metals pollutants, this study tried to develop a methodology to estimate the time to reach saturation (time of retention) of the soil so that the location of the discharge point can be changed from time to time with a defined duration of discharge. This approach helps in preventing heavy metals from reaching the groundwater and polluting it if the wastewater treatment unit is insufficient to remove heavy metals from the refinery/industry wastewater.
5. Variation of the temperature and the hydrostatic pressure inside the soil along the seepage path of the discharged wastewater (from the top of the soil to the top layer of the groundwater reservoir) and their effect on the adsorption uptake rate, vertical and horizontal velocities, and lateral diffusion rate and capacity should be considered in the future studies.
6. The results indicated that both Langmuir and Freundlich models fit the Dolomitic Limestone soil isotherms with $R^2 > 95$. The results also indicated competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from a wastewater stream in a Dolomitic Limestone soil is feasible with high removal efficiencies.
7. Lateral dispersion of the discharged wastewater may be recommended for further investigations to enhance the adsorption of heavy metals and reduce the pollution of groundwater.

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