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Recommended Citation

Alhamd, Salem Jawad; Abbas, Mohammed Nsaif; Jawad Al-Fatlawy, Hassan Jameel; Ibrahim, Thekra Atta; and Abbas, Zaid Nsaif (2024) "Removal of phenol from oilfield produced water using non-conventional adsorbent medium by an eco-friendly approach," *Karbala International Journal of Modern Science*: Vol. 10 : Iss. 2 , Article 4.

Available at: <https://doi.org/10.33640/2405-609X.3350>

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Keywords

Adsorption, mandarin peels, oilfield produced water, phenol, zero residual level (ZRL)

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RESEARCH PAPER

Removal of Phenol From Oilfield Produced Water Using Non-conventional Adsorbent Medium by an Eco-friendly Approach

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Keywords: Adsorption, Mandarin peels, Oilfield produced water, Phenol, Zero residual level (ZRL)

1. Introduction

A myriad of environmental challenges has overshadowed the natural resources of the Earth. Water, being a primary resource, is undergoing significant repercussions in different regions of the world [1]. Securing water fit for human consumption or use has grown progressively challenging and expensive, driven by the scarcity of fresh water sources and their declining quality,

exacerbated by the continuous expansion of the global population [2]. Hence, there is a need to explore sustainable water sources and implement effective solutions for treating polluted water [3]. One of the most crucial sources of sustainable water is generated water, which is abundantly present in oil-producing nations, especially in arid areas like the East, where water supplies are notably limited [4]. Produced water refers to the considerable quantity of wastewater that is separated from the oil

Received 24 January 2024; revised 23 March 2024; accepted 27 March 2024.
Available online 7 May 2024

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<https://doi.org/10.33640/2405-609X.3350>

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and gas extracted from underground formations. It naturally arises under elevated temperatures and pressures, being brought to the surface together with hydrocarbons during extraction. This wastewater represents a byproduct closely linked with oil and gas operations [5]. The composition of produced water displays considerable variation, affected by factors such as the location of gas production sites, the geographical positioning of oil extraction, specific geological formations, extraction methods, reservoir lifespan, and the concurrent operation of multiple wells extracting water [6]. This type of water contains a wide range of organic and inorganic compounds such as aliphatic and aromatic hydrocarbons including benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs), phenols, corymbos substance and soluble salts as well as various kinds of heavy metals such as barium, uranium, cadmium, chromium, lead ... etc. originating from the formations and from the water injections [7]. Additionally, various cations such as magnesium, calcium, and sodium, alongside anions like carbonate, chloride, sulfate, and others, as well as residual chemical substances, may be present. Consequently, the wastewater produced constitutes the primary waste stream originating from oil and gas operations [6]. The history of produced water is closely linked to the development of oil and gas extraction. From the inception of the petroleum industry, the concurrent extraction of water and hydrocarbons has presented an enduring challenge. As oil production has expanded globally, the volume of produced water has correspondingly grown [7]. The proportion of produced water to oil varies among wells and over their operational lifetime, typically ranging from 3 to more than 20 in specific regions globally [6]. Globally, the produced water was increased from 95,000 million barrels per day (mmb/d) in 2010 to 158,900 million barrels per day (mmb/d) in 2020 and expected reaching close to 240,000 million barrels per day (mmb/d) in 2030. The predicted rise in produced water primarily due to two reasons: (i) increased oil/gas output and (ii) increased oil/gas field age by these two variables the rise in produced water is expected to be higher than the current levels [8]. The substantial quantity of wastewater presents a legitimate environmental apprehension due to its content of detrimental substances. Among the notable pollutants frequently present in produced water, phenols emerge as a particularly significant concern [9]. Phenol, an organic compound, can be found in various types of produced water. Some phenol compounds are essential raw

Nomenclature:

b	Adsorption heat constant ($\text{J}\cdot\text{mol}^{-1}$)
C_e	Equilibrium concentration of adsorbent ($\text{mg}\cdot\text{l}^{-1}$)
C_i	Initial concentrations of adsorbent ($\text{mg}\cdot\text{l}^{-1}$)
C_f	Final concentrations of adsorbent ($\text{mg}\cdot\text{l}^{-1}$)
I	Constant of intra-particle diffusion model ($\text{g}\cdot\text{mg}^{-1}$)
K_F	Freundlich constant [$(\text{mg}\cdot\text{g}^{-1})\cdot(\text{l}\cdot\text{mg}^{-1})^{1/n}$]
K_L	Constant of Langmuir isotherm model ($\text{l}\cdot\text{mg}^{-1}$)
K_T	Temkin constant ($\text{l}\cdot\text{g}^{-1}$)
k_1	1 st order rate constant (min^{-1})
k_2	2 nd order rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)
k_{ad}	Adsorption equilibrium coefficient (–)
k_p	Intra-particle diffusion rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-0.5}$)
m	Mass of adsorbent media (g)
n	Adsorption intensity of Freundlich isotherm model (–)
q_e	Capacity of adsorption at equilibrium ($\text{mg}\cdot\text{g}^{-1}$)
q_{max}	Maximum capacity of adsorption ($\text{mg}\cdot\text{g}^{-1}$)
q	Capacity of adsorption at any time ($\text{mg}\cdot\text{g}^{-1}$)
%R	Is the percentage removal (–)
R	Universal gas constant ($8.3144 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
T	Absolute temperature (K)
t	Time of adsorption (min)
V	Volume of solution (l)
α	Initial rate of adsorption ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)
β	Desorption constant ($\text{g}\cdot\text{mg}^{-1}$)
ΔH	Enthalpy change ($\text{J}\cdot\text{mol}^{-1}$)
ΔS	Entropy change ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
ΔG	Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$)

materials in the antiseptic, germicide, and adhesive industries. Phenol and its derivatives present potential risks, with varying levels of toxicity depending on the specific type of phenol. Certain phenol compounds have been classified as “priority pollutants” by the US-EPA and EEC due to their potential threat to human and animal life at specific concentration levels [7,10]. In produced water, the origin of phenol, is natural, with transportation to the surface occurring through formation water. The concentration of phenols in produced water varied from 0.009 mg/l [9] to 43 mg/l [11]. Progress in water treatment technology, combined with an increased emphasis on environmental stewardship, has motivated ongoing efforts to develop efficient treatment approaches for produced water. This evolution seeks to shift it from a complex byproduct to a sustainable water resource, particularly vital in dry regions [10].

Various papers studied removal of phenol from aqueous solutions [12], domestic wastewater [13], oil refinery effluents [14], pharmaceutical industries [15] using different types of materials such as nanoparticles [16] or activated sludge [17]. Furthermore, numerous treatment methods, including

chemical precipitation, ultrafiltration, ion exchange, nanofiltration, reverse osmosis, flocculation, coagulation [18], flotation, ozone oxidation, and biological treatment, represent examples of traditional techniques employed in the treatment of produced water [19]. However, these methods come with various limitations, including limited efficiency in removing contaminants, increased operational costs, generation of sludge, and potential requirements for specialized equipment. Conversely, adsorption stands out as a widely adopted treatment approach for purifying produced water. This technique boasts lower energy consumption, ease of application, and moderate to high efficiency in contaminant removal [20]. The adsorption technique proved its ability to remove various types of contaminants like heavy metals including chromium [21], antimony [22], copper [23], nickel [24], molybdenum [25], and thallium [26]. Also, organic acids [27], non-organic toxic [28], dyes [29], and hardness [30] can be successfully removed from aqueous solution by this impressive technique. Not only for contaminated water, but adsorption were also used to remove organic matter [31] and toxic metals [32] from soil and sulfur ions from light [33] and heavy [34] petroleum fractions. Activated carbon is a widely acknowledged material for adsorption, extensively utilized in the treatment of various pollutants due to its distinctive properties, which encompass a high surface area and pore structure [35]. Nevertheless, this platform presents specific constraints, which have led researchers to investigate alternative options. Challenges associated with utilizing activated carbon in adsorption encompass exorbitant production expenses, the requirement for periodic regeneration, and considerable losses incurred during each regeneration cycle [36]. One viable option included agricultural and industrial residues, known for their accessibility, affordability, direct applications, and moderate effectiveness in treating various water pollutants [37]. Rice husks [38], orange peels [39], watermelon rinds [40], lemon peels [41], eggshell [42], banana peels [43], waste tea leaves [44], water hyacinth [45], aluminum foil [46], tree leaves [47], pomegranate peels [48], and others wastes are proved attractive activity to use as adsorbent. While the sole challenge encountered in the implementation of this advanced technique is the accumulation of residues post the adsorption process, this obstacle can be overcome by embracing the concept of zero residues level (ZRL) [49]. ZRL consider the wastes are sustainable source not problem. By this concept the residues of adsorption are converted to fertilizer [50], pesticide [51], concrete additives [52], bioethanol [53] and

useful substance [54], or benefit materials [55]. As previously discussed, when treated to meet agricultural or drinking water standards, produced water emerges as a substantial water source, especially vital for arid regions like Middle Eastern countries. This study aims to apply the Zero Residue Level (ZRL) approach in treating produced water by investigating the feasibility of utilizing mandarin peels, a readily available agricultural by-product, for the removal of the hazardous contaminant phenol from produced water. This is achieved through batch adsorption experiments conducted using simulated aqueous solutions, under different experimental parameters. The resulting residues are then repurposed to create a valuable material.

