

Evaluating the Efficiency of Microwaved Sludge in the Removal of 2, 4-Dinitrophenol from Aqueous Solutions: Equilibrium and Kinetics Studies

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ABSTRACT

Introduction: Nitrophenol compounds are toxic compounds found in industrial wastewaters. 2,4-dinitrophenol is the most dangerous compound among phenolic compounds. The aim of this study was to evaluate the removal of 2,4-DNP from wastewater by microwaved dried sludge adsorbent.

Materials and Methods: The results of 2,4-DNP removal were discontinuously obtained by the high performance liquid chromatography (HPLC) at a wavelength of 360 nm with various effective factors, such as contact time, pH, initial concentration of 2,4-DNP, and microwaved sludge dose. Finally, the results were analyzed using the kinetics and isotherm models. The equilibrium time was obtained 120 min. The maximum removal rate was obtained at pH 7.

Results: The findings indicated that the removal efficiency increased by increasing the adsorbent dose and decreasing the 2,4-DNP concentration. It was revealed that the removal of 2,4-DNP by microwaved sludge was 86%. The correlation coefficient value of linear and non-linear regression showed that kinetic studies follow the pseudo-second order model and isotherm studies follow the Freundlich isotherm model. The adsorption method relied entirely on pH and affected the adsorbent area attributes, ionization rate, and Delete percentage. When the pH was high, there was competition for the adsorption sites between hydroxide ions (OH) and 2,4-DNP molecules. At first, the adsorption process was high speed and gradually reached a stable level, because after a while, the adsorption sites become saturated.

Conclusion: As the adsorbent dose increases, the efficiency of the adsorption process increases, because larger amounts of adsorbent cause higher adsorption places.

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Introduction

Industrial advances have led to increased environmental pollution caused by hazardous

pollutants from human activities. These hazardous pollutants include insecticides, combustion products, hydrocarbon solvents, and nitrophenols^{1, 2}, which

contribute significantly to soil and water pollution and can affect aquatic and soil ecosystems³. Recently, phenolic compounds have been widely used in industry and daily life and have become one of the common pollutants in water⁴. Eleven phenolic compounds are classified as early pollutants by the USEPA classification, and their maximum permissible concentrations in water are 1-20 ppb⁵. The World Health Organization (WHO) recommends 0.001 mg/L as the permissible concentration of phenol in drinking water⁶. USEPA has recommended a permissible limit of 0.1 mg in wastewater⁷. Major sources of phenolic wastewaters include refineries, fuel production facilities, wood industries, and chemicals industries⁸. One of the most resistant phenolic compounds is nitrophenol, which found in industrial wastewater due to its significant solubility and stability in water. These compounds represent a significant threat to human health in the aquatic ecosystem because of their remarkable toxicity and carcinogenic nature⁹. The most toxic compound among the six types of dinitrophenol compounds is 2,4-DNP. Wastewaters containing 2,4-DNP often need treatment before being discharged into the water in order to meet the environmental standards. The environmental impacts of 2,4-DNP are of concern due to their high toxicity in wastewater. Industries such as the paint industry, explosives production industries, germicides and fungicides, tanning industries, and pharmaceutical industries generate this pollutant¹⁰. The most common methods employed for removing phenol from aqueous solutions are solvent extraction, reverse osmosis, electrochemical methods, and chemical oxidation¹¹. Since the treatment of phenol-containing wastewaters is difficult or impossible with conventional biological treatment processes, it is necessary to use advanced treatment technologies to remove these compounds and their adverse effects¹². Problems, such as high costs, low efficiency, and production of toxic byproducts are limiting factors for the widespread application of some of these removal strategies. Among physicochemical processes, adsorption technology has received widespread attention over recent years¹³⁻¹⁵. Including processes for removing contaminants from sewage,

which has been widely used recently, is the use of disposal sludge produced from wastewater treatment plants. Sludge refers to the sedimentations in wastewater treatment and water treatment processes at various stages, which can be produced by primary or secondary sedimentation basins. Most of the sludge is currently discarded, and the treatment and preparation of sludge impose high costs on wastewater treatment plants¹⁶. When the sludge is dried using microwaves, it causes the solids to coagulate and the water in the sludge solids to decrease. As a result, the sludge was almost entirely dehydrated and sterilized¹⁷. The non-living biomass is used in industrial applications as bioadsorbent, since it does not require nutrients and can be easily used in high toxicity environments¹⁸. sewage sludge is an economical adsorbent for the adsorption of organic contaminations owing to the availability of inexpensive and indigenous materials. Its efficacy for the removal of nickel, 4-chlorophenol¹⁹, and organic compounds²⁰ has been proven. In the present study, the efficacy of microwaved sludge for the elimination of 2,4-DNP from synthetic solution was evaluated.

