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Effect of the Pharmaceutical Residues on Some Physical and Mechanical Properties of Silty-Clay Soil

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ABSTRACT

The contamination caused by pharmaceuticals is recognized as one of the most severe forms of environmental pollution. Many medicines and medical waste are dumped on the land, especially near hospitals, medical clinics, stores, and others, thus the aim of the study. The physical and mechanical of soil properties and tetracycline in leachate were studied. The sample extractor device (Shelby tube) was used to take undisturbed samples with a number of (6) tetracycline solutions added monthly to the soil samples, for a period of 6 months. The obtained results showed that silty clay is a type of this soil, the unconfined compression strength decreases with months to 6 months, while the effect on Atterberg's limits (liquid and shrinkage limit) showed the soil became softer, lowering the value of the liquid limit. The tetracycline test in leachate water decreased with time, due to the soil adsorbed tetracycline. First-order is suitable for the kinetic model. Finally, the tetracycline drug effect on the physical and mechanical properties of soil was studied.

Keywords: Unconfined compression test, soil physical and mechanical properties, tetracycline drug, Atterberg Limits, underground water.

INTRODUCTION

In the last decade, pharmaceutical waste (medicines) has become an environmental issue that has attracted a lot of attention, (IUPAC, 1997). Tetracyclines are excreted by humans for treatment of diseases such as urinary tract infections, respiratory infections, relapsing fever caused by Borrelia sp, brucellosis caused by Brucella species, trachoma, syphilitic lymphogranulomatosis, and infections caused by Chlamydia kinetochores, such as uncomplicated urethra, endometriosis, as well as cervical or rectal infection, and conjunctivitis (U.S National Library of Medicine, 2022). Concerning veterinary indications, the treatment of respiratory infections includes: shipping fever (Pastrilus), bronchopneumonia, hereditary pneumonia in pigs, atrophic rhinitis, mixed infections and necrotizing bacilli, gastro-intestinal infections caused by Escherichia coli, salmonella and anaerobic, and others (Dana, 2005). The majority of tetracyclines are only partly absorbed by the body from the digestive system, leaving enough of the drug in the intestines to disrupt the normal flora and produce diarrhea. It is distributed throughout the body and across the placenta. It is excreted from the human body and from livestock mainly through urine in an unchanged form (Manjula, 2013). People in every region of the globe are administered millions of dosages of medication on a daily basis from their doctors, millions more are given to livestock. However, after administering the treatment (swallowing the pill or taking the injection), the drugs are not completely absorbed from the body and their components do not become inactive and inactive. After urination and excretion of drugs from the body, they begin to appear again in different places such as soil, sewage and groundwater, also in drinking water, where the processing is not completed in the process of metabolism. It is either released into the aquatic system (Koch, 2021) and can affect humans, wildlife and agriculture (Matthew, 2009), or it seeps directly into the groundwater (Koch, 2021). The medicines in the environment are sourced either by disposing of unwanted or expired medicines in the wastewater stream, pouring it into the sink or flushing it down the toilet (Kumar, 2020). In addition, by throwing it in the trash, it ends up in landfills, and from the leachate it enters the soil or watercourse (BNF, 2022). According to findings from previous studies, a wide range of antibiotics may be found in the sewage samples taken from hospitals, municipal sewage, wastewater treatment plant effluent, antibiotic industry sewage, livestock farm mud and sewage, surface water, groundwater, and drinking water (Dimitra, 2022). Many studies included the uptake of tetracycline in soil, including the study of tetracycline residue concentrations in soil fertilized with liquid manure using high-performance liquid chromatography and electro-ionization mass spectrometry (Gerd, 2002), Studies have been conducted on the usage of veterinary antibiotics, as well as their sales, exposure paths, incidence, and effects. In the environment (Ajit, 2006), studies investigated the fate of veterinary antibiotics in clay soils of agricultural lands after application of slurry (Paul, 2005), and the absorption of tetracycline and chlortetracycline on soil when it is saturated with calcium, calcium clay, humic substances and clay humic complexes (Jutta, 2007), and the absorption properties of tetracycline were studied by two soils, including evaluation of the role of organic matter in them (Manuel, 2020). A further investigation was conducted on the behavior of tetracyclines in the presence of sulfonamides, and their absorption coefficients were evaluated in soil; additionally, the existence of leaching into groundwater was investigated (Astrid, 2020). The study showed that there is a clear effect of the presence of tetracyclines and sulfonamides. It may be due to different uptake coefficients in the soil, indicating different kinetics in the ecosystem. In groundwater, the genes for resistance to tetracyclines were discovered, and this is an indication of the presence of tetracyclines in them (Cycoń et al., 2019). The wastewater discharge from pharmaceutical plants was associated with an increased prevalence of resistance to single and multiple antibiotics in indicator organisms. Here, studies have shown several environments that altered the susceptibility of microbes to antibiotics in those environments and/or other than the dominant microbes.