2. Materials and methods

2.1. Collecting of real produced water

During April–August, 2023 several samples were collected of produced water from three Iraqi oil field according to the method described by (Abbawi and Hassan, 1990) [56] through taking a clean and sterile 1L bottle and submerging it in the produced water collection basin. The sample taking covered tightly, then wrapping it by two layers of aluminum foil, recording the sample number and the date of its withdrawal. The samples were taken from Baba Gur-Gur, Al-Ahdab, and Al-Zubair oilfields; in Northern, central and southern of Iraq, respectively. The samples collected were transported as soon as possible to the laboratory for analysis of their composition. The laboratory test of the phenol was performed accurately and in triplicates, and the average of measurements was taken. The analysis of phenol concentration in the collected produced water was conducted using the method described by (Tabaraki and Heidarizadi, 2019) [57]. The tests show that it was less than 10 mg/l of phenol in all samples examined. However, from a review of the literature, it was found that the concentration of phenol in the produced water ranges from 0.009 to 43 mg/l as mentioned by (Miranda et al., 2022) [9] and (Ekins et al., 2005) [11], respectively. Thus, the concentration of phenol investigated in adsorption experiments of this study is ranged between 0.005 and 50 mg/l, to include wide range of pollution.

2.2. Materials

The chemicals and materials employed in this study included Liquid phenol AR of a chemical formula C_6H_5OH , having a purity of 99.5%, which was supplied by Central Drug House, CDH India.

The solutions of pH adjustment, i.e., sodium hydroxide (NaOH) pellets with a purity of 99.99% and hydrochloric acid (HCl) with a purity of 37% were purchased from MERCK Company, Germany. All of these materials were used without further treatment. Double distilled water used in the experimental procedures was prepared in the laboratory using a distillation unit (2014 GFL Double distiller apparatus, Germany) at room temperature.

2.3. Mandarin peels adsorbent

The Iraqi origin mature mandarin peels of scientific name *Citrus reticulata* used in this investigation were obtained from grocery retail store in Baghdad. Subsequently, the collected peels, in their original size, underwent three washes with tap water and soaked in distilled water overnight to get rid of any impurities or dust might be adhering to them. The cleansed peels were naturally dried over several days by exposure to fresh air and sunlight in September, where the weather temperature ranges between 25 and 30 °C. After that, the peels underwent drying by oven using (TR 450 drying oven-Nabertherm, Germany). The oven temperature commenced at the laboratory temperature and gradually increased until reaching 50 °C. The drying process persisted until the peel weight stabilized. Finally, the clean and dried peels were manually crushed using a 200 ml volume laboratory ceramic mortar and pestle with a rough friction surface (Rotilabo®, Carl ROTH, Germany). The clean and dried peels were stored in amber glass jars, covered with aluminum foil and kept in a dry place until used.

2.4. Determination of the point of zero charge (pH_{PZC})

The pH_{PZC} , an important parameter governing the reactivity and adsorption characteristics of the adsorbent, was determined using the solid addition method—a foundational technique in surface chemistry and adsorption investigations according to the method described by Mondal and Kar (2018) [58]. This method establishes the pH at which the surface of adsorbent carries no net charge. A series of 100 ml Pyrex™ Borosilicate Glass Erlenmeyer Flasks, equipped with screw caps, were utilized to prepare suspension solutions. In each flask, 100 ml of 0.01 N KNO_3 solution—prepared in advance—was introduced, and the pH of each solution was measured using the HI-83141-1 pH Meter from Hanna-USA, accurately adjusted to cover a range from pH 1 to 14. This adjustment was accomplished

by judiciously utilizing either 0.1 N HCl or NaOH solutions, establishing these pH values as the initial conditions. Subsequently, one gram of finely ground mandarin peel samples (45 mesh), pre-dried, was added to each flask under controlled conditions using a hotplate magnetic stirrer (C-MAG MS 7, IKA™) operating at 200 rpm and ambient temperature. Stirring continued for 15 min to ensure a uniform suspension. After mixing, the flasks were sealed promptly with aluminum foil and securely fastened with rubber bands to prevent localized variations in pH measurements. For consistent conditions, the flasks with the suspension underwent overnight agitation in an orbital water bath shaker (Marshall Scientific Barnstead MaxQ 7000) at a constant temperature of 25 °C and an agitation speed of 100 rpm. After a 24-h equilibration period, the average pH values were determined based on five separate measurements of the liquid supernatant to ensure the accuracy and reliability of the obtained pH_{PZC} value.

2.5. Stock solution of phenol

Avoiding to any additional pollutants or materials that could affect the accuracy and quality of the results, the adsorption experiments were carried out by preparing previously prepared simulated solutions with the required concentrations, by preparing a stock solution of 1000 ppm of phenol concentration. Amount of 1 g \approx 0.9346 ml of liquid phenol was dissolved in one liter of double distilled water prepared by distillation apparatus of a type (GFL Double Distiller, 2014). The dissolving process was conducted by a magnetic mixer of type (Fisher Scientific, IKA™ C-MAG MS 7) for 15 min at room temperature. The concentration of prepared stock solution was 1000 ppm, i.e. each 1 ml of the stock solution contains 1 mg of phenol.

2.6. Calibration curve

The stock solution and the solutions of adsorption-treated were tested by UV/VIS spectrophotometer device (Shimadzu UV-1800 spectrophotometer, Japan) with the assistant of the calibration curve graphed previously prepared for this goal. The purpose of the calibration curve is to detect the concentration of phenol remaining in the solution after the end of the adsorption process in order to determine the value of the percentage removal and to determine the efficiency of the adsorbent material by calculating the adsorption capacity. The calibration curve was prepared by the method described by Ref. [59] through examining several known

concentrations of phenol solution at a wavelength of 270 nm, and then by recording the level of absorbance, the correction curve was drawn. Each concentration was rechecked at least triplicate to reduce the percentage error and record the average results. Fig. 1 shows the calibration curve prepared and used to determine the concentrations of phenol in this study.

2.7. Adsorption unit

This study systematically investigated six crucial design parameters to identify the optimal conditions for eliminating phenol from aqueous solutions simulating “real oilfield produced water”. The treatment process was conducted in a batch-type adsorption unit utilizing mandarin (*C. reticulata*) peels as the adsorbent material. The batch adsorption unit stands out as one of the simplest and most effective types, characterized by its suitable size, portability without the need for reconstruction, low energy consumption, absence of preliminary preparations, and minimal additional equipment requirements. Moreover, it boasts low operational costs in comparison to continuous adsorption units. This approach facilitates the acquisition of useful and precise results using small, limited volumes of contaminated solutions, providing a contrast to continuous systems that necessitate large and continuous quantities of contaminated solutions. The experiments adsorption were conducted via benchtop orbital digital water bath shaker (Thermo-Fisher SHKE7000 MaxQ 7000) using 100 ml

Erlenmeyer flask with screw cap (Witeg Labor-technik GmbH) completely covered with aluminum foil to ensure there isn't any effect of the light on the content of flasks.