Materials and Methods

This experimental research investigated the ability of microwaved sludge to eliminate a synthetic solution of 2,4 DNP. 2,4-DNP obtained from a German company called Merck KGaA²¹. The 2,4-DNP structure and its physicochemical characteristics are shown in Table 1. A stock solution was prepared by dissolving 1 g of 2,4-DNP in deionized distilled water and diluted to 1000 ml. The phenolic solution for the adsorption analysis were prepared by diluting the stock solution to give different concentrations within the range of 10 to 100 mgL⁻¹ for 2,4-DNP. Stock solution was preserved in a covered dark bottle until ready to use. The pH of the experiment solution was set by 0.1 normal hydrochloric acid and sodium hydroxide (pH meter HQ40d, USA). To prepare the microwaved sludge, the required discharged sludge was first obtained from a treatment plant in the south of Tehran. The collected sludge samples were washed several times with water to remove excess contaminants and then dried in an oven for 48 hours

at 60 °C¹⁸. For manufacturing of the sludge microwaved, The dried adsorbent in the previous step was chemically processed with a chemical solution of ZnCl₂, KOH and H₃PO₄ 2 M, 2 M and 3 M respectively. For these chemical solutions, the pH of the solution was fixed at 6.5. The Distilled water was used to wash the prepared adsorbent and then passed through a filter paper. The modified adsorbent was heated in a microwave for 7 min. In the next step, it was screened in sizes of 0.2 to 0.3 mm using standard sieves²².

Kinetics experiments

The aim of these assays was to determine the changes of 2,4-DNP adsorption at concentrations 10, 30, 50, 70 and 100 mg/L, pH levels 3,5,7,9, and 11, contact times 10, 30, 45, 60, 90, 120, and 150 min and to obtain the equilibrium time of the pollutant adsorption onto the adsorbent and determine their optimum values. All samples were filtered by Whatman filters, passed through 0.45 µm pore size PTFE syringe filters and then measured using the high performance liquid chromatography (HPLC) model CECIL CE4900 at a wavelength of 360 nm.

Equilibrium experiments (isotherms)

These experiments were performed by varying the adsorbent dose used (0.1, 0.5, 1, and 1.5 g) and the optimized values of the factors, such as time, pH, and concentration. Finally, Langmuir and Freundlich adsorption models and kinetics equations for the adsorption of 2,4-DNP onto the adsorbent were separately studied.

$$q_{eq} = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$R = \frac{C_0 - C_t}{C_0} \quad (2)$$

The equation (1) was used to calculate the adsorption capacity (q_e) and the equation (2) was used to calculate the removal efficiency of the solution. C_t and C_0 are the primary and final concentrations of the contaminant in aqueous solution (mgL⁻¹), M (g) and V (mL) are the mass of the sludge adsorbent and the volume of the aqueous solution, respectively^{23,24}.

The Information gathered from the several stages of the examinations and the findings of the analysis of the collected samples and other measured parameters were analyzed using Excel software.

Table 1: Specifications of 2, 4-DNP

Color	Form	Characteristic	Chemical formula	Molecular weight (g/mol)
Yellow	Crystalline solid	2,4-dinitrophenol	C ₆ H ₄ N ₂ O ₅	184.11

Ethical Issue

The present study was conducted with the approval of Iran University of Medical Sciences, Tehran, Iran (Code: IR.IUMS.REC 1396.9511388008).

Results

The properties of the adsorbent used are described in Table 2. Also, SEM images of microwaved sludge adsorbent are indicated in Figure 1.