- Household products. There are more than 700 "anti-bacterial" household products, such as sweat socks, kitchen plastic utensils, toothpastes, cement and paints. It was also found that most compounds are considered antibacterial, such as quaternary ammonium compounds, triclosan, alcohol, bleach and others.
- Spray on crops. About 300,000 pounds of antibiotics are sprayed annually on high-value agricultural crops, such as fruit trees, within plant production to prevent bacterial infections.
- Animal production. Antibiotics are commonly added to feed as a growth promoter and at subtherapeutic levels. It is also added to fishing water (Andrew, 2016) and other veterinary medicines. The sludge that is left over following the treatment of wastewater is used in agriculture as a fertilizer and a source of nutrients; nevertheless, this material also includes pharmaceuticals that are intentionally hidden from view (Bethany, 2008).

A number of studies on the impact of waste on soil properties, including (Qassem, 2009) the effect of sewage water for the city of Baghdad on the physical and chemical properties of clay soil with a depth of 1 m to 2 m was studied and this effect was shown on the foundations of buildings and engineering facilities when they suffer from leakage of that water under them as a result of cracks in pipe carrier or as a result of brackish water penetrating into the soil in the case of surface runoff of sewage water in the areas that do not contain a sewage network. The study included samples of disturbed and undisturbed soils and their treatment with sewage water. Some variables and time factor, such as temperature, organic matter and dissolved salts were studied and their effect on groundwater was studied. The study found an increase in plasticity, fluidity and density, while the specific weight decreased, the dissolved salts, sulfates and carbonates decreased, and the organic matter increased. The amount of specific weight (G_s) increased significantly and returned to recover over time with a clear increase in the amount of leaching the unstable (q_u) covered and marked change in the separating marks (C, $ø$) of the soil over time. It was also noted that an initial decrease and then a gradual increase in the amount of soluble salts (TSS), sulfates (SO_4) and carbons (CO_3), and there was also an expected increase in the amount of organic substances ($O.M$) and chlorides (Cl), with a relative stability of the amount of chlorides over the time of the effect. A number of important curves were obtained that clearly showed the effect of wastewater on the physical and chemical properties of clay soils. (Ghayda, 2010) The effect of sewage water on some physical and chemical properties of clay soil and knowing the extent of its impact on the properties of joining and on the foundations of facilities and buildings when they suffer water leakage under them as a result of sewage pipes breaking or as a result of the penetration of brackish water into the soil or the flow of water on abandoned lands. By taking disturbed and undisturbed samples, the results of soil treatment with sewage water showed an increase in the limit of fluidity, plasticity and plasticity index and for the two models, disturbed and undisturbed, and a decrease in the specific weight of soil with time was observed as a result of the chemical contents of wastewater. An increase in the percentage of voids and a decrease in the pressure of pre-joining were observed due to the dissolution of the dissolved salts and the breaking of physicochemical bonds when stress was applied to the carbonate content in the soil. The results also showed an increase in soil compaction, as the compressive index (C_c) and the values of the swelling index (C_r) increased.

There is no study concerned with pharmaceutical pollutants and their effects on engineering soils, in the case of using contaminated soils with antibiotics and their effect on construction, and knowing the effect of these pollutants on its mechanical and physical properties. Therefore, the aim of this study was to determine the effect of tetracycline, as a drug that is widely used for humans, veterinarians, and with and without a doctor's prescription, on the mechanical and physical properties of soil.

EXPERIMENTAL WORK

Material

Tetracycline with the chemical formula $C_{22}H_{24}N_2O_8$ was used and the chemical form is shown in Figure 1, i.e. capsules with a dose of 500 mg that was prepared from local pharmacies,

Preparation of tetracycline solution

The concentration of tetracycline has been prepared by dissolve 500 mg of tetracycline in a liter of water, which is equivalent to a one capsule in a liter of water.