The pH of the solutions were adjusted by 0.1 N solution of sodium hydroxide (NaOH) as a base or hydrochloric acid (HCl) or as an acid respectively. After preparing the required phenol concentration and setting the agitation speed and unit temperature, a predetermined dose of adsorbent was introduced into the flask to initiate the adsorption experiment. The experiment continued until the specified time was reached. Subsequently, the samples underwent filtration using Whatman® qualitative filter paper. The remaining phenol concentration was measured using a UV-VIS spectrophotometer and a calibration curve. To ensure precision, each experiment was replicated three times, and the average value was computed. The studied design factors included pH, agitation speed, initial concentration, adsorbent dose, contact time, and temperature, with variations in the ranges of 1–12, 100–500 rpm, 0.005–50 mg/l, 0.5–5.0 g, 10–180 min, and 20–50 °C, respectively. According to the spectrophotometer measurements, the calculation of adsorption efficiency and capacity can be achieved via equations (1) and (2), respectively [60]:

$$\%R = \frac{C_{Ads}}{C_o} = 1 - \frac{C_f}{C_o} \quad (1)$$

$$q = \frac{V}{m} \cdot C_{Ads} \quad (2)$$

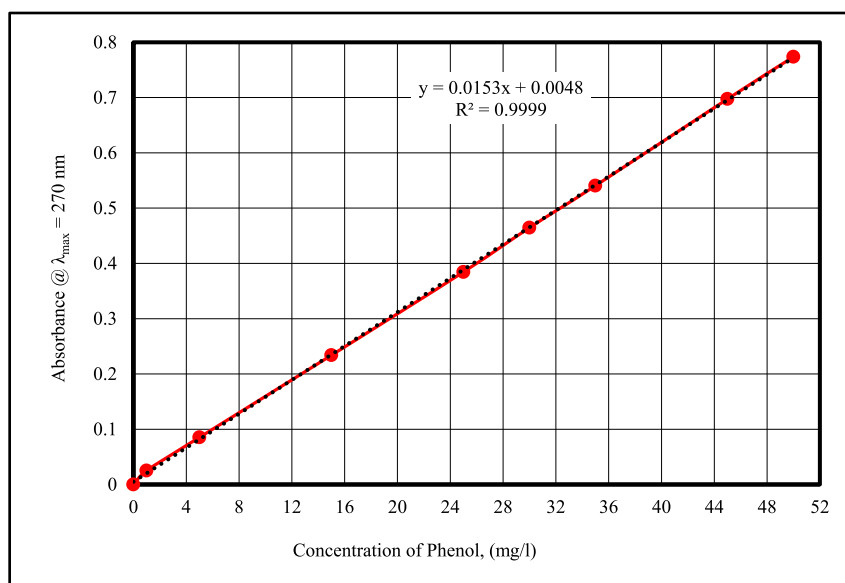


Fig. 1. Calibration curve of phenol concentration using UV-VIS Spectrophotometer applied in the current study.

3. Results and discussion

3.1. Point of zero charge (pH_{PZC})

The determination of the point of zero charge (pH_{PZC}) for mandarin peels was conducted using alkali metal nitrate, particularly potassium nitrate (0.01 N), as is customary for such estimations. The pH_{PZC} values, crucial for pinpointing where the resulting curves intersect with the pH_0 axis, were identified for mandarin peels, with a recorded pH_{PZC} value of 6.4, as illustrated in Fig. 2. This value holds significance in predicting the surface charge of the adsorbents. Specifically, when adsorption takes place at a pH below the point of zero charge of the adsorbent, the surface will be positively charged. Conversely, if adsorption occurs above the pH at the point of zero charge, the adsorbent surface will carry a negative charge. The relationship between ΔpH and pH_{PZC} for mandarin peel is depicted in Fig. 2.

3.2. Influence of pH

The pH level of a solution plays a significant role in determining the adsorption efficiency of the entire system. The interactions between the adsorbent and adsorbate are notably impacted by the pH of the solution, given its influence on the extent of dissociation and ionization of the adsorbate molecules, alongside the resulting charge on the adsorbent surface. This investigation delved into the adsorption of phenol on mandarin peels across a pH levels spanning from 1 to 12, at agitation speed of 450 rpm, initial phenol concentration of 10 mg/l,

mandarin peel quantity of 1 g, contact time of 180 min, and a temperature of 20 °C with the outcomes depicted in Fig. 2. The efficiency of adsorption is prominently pronounced in acidic conditions, showing a gradual decline post $pH = 1$, stabilizing around the pH range of 6–7. Conversely, in an alkaline setting, a gradual decrease in adsorption effectiveness is evident, with the lowest observed efficiency occurring at the highest alkaline pH of 11. The logarithmic representation of the acid dissociation constant signifies the molecular state of the adsorbate in the solution. Consequently, in a solution where the pH is below the pK_a value of phenol ($pK_a = 10$), the molecule persists in a non-dissociated, protonated state. Conversely, when the solution pH surpasses the pK_a value, the adsorbate adopts a dissociated form, transforming into a negatively charged phenolate ion ($C_6H_5O^-$). As previously indicated, the pH of a solution plays a role in determining the charge on the adsorbent surface. This characteristic is effectively captured by the point of zero charge (pH_{PZC}), denoting the pH value at which the surface charge is neutral. The determined pH_{PZC} for mandarin peels stands at 6.6. In solutions with a pH below this value, the adsorbent surface carries a positive charge, while in solutions with a pH exceeding pH_{PZC} , the surface acquires a negative charge. The determined pH_{PZC} for mandarin peels is approximately 6.6. This indicates that in an acidic environment, the surfaces of the mandarin peels will carry positive charges. Conversely, in an alkaline environment, characterized by a pH greater than the pH_{PZC} , a negative charge will be present on the surfaces of the

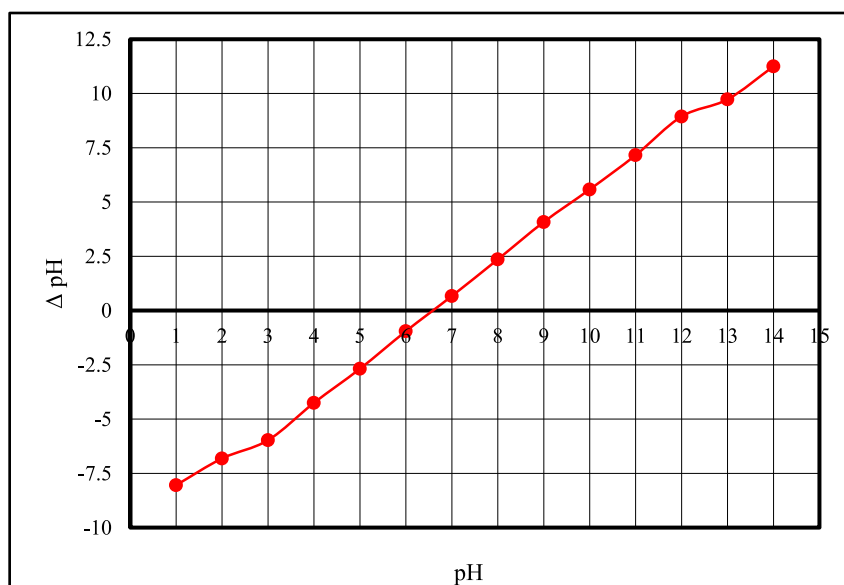


Fig. 2. Point zero charge pH_{ZPC} analysis of mandarin peels.

mandarin peels. The relationship depicted in Fig. 3 reveals a preference for adsorption in an acidic setting, implying that the interaction between non-dissociated (protonated) adsorbate molecules and the positively charged surface of each adsorbent is most favorable. Conversely, the least efficient adsorption occurs in an environment with a pH of 11, where phenol molecules exist as phenolate anions, and the surface of the adsorbent material carries a negative charge. In such circumstances, repulsion occurs between the negatively charged adsorbate ions and the negatively charged surface of the adsorbent, leading to a decrease in adsorption efficiency. Consequently, the adsorption of phenol on mandarin peels is governed by the electrostatic interactions—whether attractive or repulsive—between the adsorbate and the adsorbent. Comparable phenomena have been observed in the adsorption of phenol using *Ulva lactuca* algae [10].

3.3. Influence of agitation speed

*Special description of the title. (dispensable).