Effect of time

The adsorption of 2,4-dinitrophenol onto the microwaved sludge was investigated by examining the contact time to determine the equilibrium time. The findings indicated that the highest elimination percentage was at 60 minutes and then decreased

and reached equilibrium at 120 minutes (Figure 2).

Effect of initial pH

The data showed that the adsorption was highly correlated with pH, as it affected the adsorption efficiency, the degree of ionization and the adsorbent surface characteristics. The highest removal percentage of the pollutant was generated at pH 7, so that the removal efficiency increased from the acidic pH to the neutral pH, and decreased from the neutral pH to the alkaline pH (Figure 3).

Effect of concentration 2,4-DNP

The effect of primary concentration of 2,4-dinitrophenol on the elimination percentage was investigated by microwaved sludge in the range of 10 to 100 mg/L. The findings showed that the

removal rate of 2,4-dinitrophenol decreased by increasing the concentration of 2,4-DNP. So that by increasing the concentration of 2,4-dinitrophenol from 10 mgL^{-1} to 400 mgL^{-1} , the removal rate of 2,4-DNP decreased from 78.3% to 49.9% (Figure 4).

Effect of various doses of microwaved adsorbent

The adsorption dependence of 2,4-DNP on adsorbent dose at doses of 0.1 to 1.5(g 40 l/mL) of the sample was investigated. in this stage, only the

adsorbent dose parameter was variable and the other optimized parameters were constant. The results showed that the adsorption rate decreased by decreasing the amount of adsorbent (Figure 5).

Table 2: Chemical and physical properties of microwaved sludge adsorbent

Characteristics	Microwaved sludge
Color	Brown
BET surface area (m^2/g)	98.76
pHzpc	7.2
Particle size (mm)	0.2-0.3
Particle porosity	0.79

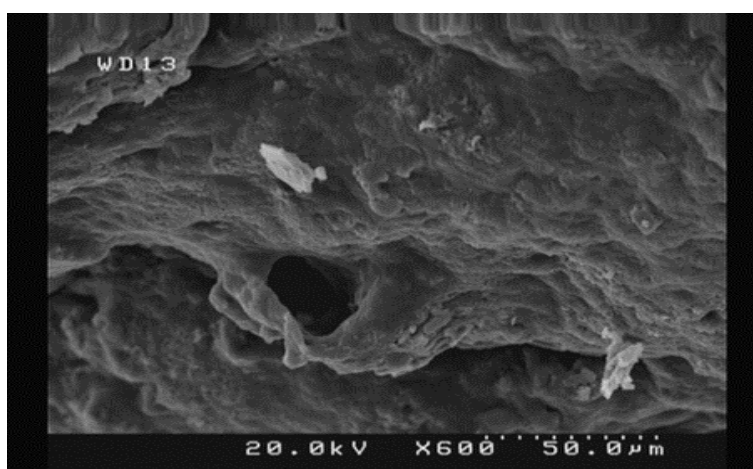


Figure 1: Scanning electron microscopy (SEM) of microwaved sludge

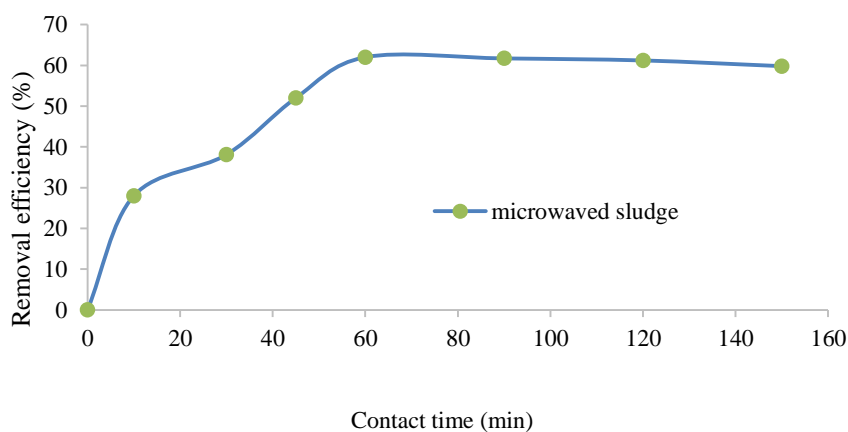


Figure 2: Effect of contact times on the removal of 2, 4 DNP by adsorbent microwaved sludge (experimental condition; adsorbent dosage = $0.5 \text{ g } 40 \text{ mL}^{-1}$, $C_0 = 50 \text{ mg L}^{-1}$ and initial pH = 7)