Lab work investigation

In order to know the effect of tetracycline as an antibiotic on the soil, the soil samples are collected from a depth of approximately 1.5 m to reach the natural soil, using the Shelby tube model extractor device. Thus, 6 samples of undisturbed soil samples were taken and transferred to the laboratory, as shown in Figure 2. The tetracycline solution was prepared with 500g of tetracycline tablet to one liter water as reveal in Figure 3, and added periodically to soil samples every month for 6 months except for one sample as reference. Each month, the soil sample was raised and taken for examination. The soil properties and unconfined compression strength of a reference soil sample were studied. The hydrometer analysis for the soil sample was tested to find out the soil type, and Atterberg limits (liquid limit, plasticity limit) were tested according to ASTM D4318-17e1 (ASTM, 2018) as in Figure 4, in addition, to testing the unconfined compression according to ASTM D2166-06 (ASTM, 2010). Leachate samples were collected and

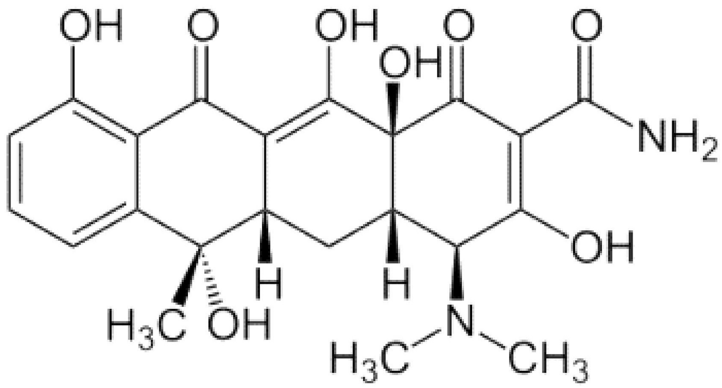

Figure 1. Tetracycline chemical formula

Figure 2. Undisturbed soil samples

Figure 4. Atterberg limits test

Figure 3. Tetracycline Solution

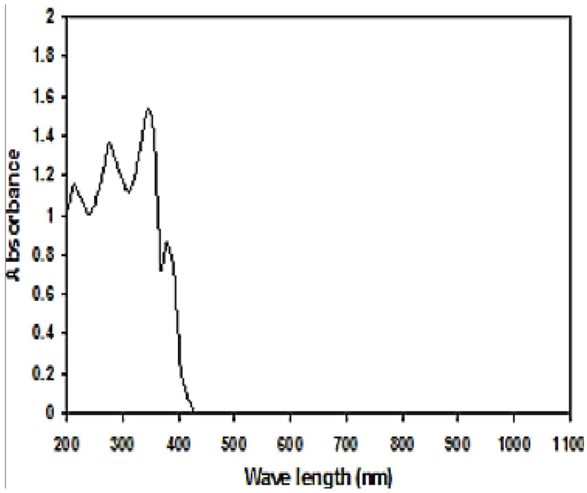

Figure 5. Absorption spectrum of tetracycline concentration versus a blank solution

periodically checked for tetracycline concentration using UV-visible at 344 nm (Nief, 2018), the maximum spectrum absorption of tetracycline concentration in ultraviolet-visible in UV instrument at different max (213 nm, 271 nm, 344 nm, and 363 nm) with versus as blank solution as explain in Figure 5, tetracycline kinetics model are studied.

RESULTS AND DISCUSSION

Results of the physical properties

Hydrometer test

The hydrometer was examined for the reference soil samples and the samples exposed to contamination by adding tetracycline, and the results are shown in Figure 6 the classification triangle, i.e. soil texture triangular. It was found that the type of soil is silty clay.

Atterberg's limits (liquid and plastic limits)

The consistency of a soil sample changes with the amount of water present. The physical state of the soil is evaluated using Atterberg's limits, which vary depending on the amount of water present in the soil. At different moisture levels, these limitations might be interpreted as indications of the workability of the soil. These aspects are determined by the soil's texture, level of organic matter, and percentage of clay content. The consistency of limit test is a type of test that is performed on fine-grained soil, particularly clay and silt soil. This test is performed because sufficient water can be added to the soil until the soil grains are dispersed in a suspension. After this, the water