The investigation into the effect of agitation speed involved altering its range from 100 to 500 rpm, at pH of 1, initial phenol concentration of 10 mg/l, mandarin peel quantity of 1 g, contact time of 180 min, and a temperature of 20 °C. Fig. 4 illustrates the impact of agitation speed on the efficiency of phenol adsorption removal using mandarin peels as adsorption medium. The depicted figure underscores a clear and direct correlation between the efficiency of phenol removal and the agitation speed

of the solution, revealing a notable increase with higher speeds. This noteworthy observation can be attributed to the interplay of two pivotal factors that intricately influence the adsorption process. Firstly, the heightened agitation speed facilitates the enhanced diffusion of phenol ions from the aqueous solution towards the adsorbent material, which, in this case, is mandarin peels. The vacant active sites within the porous structure of mandarin peels, capable of attaching phenol via functional groups on their surfaces, play a crucial role in this phenomenon. Furthermore, as agitation speed rises, the turbulence within the solution induces a reduction in the thickness of the boundary layer enveloping the particles of the adsorbent media. This phenomenon holds important effect for the adsorption process. The reduction in the boundary layer thickness is instrumental in facilitating more facile access to the active sites on the surface of the adsorbent material, thereby promoting a heightened efficacy in the adsorption of phenol [58]. The relation between increased agitation speed and boundary layer thickness elucidate the optimized conditions for phenol removal. At elevated agitation speeds, the enhanced convective mass transfer accelerates the diffusion of phenol molecules toward the adsorbent material. Simultaneously, the decreased boundary layer thickness minimizes the mass transfer resistance, ensuring that a greater number of phenol ions can readily access the available active sites on the adsorbent surface. This result confirmed the important role of agitation speed in dictating the efficiency of phenol removal. As can be seen from

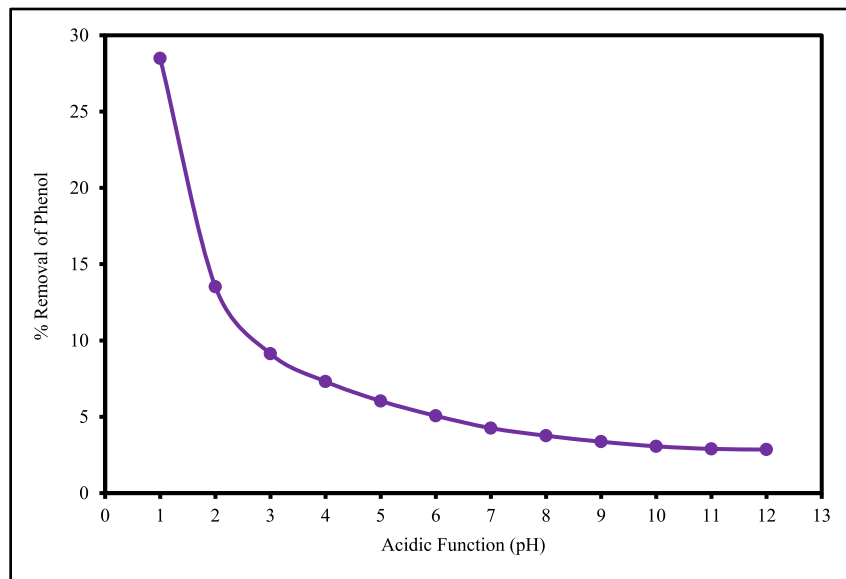


Fig. 3. pH influence on the removal efficiency of phenol using mandarin peels.

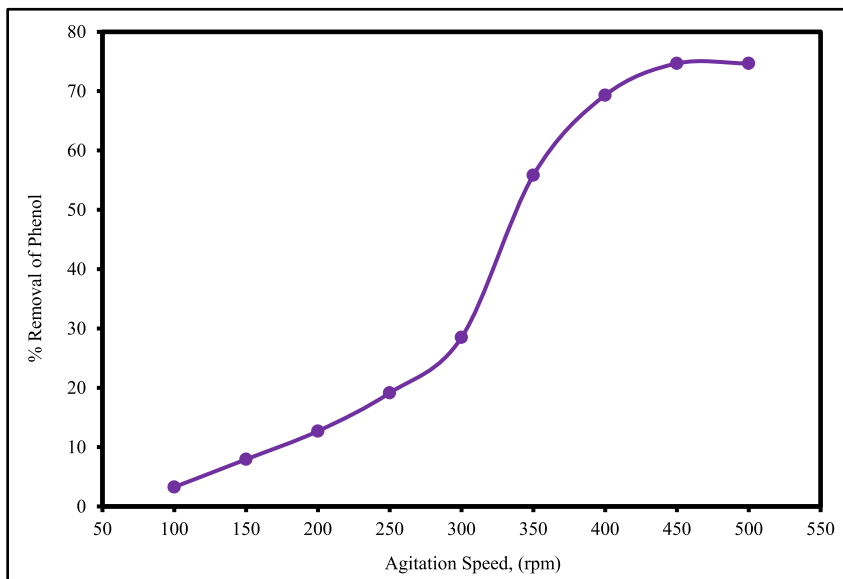


Fig. 4. Agitation speed influence on the removal efficiency of phenol using mandarin peels.

Fig. 3, the optimum agitation speed is 450 rpm and surpassing this value does not yield further enhancement in adsorption efficiency using the adsorbent biomass. This implies a state of saturation, signifying the optimal speed for phenol adsorption using mandarin peels is 450 rpm. This result agrees with [30].

3.4. Influence of initial concentration

The results indicate that the utilization of mandarin peels as an adsorbent led to a decrease in the

percentage of phenol removal from contaminated solutions as the initial concentration increased. Keeping other variables constant at agitation speed of 450 rpm, pH of 1, mandarin peel quantity of 1 g, contact time of 180 min, and a temperature of 20 °C, as illustrated in Fig. 5, this decline can be explained by the limiting impact of the initial phenol concentration on the removal capacity. In essence, the adsorbent medium has a finite number of adsorption sites, reaching to saturation at a specific phenol concentration. Consequently, an increased number of phenol molecules compete for the available

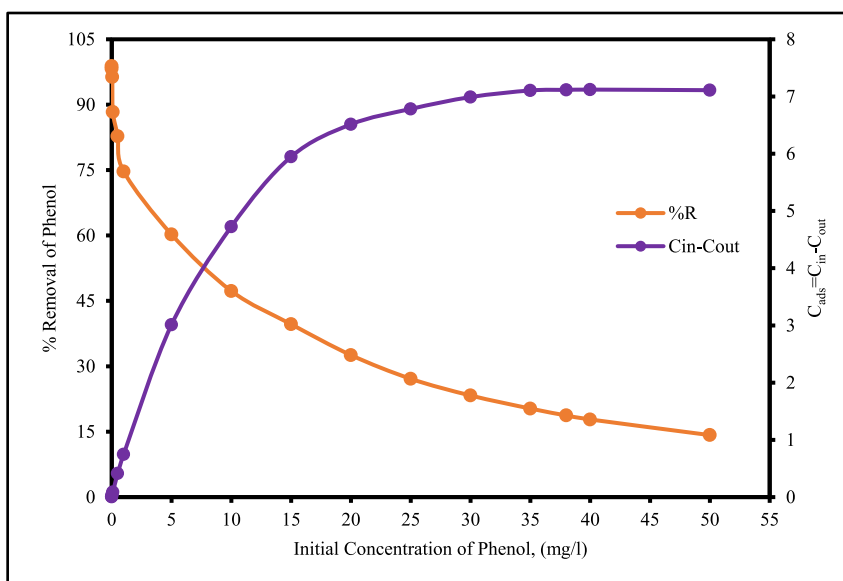


Fig. 5. Initial concentration influence on the removal efficiency of phenol using mandarin peels.

adsorption sites on the surface of adsorbent medium. Solutions with low concentration contain fewer phenol molecules compared to those of higher concentration, resulting in decreased removal efficiency with an increase in the initial concentration. The highest percentage removal was observed at 98.86% for an initial phenol concentration of 0.005 mg/l and 14.22% at 50 mg/l. Furthermore, the adsorption concentration increase with the initial concentration until reaching a constant value at 38 mg/l due to equilibrium state. Mandarin peels demonstrated effectiveness in efficiently removing polluted phenol from aqueous solutions at an optimal concentration of 38 mg/l. A study by Ref. [38] yielded results similar to those of the current investigation.