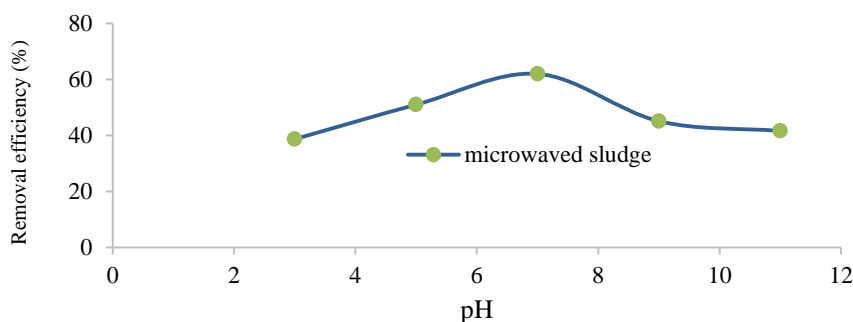


Figure 3: Effect of pH on the removal of 2,4 DNP on adsorbent microwaved sludge (experimental condition; adsorbent dosage = 0.5 g 40 mL⁻¹, C₀ = 50 mg L⁻¹ and contact time = 60 min)

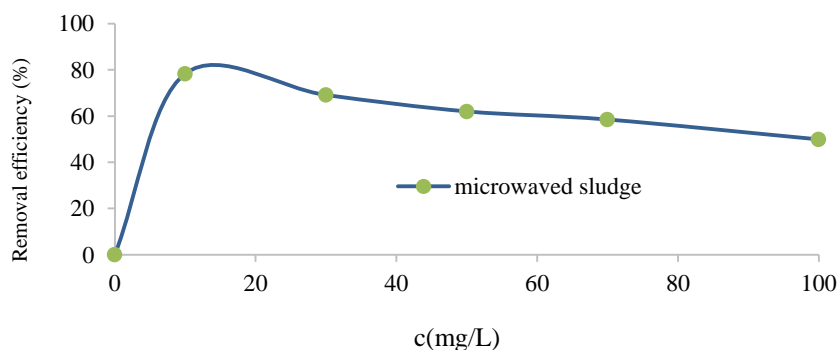


Figure 4: Effect of various concentrations of 2,4-dinitrophenol on adsorbent microwaved sludge (experimental condition; adsorbent dosage = 0.5 g 40 mL⁻¹, optimal time and optimal pH)

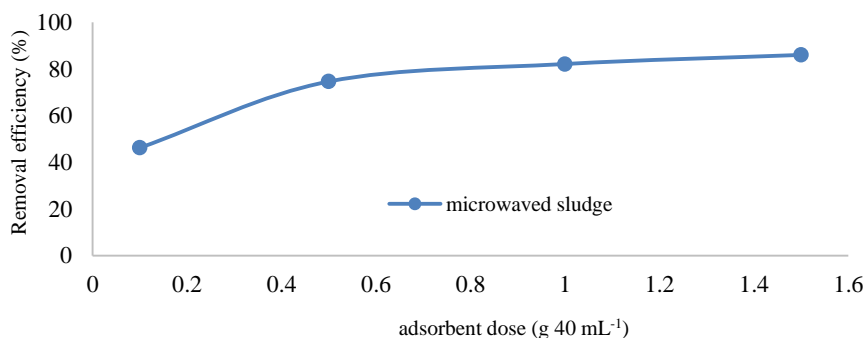


Figure 5: Effect of adsorbent dose of adsorbent microwaved sludge on the removal of 2,4 DNP (experimental condition; optimal pH, optimal concentration and optimal time)

Adsorption kinetics

Due to the mass transfer process and physicochemical properties of adsorption, kinetic studies are used to evaluate the adsorption performance. Given most kinetics models for adsorption are pseudo-first-order and pseudo-second-order models^{25, 26}, The formula for the pseudo-first-order relation is as follows^{27, 28}:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{3}$$

The adsorption rates of 2,4-DNP per every gram of adsorbent at the equilibrium time and t time were indicated by q_e and q_t. K₁ is the first-order kinetics constant (1/min) and determined from the plot of log (q_e - q_t) versus t. The pseudo-second-order relation formula, which is based on the adsorption capacity in the solid phase, can also be used for adsorption kinetics^{1, 29}:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \tag{4}$$

In the above equation, the plot t/q versus t indicates a linear relationship.