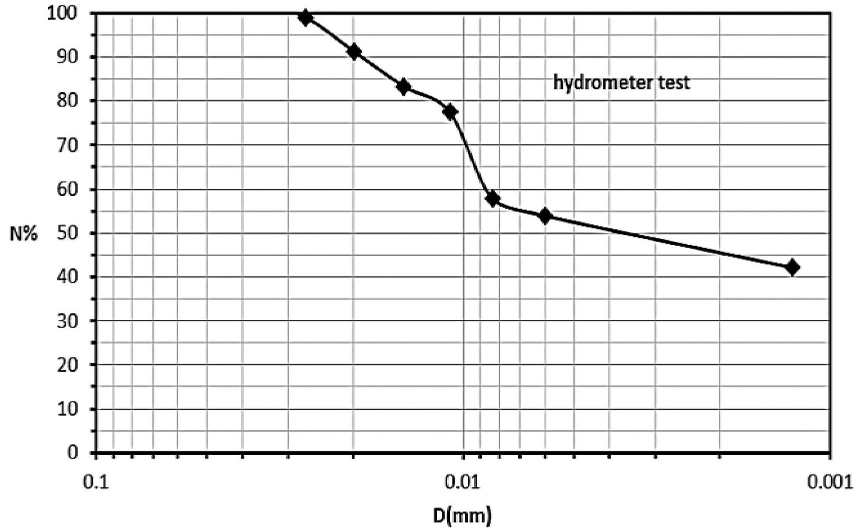

Figure 6. Hydrometer test

Table 1. The results of the liquid and plastic limits

Time (days)	L.L%	P.L%
0	50	32
30	48	29
60	34	25
90	28	21
120	23	20

is evaporated from such a soil suspension. Consistency limits, also known as Atterberg's limits, are the water contents at which the soil changes from one state to another as it goes through its progression from a solid to a semi-solid to a plastic to a liquid state. The soil goes through these stages as it moves from a solid to a liquid state. Adding the polluting material dissolved in water to the soil over time, causes the soil to become softer, lowering the value of the liquid limit, see Table 1 and Figure 7.

Mechanical properties

Unconfirmed compressive strength

The soil samples were examined for unconfined compression, firstly, the pollution-free reference sample was examined, and then successively the samples were checked every month. Several samples were analyzed at various times of pollution. When clay soil is exposed to pollution for 30 days, its compressive strength drops to (27 kPa) compared to when it is not exposed to pollution. When the pollution time is increased to 60, 90, 120, and 150 days, the compressive strength is reduced till it reaches (9 kPa). After 120 and 150 days, the pollution of clay soil reduced the compressive stress of the soil by 70%, as demonstrated in Figure 8. Because pollution affected the texture of the soil, different liquid and plastic limit values were obtained.