3.5. Influence of adsorbent dose

Examining the influence of mandarin peel dosage on the sorption efficiency of phenol was conducted within the 0.5–5.5 g mandarin peel range, while maintaining other operational parameters constant at agitation speed of 450 rpm, initial phenol concentration of 38 mg/l, pH of 1, contact time of 180 min, and a temperature of 20 °C. The findings from this study unveil a direct correlation between the efficiency of phenol removal and the mass of the adsorbent medium. Notably, a reduction in mandarin peel amount in the adsorption unit resulted in a decrease in phenol adsorption capacity, as clarified in Fig. 5. Conversely, the peak phenol adsorption efficiency was observed at 5 g. This observation

aligns with the significance of active sites within the adsorbent material; wherein lower adsorbent amounts correspond to a reduced surface area and availability of active sites. Consequently, fewer phenol molecules are adsorbed from the pollutant solution on the surface of the adsorption medium compared to higher adsorbent dosages. It is also evident that increasing the dose of mandarin peels beyond 5 g has no effect on the adsorption efficiency, a result attributable to equilibrium state at these conditions. Fig. 6 also indicates that the maximum adsorption capacity is 0.72 mg/g, achieved at an adsorption dose of half a gram. Subsequently, adsorption capacity starts to decrease according to the adsorption capacity law according to Equation (2), where the adsorption capacity is inversely proportional to the amount of the adsorbent material. Thus, the optimum dose of mandarin peels for achieving the maximum removal of phenol molecules from contaminated water solutions was identified as 5 g. The results depicting the effect of the adsorbent dose are illustrated in Fig. 6. Similar results have been reported by Ref. [49].

3.6. Influence of contact time

Fig. 7 illustrates the impact of contact time on phenol removal efficiency from simulated aqueous solutions, with other variables held constant at agitation speed of 450 rpm, initial phenol concentration of 38 mg/l, pH of 1, adsorbent dose of 5 g, and a temperature of 20 °C. The outcomes revealed that as the contact time increased, phenol removal

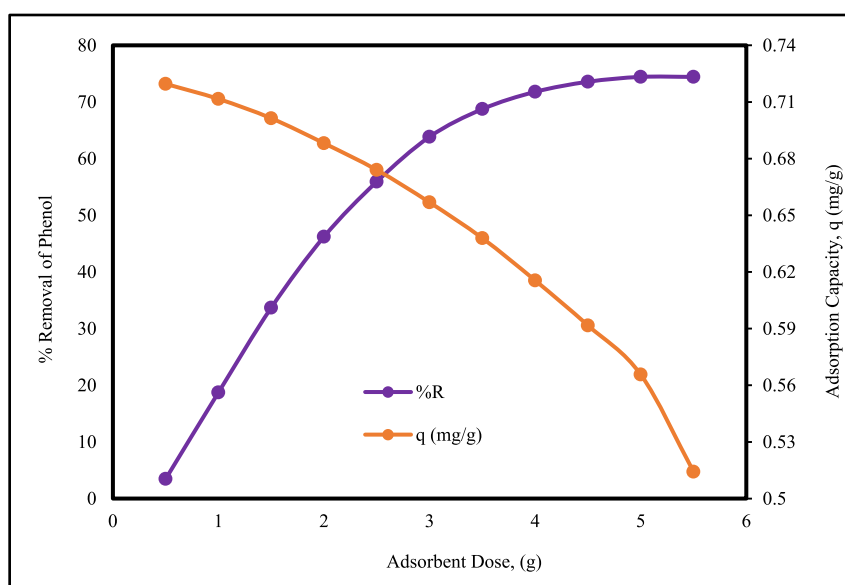


Fig. 6. Dose of mandarin peels influence on the removal efficiency of phenol.

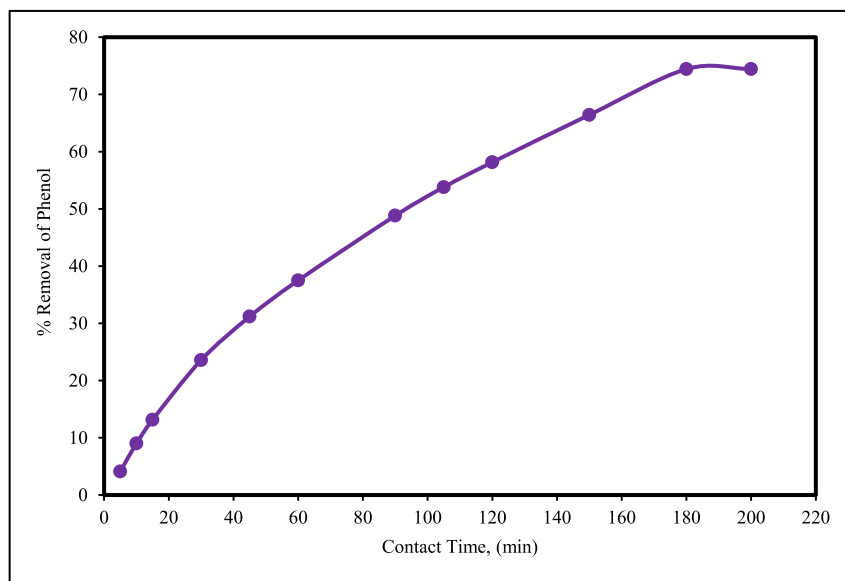


Fig. 7. Contact time influence on the removal efficiency of phenol using mandarin peels.

efficiency also increased, reaching constancy at 180 min. This phenomenon is ascribed to the prolonged exposure of the polluted solution to treatment and the consistent agitation speed of the shaking with the mandarin peels. The extended contact allowed mandarin peels to absorb more phenol molecules from the simulated contaminated solution, resulting in the continuous recovery of phenol until equilibrium was achieved at 180 min. After this time, no further ions were adsorbed despite an increase in contact time. This result is explained by the initially abundant active sites on the surface of biosorbent material (mandarin peels), which gradually decreased as they became filled with adsorbed ions. The diminishing number of active sites persists until saturation, establishing an equilibrium where the ions attaching to the surface by adsorption equals that of leaving it. An identical result was concluded by Ref. [43].

3.7. Effect of temperature

The effect of changing temperature on the adsorption efficiency of phenol using mandarin peels as an adsorbent was conducted in the range of 20–55 °C, keeping all other variables constants at agitation speed of 450 rpm, initial phenol concentration of 38 mg/l, pH of 1, contact time of 180 min, and adsorbent dose of 5 g. The behavior of phenol recovery from polluted solution due to altering this operating factor was illustrated in Fig. 8. It's obvious from this figure that there is an inversely relation between the removal efficiency and temperature, and the maximum efficiency was achieved at lower

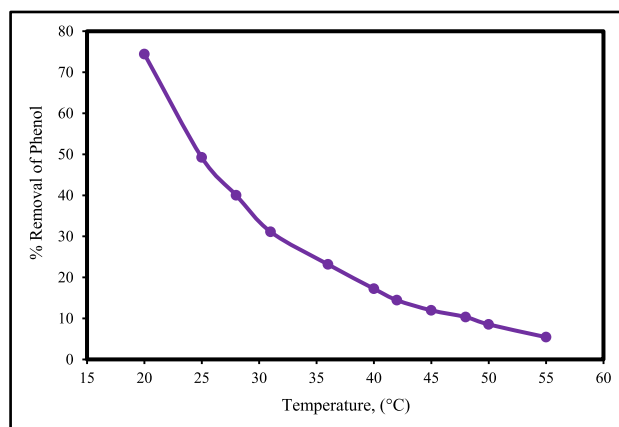


Fig. 8. Temperature influence on the removal efficiency of phenol using mandarin peels.

temperature. The decline in phenol adsorption efficiency from polluted solutions using mandarin peels at elevated temperatures can be ascribed to various factors. Firstly, higher temperatures may accelerate desorption kinetics, leading to a faster release of adsorbed phenol molecules from the mandarin peels. Additionally, increased temperatures can promote competitive reactions that interfere with the adsorption process, complicating the binding of phenol to the mandarin peels. The raise in temperature may be changed the properties of the adsorbent, which could affect surface characteristics and the sites available for phenol adsorption. Moreover, higher temperatures promote the solubility of phenol (82.8 mg/l at 20 °C and 117.7 mg/l at 50 °C). So, reducing the concentration of phenol accessible for adsorption onto the mandarin peels.