Determination of K_2 and q_e is done by the intersection point and slope of the diagrams. The kinetics constant is the same as K_2 . Also the intracellular diffusion model (IDP) is used to express the adsorption kinetics whose mathematical expression is as follows³⁰:

$$q_t = K_{dif} t^{0.5} + C \quad (5)$$

In this equation, C and K_{dif} represent the diffusion constant (mg g^{-1}) and the intraparticle diffusion rate constant (mg g^{-1}), respectively. Also in this study, non-linear shapes of these kinetics models (Equation 6 and 7) were used.

$$q = q_e (1 - e^{-kt}) \quad (6)$$

$$q = \frac{q_g^2 + K_t}{1 + q_e K_t} \quad (7)$$

Where Kt , q and t are the pseudo-second-order rate constants ($\text{g mg}^{-1} \cdot \text{min}^{-1}$), the amount of adsorbate adsorbed per unit mass of solid at the time, and the pseudo-first-order rate constants (mg g^{-1}), respectively. In this study, the findings of kinetic studies are reported in Table 3.

The correlation coefficient (R^2) value in the pseudo-first-order kinetic and the intraparticle diffusion kinetic was relatively weaker than in the pseudo-second-order kinetic. Therefore, the adsorption of 2,4-dinitrophenol onto the microwaved adsorbent was more proportional to the pseudo-second-order kinetic. The figure of data compliance with pseudo-second-order kinetic is shown in Figure 6. Also figure 7 shows that the diagrams of the non-linear fitting findings for the adsorbent demonstrate adherence to pseudo-quadratic kinetics.

Table 3: Correspondence between the obtained data and adsorption kinetics linear models

Adsorbent	Intraparticle diffusion kinetic			Pseudo-first order kinetic			Pseudo-second order kinetic		
	K_d	R^2	C	k_1	R^2	Q_e	k_2	R^2	q_e
Microwaved sludge	0.046	0.917	0.198	0.0019	0.529	0.03	1/23	0.993	29.54