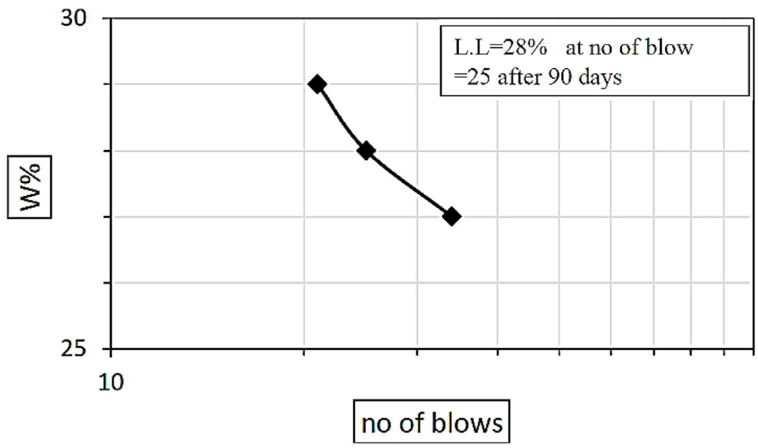

Figure 7. Liquid and plastic limits

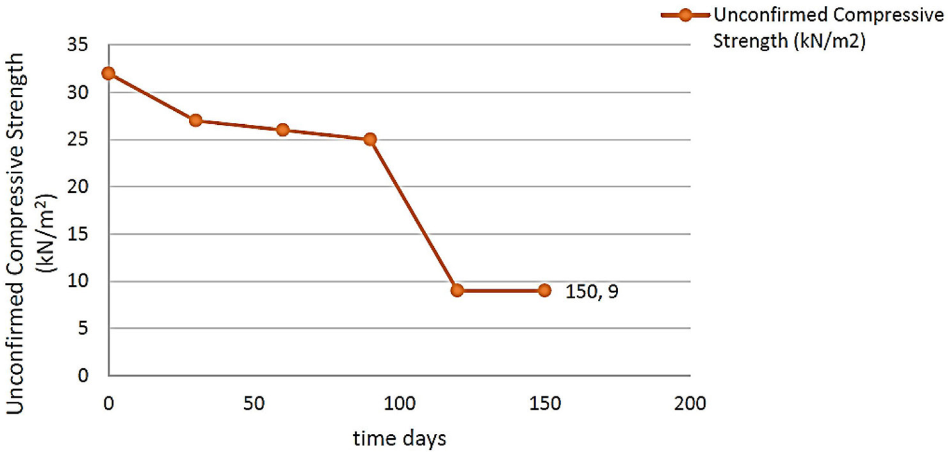

Figure 8. Unconfirmed compressive strength (kN/m²)

Tetracycline leachate test

The liquid leaching from the samples was examined after adding contaminated water with tetracycline. In the first period, from the results were shown, the adsorption of tetracycline is high in (0–30 and 60 days), so tetracycline concentration in the filtrate was very poor, and this is evident in Figure 9. However, tetracycline concentration in liquid leachate increased in remained months, since all the sites of adsorption were filled, and the liquid contamination was leachate with a high concentration

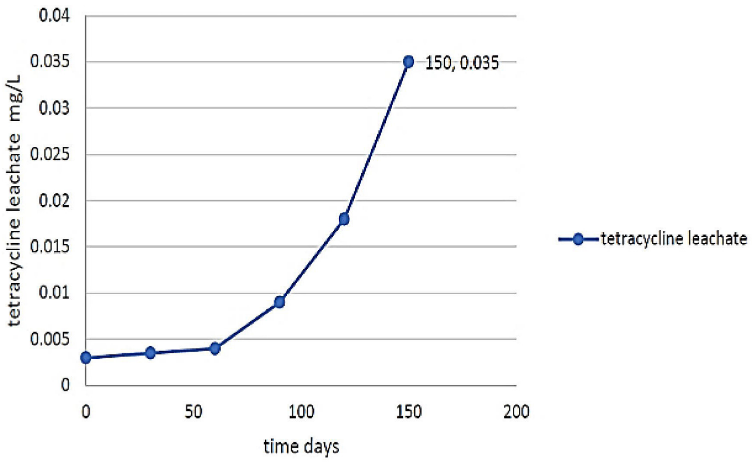

Figure 9. Tetracycline concentration leachate

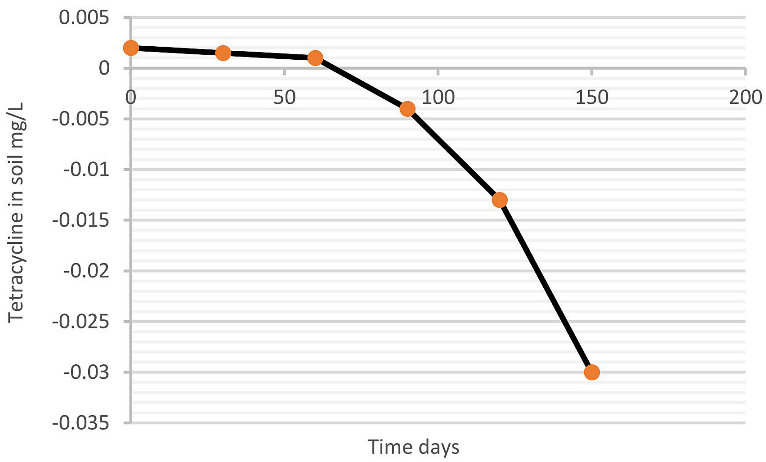

Figure 10. Tetracycline concentration in soil

of tetracycline and the negative effect of tetracycline on the properties of soil (especially Atterberg's limits). From the foregoing, it was found that the concentration of tetracycline in the soil is equal to the difference between the concentration added to the samples and the concentration in the leaching liquid, which is displayed in Figure 9.

Tetracycline kinetics model

The investigation of kinetics is an essential part of research into the adsorption processes (Wang, 2008). The kinetic equation is given in the form of Equation 1, which represents the n^{th} order of absorption.

$$\frac{dC}{dt} = -kCn \quad (1)$$

where: k – adsorption rate coefficient;
C – Ibuprofen concentration;
t – time of adsorption;
n^{th} – reaction order.