This aligns with the thermodynamic principles governing the adsorption process. These results are consistent with many results such as [10].

4. Adsorption behavior

4.1. Adsorption isothermal study

In this investigation, three renowned isotherm models—Langmuir, Freundlich, and Temkin—are employed to elucidate the connection between concentration and the adsorbent amount during the equilibrium state, a relationship known as the adsorption isotherm [46]. These models are utilized to ascertain the isothermal correlation of phenol adsorption from aqueous solutions using mandarin peels as a cost-effective medium.

4.1.1. Langmuir isotherm model

It embodies a semi-empirical correlation derived from a proposed kinetic mechanism of particles (e.g., molecules, ions, etc.). This model presupposes the homogeneity of the adsorption surface, non-reactivity among adsorbed particles, and the formation of a monolayer and its equivalency during adsorption. The mathematical expression of the Langmuir isotherm model of adsorption is articulated by equation (3), with its linear form presented in equation (4). An integral feature of this model is its capability to ascertain the preferential nature of adsorption, detected by the separation factor R_L , which is determined using Equation (5).

$$q_e = \frac{q_{max} \cdot k_L C_e}{1 + k_L C_e} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_{max} k_L} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (4)$$

$$R_L = \frac{1}{1 + k_L C_e} \quad (5)$$

The constants of this isotherm model can be calculated from the slope and intercept of graphical representing of dependent and independent variables of Equation (4) and Fig. 9. Thus, when plotting $(1/q_e)$ vs. $(1/C_e)$, the slope and intercept are $(1/K_L q_{max})$ and $(1/q_{max})$, respectively.

4.1.2. Freundlich isotherm model

The Freundlich isotherm model acts as an empirical template depicting the mathematical relationship between solute concentration on the surface of the adsorbent and the solute concentration in the liquid bulk in contact with it. This model posits the presence of multiple layers for adsorption, with a heterogeneous surface and non-equivalent or independent active sites. The overall Freundlich isotherm model, whether in its general or linear form, can be articulated by equations (6) and (7), respectively.

$$q_e = k_F C_e^{\frac{1}{n}} \quad (6)$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

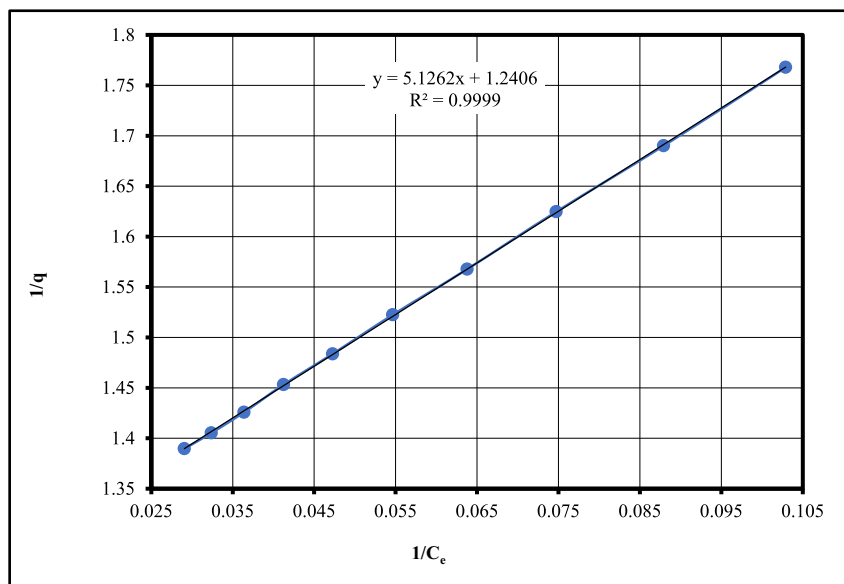


Fig. 9. Langmuir isotherm for phenol adsorption using mandarin peels.

This model is clarifying the adsorption isotherm behavior by plotting $\ln q_e$ against $\ln C_e$ in a straight line, as in Fig. 10, to obtain $\ln k_F$ and $1/n$ as slope and intercept of Equation (7), respectively.

4.1.3. Temkin isotherm model

This model posits a linear decrease in the adsorption temperature of all molecules, rather than an exponential decrease, as the surface of adsorption increases.

It assumes a uniform distribution of binding energies over the adsorbent media's surface, extending beyond the maximum binding energy. The interaction between the adsorbate and adsorbent considers the interfacial layer between them. The general formula is expressed in Equation (8), while Equation (9) illustrates the linear expression of the Temkin isotherm model.

$$q_e = \frac{RT}{b} \ln K_T C_e \quad (8)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (9)$$

The constant of Temkin model can be obtained from graphical plotting of linear form, i.e. Equation (9) and Fig. 11. The slope of this relation is RT/b and the intercept is $(RT/b) \ln K_T$ can be guessed from plotting q_e vs. $\ln C_e$ to give a straight line. The constant of Temkin model can be obtained from graphical plotting of linear form, i.e. Equation (9) and Fig. 11. The slope of this relation is RT/b and the intercept is $(RT/b) \ln K_T$ can be guessed from plotting q_e vs. $\ln C_e$ to give a straight line. Table 1

presents the parameters of the adsorption isotherm models investigated in this study, obtained from the slopes and intercepts of linear equations. The calculated correlation coefficients (R^2) were clearly higher for the Langmuir model compared to the Freundlich and Temkin models. This indicates that the Langmuir isotherm model provides a more accurate description of the adsorption process, surpassing the other models. Under constant temperature conditions, mandarin peels demonstrated a maximum phenol removal capacity of 0.81 mg/g, underscoring their exceptional adsorption efficacy for phenol removal.

4.2. Adsorption kinetic study

Four established kinetic models are employed in this study to elucidate the relationship between time and the adsorption capacity at the equilibrium state. This facilitates the prediction of the adsorption mechanism through a concept known as adsorption kinetics [16]. The investigation utilizes the pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion models to delineate the kinetic dynamics governing the adsorption of phenol from aqueous solutions using mandarin peels.

4.2.1. Pseudo-first order kinetic model

The pseudo-first order kinetic model assumes that the rate-limiting step in the adsorption process is the interaction between the adsorbate (phenol, in this context) and an active site on the adsorbent surface. The model follows the first-order reaction kinetics, where the rate of adsorption is directly

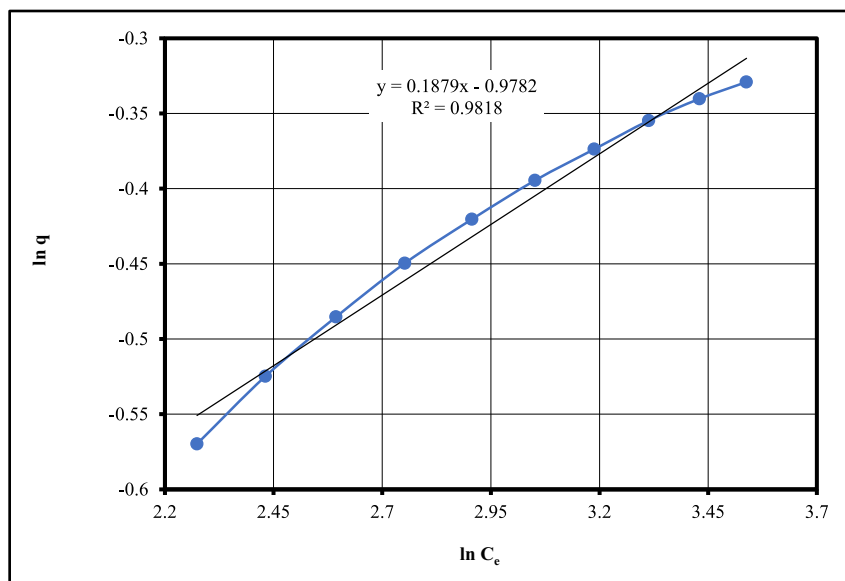


Fig. 10. Freundlich isotherm for phenol adsorption using mandarin peels.