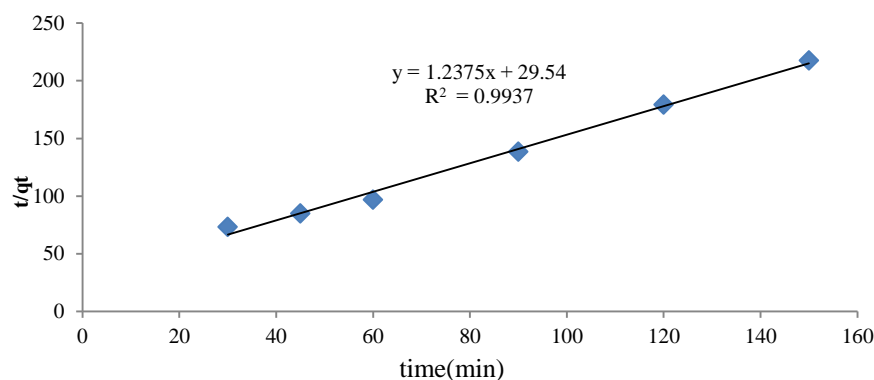


Figure 6: Data compliance with pseudo-second-order model

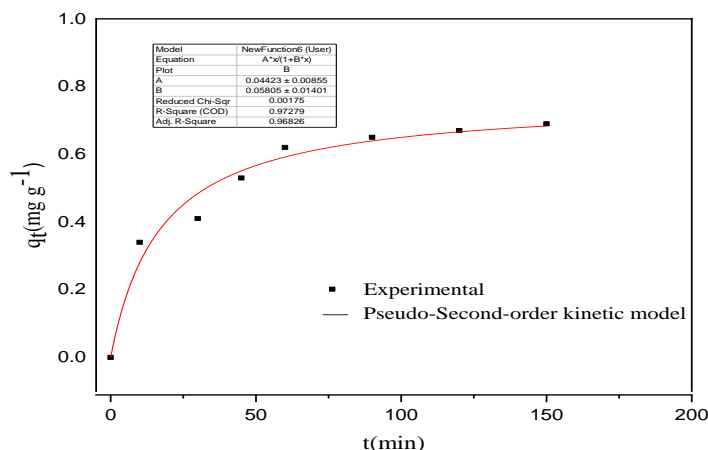


Figure 7: Non-linear pseudo-second-order diagram of the microwaved adsorbent

Adsorption isotherm

Adsorption isotherm parameters are used to access the adsorption capacity characteristics of an adsorbent^{31, 32}. The constant and specific values in the isotherm represent the surface characteristics and dependence of the adsorbent and can be used to compare the adsorption capacity of the adsorbent for various contaminants. This type of isotherm often fits the Langmuir and Freundlich model³³. The Langmuir model is designed for the monolayer adsorption onto a area with a small amount of adsorption places. The sites are uniformly dispensed over the adsorbent surface whose linear form is as follows^{34, 35}:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b} \tag{8}$$

C_e (mg L⁻¹) and q_e (mg g⁻¹) are the equilibrium concentrations of 2,4-dinitrophenol in equilibrium and the amount of 2,4-DNP absorbed per gram of adsorbent, respectively. q_m is the maximum adsorption capacity, and b is the adsorption correlation energy. Freundlich model is also an adsorption equation for multilayer adsorption onto heterogeneous surfaces^{36, 37}, which implies that the places of correlation are not the same or independent, and the equation is as follows^{27, 38}:

$$\ln q_e = \frac{1}{n} \ln c_e + \ln K_F \tag{9}$$

Where 1/n and C_e and K_F indicates the degree of adsorption, equilibrium concentration (mg L⁻¹) and adsorption capacity per unit concentration, respectively. 1/n describes the method of this process;

If 1/n = 0, 0 < 1/n < 1 and 1/n > 1, it indicates that the adsorption process is irreversible, favorable and unfavorable, respectively³⁹⁻⁴¹.

In order to measure the adsorption equilibrium data, Equations 10 and 11 were used for non-linear methods of Freundlich and Langmuir isotherms, respectively.⁴²

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{10}$$

$$q_e = K_F \frac{1}{C_e^n} \tag{11}$$

Where K_L, q_e, C_e and q_m are the constant adsorption equilibrium (L mg⁻¹), the amount of adsorbate adsorbed per unit mass of solid at the time of t (mg g⁻¹), the equilibrium concentration and the maximum adsorption capacity, respectively. n and K_F are Freundlich constants in which the K_F and n indicates constants associated with the sorption capacity (mg/g) and intensity. In this study, two Langmuir and Freundlich models were selected to evaluate the amount of 2,4-DNP on microwaved sludge adsorbent and its equilibrium concentration in aqueous solution. Table 4 reveals the isotherm constants, and the adsorption information for 2,4-DNP follows the Freundlich isotherm well (Figure 8). The results of non-linear fitting for adsorbent follows Freundlich's model according to Figure 9. Table 5 compares the adsorption capacity of the adsorbent used in this study with other studies.

Table 4: Isotherms parameters for adsorption 2,4-DNP by microwaved adsorbent

Adsorbent	Isotherms					
	R^2	Langmuir b	q_{max}	R^2	Freundlich $1/n$	K_F
Microwaved sludge	0.9835	0.050	5.494	0.9933	0.60	0.411