Following on from the preceding equation, the pseudo first order kinetic equation was presented as Equation 2 (First Order), and the faux second order kinetic equation was displayed as Equation 3 (Second Order), respectively (Emami et al., 2010):

$$log\,(q_e - q_t) = log\,q_e - k_1\,t \quad (2)$$

The following equation summarizes the definition of the initial sorption rate:

$$h = k_2 \times q^2 \quad (3)$$

Due to the high value of $R2$, this kinetic analysis was performed on various concentrations of

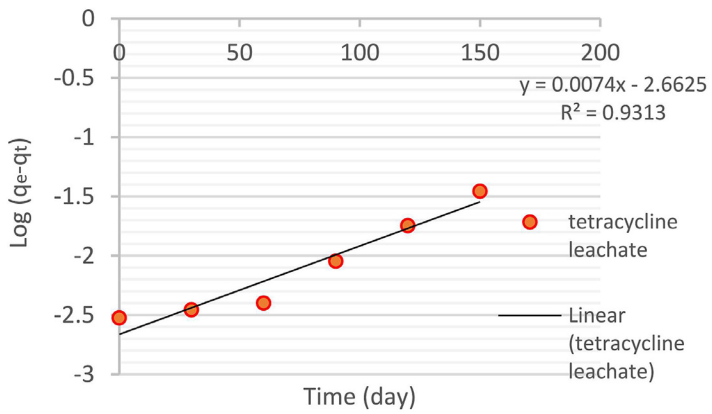

Figure 11. Linear plots of kinetics data of the first order model

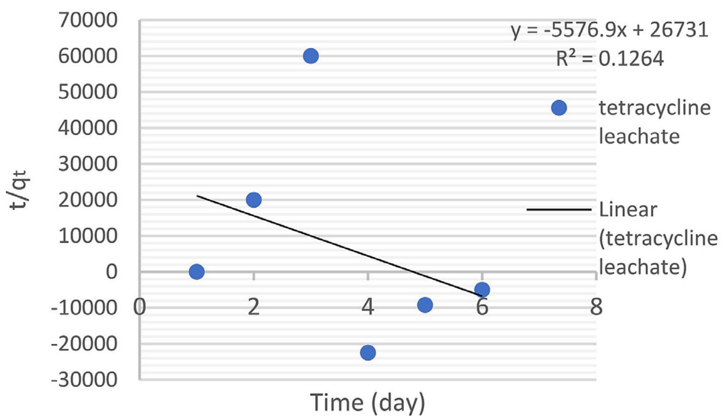

Figure 12. Linear plots of kinetics data of the second order model

Table 2. Kinetic parameters

First-order			Second-order			
$R2$	k_1 (min^{-1})	Calculated eqilb. uptake q_e ($mg \cdot g^{-1}$)	k_2 ($mg \cdot g^{-1} \cdot min^{-1}$)	h ($mg \cdot g^{-1} \cdot min^{-1}$)	$R2$	Calculated eqilb. uptake q_e ($mg \cdot g^{-1}$)
0.9313	0.0074	2.6625	-5576.9	-3.98495E+12	0.1264	26731

ibuprofen. Figures 10 and 11 as well as Table 2 provide visual representations of the results *k* and *R2* for the first and second orders, respectively. In light of the findings, it was determined that the pseudo first order provided the optimal solution on account of the high *R2* value. The findings demonstrated that the faux first order equation provided a good match to the experimental data with a correlation coefficient (R2) that was closer to one than the second order did. This was the case because the pseudo first order equation was simpler. The rate of departure from the straight line of sorption, as shown in the pseudo first order and second order model, and the rate of adsorption observed in this investigation were both rather sluggish, particularly in the early stages of the reaction. The first order model was a reaction pathway for the sorption of ibuprofen by activated Moringa oleifera. This conclusion was reached on the basis of the correlation coefficients (Kawanga et al., 2016). Figure 12 represents the linear plots of kinetics data of the second order model.

CONCLUSIONS

In this work, an environmental problem was highlighted, which is the disposal of tetracycline treatment residues in the soil without treatment, and the effect of the disposal of these drug residues on some of the physical and mechanical properties of silty-sand soil was also examined. The following conclusions were drawn:

1. The results of unconfined compression strength decrease with months due to tetracycline in space of soil.
2. The concentration of tetracycline absorbed in the soil is increasing so that these concentrations decrease in water.
3. The effect of pollutants on soil texture Atterberg's limits (liquid and shrinkage limit).
4. The ratio of the limit of liquidity and plasticity decreases over time.

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