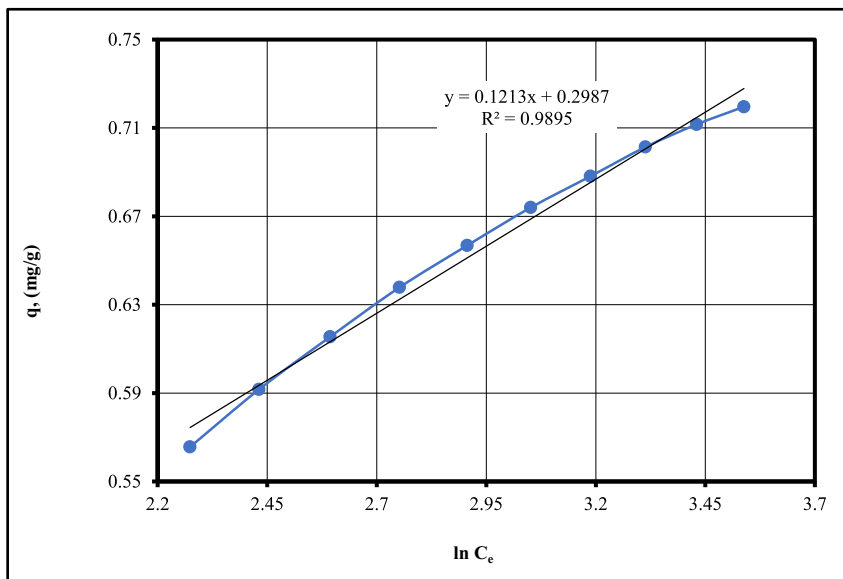


Fig. 11. Temkin isotherm for phenol adsorption using mandarin peels.

proportional to the number of unoccupied active sites. The hypothesis suggests that the process occurs through a monolayer adsorption mechanism, and it assumes that the concentration of the adsorbate in the solution significantly exceeds the concentration of active sites on the adsorbent surface. The initial expression and linear representation of this model outlined by Equation (10) and Equation (11), respectively.

$$q_e - q = e^{-k_1 t} \tag{10}$$

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{11}$$

The constants k_1 , and q_e which are represent the slope and intercept of this kinetic model, can be guessed by plotting $\ln(q_e - q)$ vs. t as in Fig. 12.

4.2.2. Pseudo-second order kinetic model

The premise of this model is rooted in the adsorption mechanism occurring between the solid-phase adsorbent and the liquid-phase adsorbate, unfolding

in two layers on the adsorption surface. This depiction is articulated by Equation (12), and it can be transformed into linear form using Equation (13)

$$q = \frac{q_e^2 k_2 t}{1 + q_e^2 k_2 t} \tag{12}$$

$$\frac{t}{q} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \tag{13}$$

By plotting (t/q) against t , as in Fig. 13, the slop of Equation (13) is calculated by $(1/q_e)$ while the intercept is determined by $(1/q_e^2 k_2)$.

4.2.3. Elovich kinetic model

The Elovich model is a kinetic model used to describe chemisorption on solid surfaces, particularly in the context of adsorption processes. It is often applied to describe the initial rapid adsorption phase, when the adsorbate interacts strongly with the adsorbent surface. The physical meaning of this model lies in its representation of a multistep adsorption.

The model suggests that adsorption occurs through two distinct processes. The first one is chemical adsorption (chemisorption), which is represented by the first term in the Elovich equation. It reflects the initial rapid adsorption where the adsorbate molecules chemically bind to specific sites on the adsorbent surface. The rate of chemisorption is influenced by factors like the availability of active sites and the strength of the chemical bonds formed between the adsorbate and the adsorbent. While the second process is desorption and diffusion which is represented by the second

Table 1. Parameter values of isothermal models utilized for Phenol adsorption using Mandarin Peels.

Model	Parameter	Value
Langmuir	q_{max}	0.81
	k_L	0.24
	R_L	0.1
	R^2	0.9999
Freundlich	k_F	0.38
	n	5.32
	R^2	0.9818
Temkin	b	20.09
	k_T	11.73
	R^2	0.9895

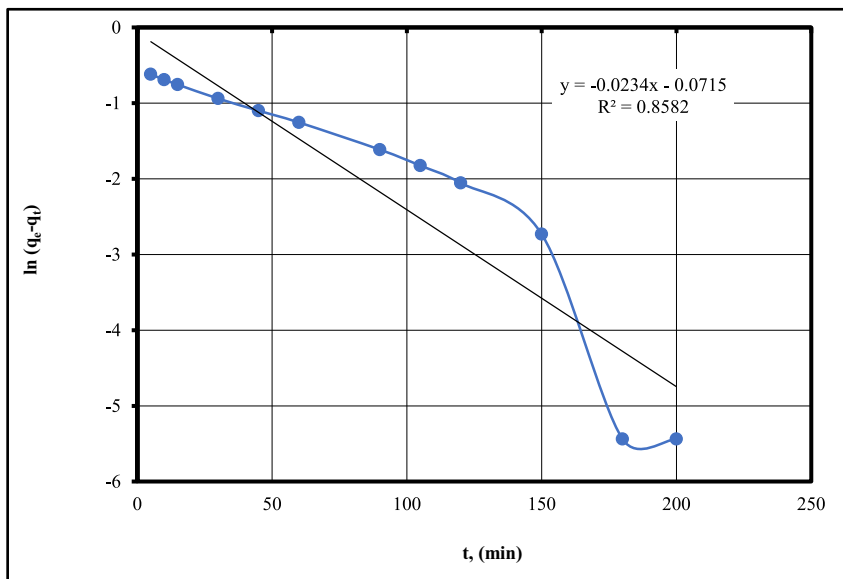


Fig. 12. Pseudo-first order kinetic for phenol adsorption using mandarin peels.

term in the Elovich equation accounts for desorption and diffusion processes. After the initial chemisorption, subsequent adsorption becomes slower and is influenced by desorption of molecules from the surface and their diffusion to new adsorption sites. Therefore, this model can be represented mathematically as shown in Equation (14). By integrating Equation (15) at the boundary conditions from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$. By arranging the terms, yielded the linear form for this model which is described in Equation (15). When the system closer to equilibrium state, $t \gg (1/\alpha\beta)$.

So, Equation (15) can be written as in Equation (16). The linear relationship of this kinetic model can represents by plotting q against t , as in Fig. 14. The slop and intercept are $1/\beta$ and $(1/\beta) \ln(\alpha\beta)$, respectively.

$$\frac{dq}{dt} = \alpha e^{-\beta q_t} \tag{14}$$

$$q = \frac{1}{\beta} \ln\left(\frac{1}{\alpha\beta} + t\right) + \frac{1}{\beta} \ln(\alpha\beta) \tag{15}$$

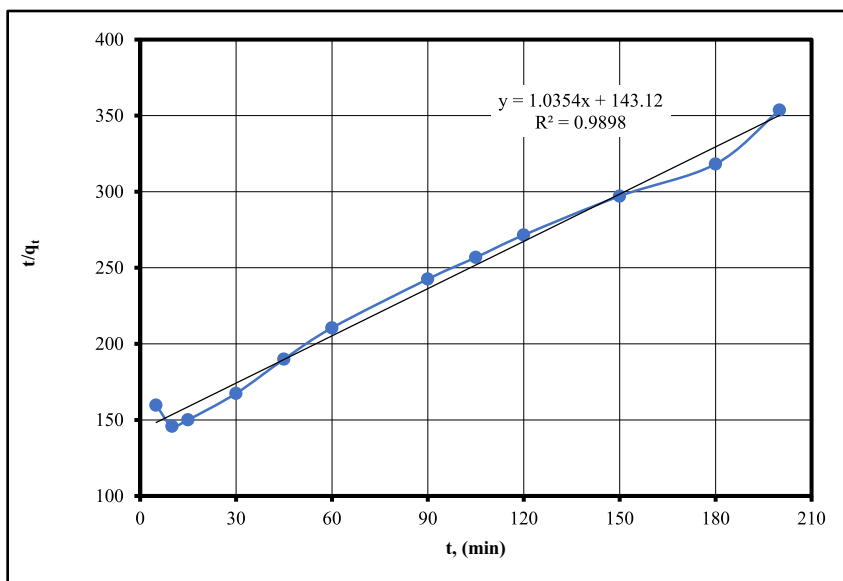


Fig. 13. Pseudo-second order kinetic for phenol adsorption using mandarin peels.