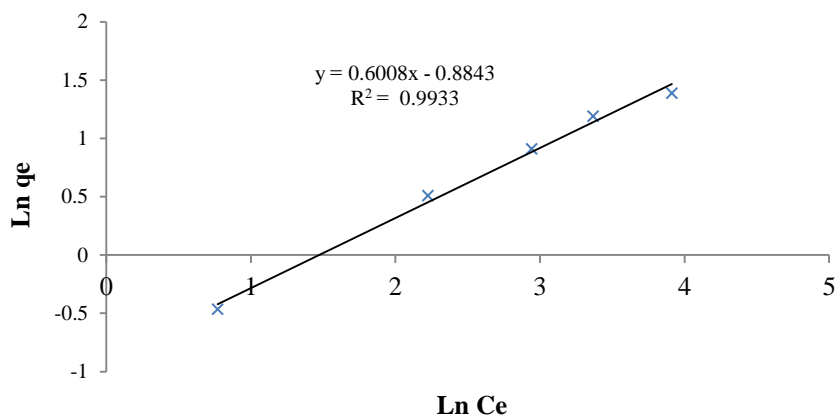


Figure 8: Freundlich isotherm for 2,4-DNP adsorption by microwaved sludge

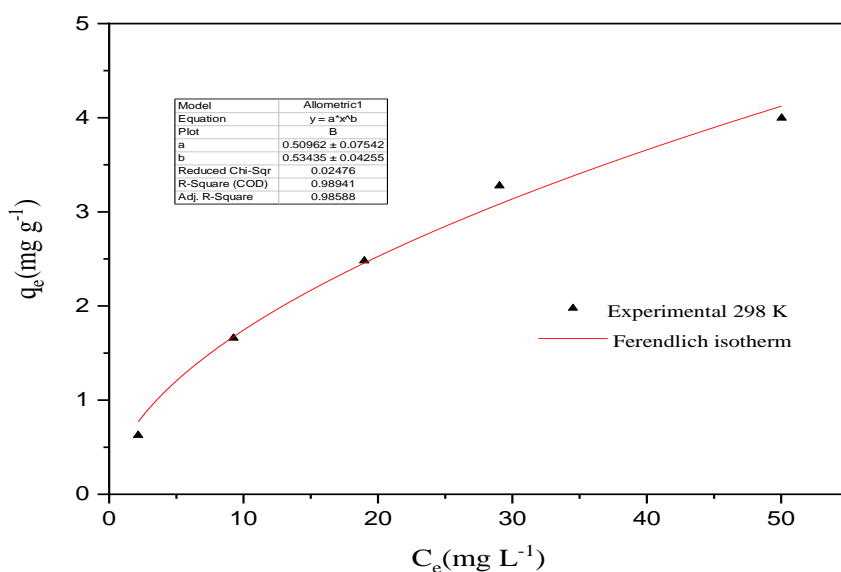


Figure 9: Non-linear diagram of Freundlich isotherm of the microwaved sludge

Table 5: Comparing different kinds of adsorbents in the absorption of 2,4-dinitrophenol

Adsorbent	q_{max} (mg/g)	Data sources
Powder activated charcoal	1.01	43
Activated carbon fibers	2.3	44
Imprinted polymer	2.9	45
Activated carbons	2.96	46
Microwaved adsorbent	5.5	This work

Discussion

In this study, It was determined that the removal rate raised by increasing the time and decreasing the primary concentration of 2,4-dinitrophenol. At the beginning of the adsorption process, because of the large number of adsorption places, there was a large concentration difference between the adsorbed material in the solution and its amount on the adsorbent surface. adsorption increases in the initial stages due to the increase in concentration difference⁴⁷. The findings showed that, the maximum removal efficiency was 60 min, and by increasing time, due to the accumulation of 2,4-dinitrophenol in the adsorption places, the adsorption rate decreased and reached a fixed amount in 120 minutes. The increase in mass creates a driving force, resulting in a velocity that results in the transfer of 2,4-DNP molecules from the high-concentration solution onto the particle surface⁴⁸.

The pH of the solution, in addition to the surface charge of the adsorbent, affects the chemistry of the solution, the separation of functional groups at the adsorbent places, and the ionization rate of the materials present in the solution⁴⁹. The results obtained from the experiment showed that the pH_{zpc} isoelectric point was 7.2 for the microwaved sludge. At a pH lower than pH_{zpc} , the adsorbed surface protonates and results in positive charges. The electrostatic force of the adsorbent surface attracts more phenolic compound, because it is a weak phenolic acid, so its decomposition in solution is strongly dependent on pH. At acidic pH, the adsorbent surface is surrounded by the carboxylate ions, and due to the anionic conditions of 2,4-DNP under these conditions, the electrostatic attraction between the adsorbent and the pollutant increases. However, at alkaline pH, the overall charge of the cells is negative and the binding and absorption sites of the adsorbent surface are reduced. It may be due to the negative load at the adsorbent surface and rivalry among OH^- ions and 2,4-dinitrophenol molecules for the adsorption places. At pH higher than pH_{zpc} , the dominant electrical charge on the adsorbent surface is negative and the number of negative charges

increases by increasing pH. Due to the anionic nature of 2,4-DNP, the electrostatic attraction between the pollutant and the adsorbent surface reduced and the adsorption efficiency decreased⁵⁰. Siva Kumar also reported similar results. He also attributed the effect of adsorption decrease by increasing pH on the adsorbent surface to the relationship between pH and electrical charge of the adsorbent surface⁵¹. As the primary concentration of pollutants increased, their removal percentage decreased but their adsorption capacity increased. This is probably due to the fact that by increasing the surface charge of the adsorbates on the adsorbent, the adsorption places of the upper surfaces on the adsorbent are saturated, and the removal efficiency of the adsorbent decreases⁵². The effect of adsorbent dose at different times indicates that removal efficiency Improves by increasing the adsorbent dosage. It is due to the presence of more accessible sites and higher surface area at higher dose values, with the highest removal rate being 1.5 g at adsorbent dose. Analyses have shown that adsorption capacity decreases by increasing adsorbent dose. These results have also been confirmed in other studies. In this study, lack of adsorbate agent in vacancies was the reason cited for decreased adsorption capacity^{53, 54}. Studies on the kinetics of adsorption of pollutant onto the microwaved adsorbent have shown that this process follows the pseudo-second-order kinetic. This model emphasizes on the hypothesis that the rate-determining stage of the reaction may be the chemical adsorption.

It involves the valency force through the sharing or exchange of electrons between the adsorbent and the adsorbate⁵⁵. In this study, the best correlation coefficient created by the non-linear method was in pseudo-second order kinetic.

Darwishi et al. investigated the adsorption of cadmium on dried extruded sludge. They reported that cadmium adsorption onto dried sludge followed a pseudo-second-order kinetic and chemical reactions determined the reaction rate¹⁸. Findings created in this study indicated that the absorption of pollutants in linear and non-linear techniques follows Freundlich studies. This

isotherm shows the adsorption of multilayer in the adsorbent⁵⁶. The linear graph $\log q_e$ against $\log c_e$ is used to show the Freundlich coefficients KF and $1/n$. Table 5 compares the studied adsorbent with other adsorbents used to remove 2,4-dinitrophenol from Synthetic solution. The studies mentioned in this table show that the microwaved adsorbent used in this study has a higher absorption capacity and efficiency in removing contaminants than other studies.

Conclusion

In this study, it was found that the maximum rate of 2,4-dinitrophenol adsorption onto the microwaved sludge adsorbent was 60 min, and over time, the removal efficiency gradually decreased until it reached an almost constant rate, so that this equilibration time was 120 min. The removal efficiency of 2,4-dinitrophenol was highly dependent on pH. The maximum removal percentage was obtained at $pH = 7$, and the removal efficiency decreased with higher slope in pH less than 7 and decreased with lower slope in pH greater than 7. The results obtained from investigating the effect of concentration changes on removal rate showed that the removal rate of 2,4-dinitrophenol decreased as the concentration of 2,4-dinitrophenol increased. With respect to the effect of the adsorbent dose, it was found that the removal rate of 2,4-DNP increased by increasing the concentration of 2,4-DNP. Increasing the adsorption capacity by increasing the concentration of 2,4-DNP indicated that the microwaved sludge was a suitable adsorbent for the elimination of this pollutant from Synthetic solution. In kinetics studies, the results of experiments for 2,4-DNP followed the pseudo-second-order kinetics equations. Finally, the results of equilibrium studies showed that the removal of 2,4-DNP followed the Freundlich isotherm.

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Conflict of interest

The authors declare that there is no conflict of interest.

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