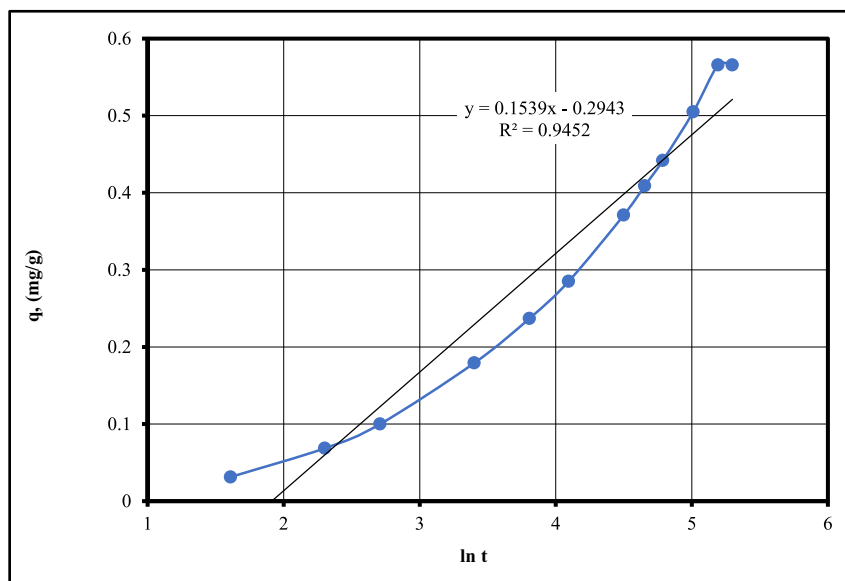


Fig. 14. Elovic kinetic for phenol adsorption using mandarin peels.

$$q = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln \alpha \beta \quad (16)$$

4.2.4. Intra-particle diffusion kinetic model

According to the model hypothesis, the solute transfer from the solution to the adsorption surface encompasses four sequential steps. The initial phase is mass transfer (bulk movement), characterized by the rapid movement of solute molecules in the presence of the adsorbent substance. Subsequently, film diffusion ensues, involving the movement of solute within the boundary layer of the adsorbent material. The third stage involves the diffusion of solute particles towards the pores of the adsorption surface, referred to as surface diffusion. The final step entails the adsorptive attachment of solute molecules to the active sites on the adsorption surface, denoted as pore diffusion. The mathematical expression representation of this model is elucidated by Equation (17).

$$q = k_p t^{0.5} + I \quad (17)$$

This equation is linear, thus, by plotting q against $t^{0.5}$, as in Fig. 15, the slope of the straight line represents the time-constant constant k_p , while the constant I can be calculated from the intercept. Table 2 presents the parameter values of the four kinetic models employed for depicting the adsorption of phenol from aqueous solutions by mandarin peels. It is evident from Table 2 that the intra-particle diffusion is most suitable model for representing the experimental data, followed by the pseudo-second-order model, as evidenced by higher correlation

coefficients for both. If the adsorption kinetics of phenol follows the intra-particle diffusion model, it implies that the process is significantly influenced by intra-particle diffusion, which refers to the movement of adsorbate molecules within the pores or particles of the adsorbent material. The physical meaning of the intra-particle diffusion model in the adsorption of phenol can be explained through pore structure and rate-limiting step. The model provides an important view into the pore structure of the adsorbent material and the accessibility of phenol molecules to adsorption sites. Furthermore, Intra-particle diffusion is identified as the rate-limiting step, implying that the overall adsorption kinetics are predominantly controlled by the speed at which phenol molecules move within the pores. In other words, this model suggests that the rate-limiting step in the adsorption process is the intra-particle diffusion of phenol molecules into the pores of the adsorbent material to reach active sites on the surface of adsorbent where adsorption occurs.

Thus, the adoption of the intra-particle diffusion model for describing the kinetics of phenol adsorption indicates that the movement of phenol molecules within the pores of the adsorbent material plays an important role in determining the overall adsorption process.

4.3. Thermodynamics of adsorption study

The determination of thermodynamic functions assumes paramount importance in elucidating reactions, particularly in the domain of adsorption processes. Enthalpy (ΔH), Gibbs free energy (ΔG),

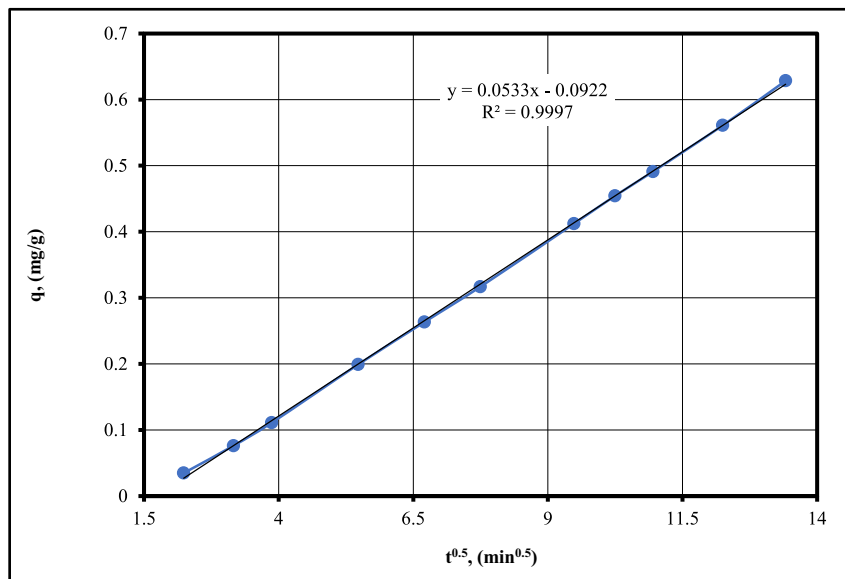


Fig. 15. Intra-particle diffusion kinetic for phenol adsorption using mandarin peels.

and entropy (ΔS) are indispensable metrics for unraveling the underlying dynamics of these reactions. The enthalpy value (ΔH°) provides a direct quantitative measure of the forces influencing the interaction between the adsorbed particle and the surface of the adsorbent. Concurrently, the entropy value (ΔS°) furnishes a quantitative gauge of the disorder and randomness inherent in the molecular arrangement on the adsorption surface. The Gibbs free energy (ΔG°) represents a pivotal thermodynamic parameter, playing a critical role in discerning the spontaneity or non-spontaneity of a given reaction or change [10]. For the adsorption of phenol using mandarin peels, these thermodynamic variables were calculated through the application of the van't Hoff relation, expressed by Equation (18):

$$\ln k_{ad} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (18)$$

Table 2. Parameter values of kinetic models utilized for Phenol adsorption using Mandarin Peels.

Model	Parameter	Value
Pseudo-first order	q_e	0.93
	k_1	0.02
	R^2	0.86
Pseudo-second order	q_e	0.97
	k_2	6.52×10^{-3}
	R^2	0.9898
Elovich	α	0.02
	β	6.50
	R^2	0.95
Intra-particle diffusion	k_p	0.05
	I	0.09
	R^2	0.9997

Equation (18) enables a thorough exploration of the thermodynamic fundamentals governing adsorption phenomena, thereby enhancing understanding and predictive capability in the field of processes associated with surface phenomena. However, the thermodynamic equilibrium coefficient of adsorption (k_{ad}) can be calculated using Equation (19)

$$k_{ad} = \frac{q_e}{C_e} \quad (19)$$

By plotting the relation between $\ln k_{ad}$ and $1/T$ in Equation (18), the slope ΔH and intercept of ΔS can be calculated from a straight line obtained. The Gibbs free energy (ΔG°) of the system can be determined from Equation (20)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (20)$$

The values of thermodynamic functions of phenol adsorption from aqueous solutions using mandarin peels are calculated and listed in Table 3.

Table 3. Thermodynamic Behaviors of phenol adsorption using mandarin peels.

T (°C)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol)
20	-903.12	-260.34	-13.99
25			-12.69
28			-11.91
31			-11.13
36			-9.83
40			-8.79
42			-8.26
45			-7.48
48			-6.70
50			-6.18
55			-4.88

The rise in temperature initiates the disruption of bonds between adsorbent ions and the active sites on the adsorption surface, resulting in the release of phenolate anions back into the solution. The observed enthalpy change was negative, signifying that the adsorption of the examined phenol onto the adsorbent surfaces is an exothermic process. Notably, the adsorption of phenol using mandarin peels was characterized as a chemical process, with an enthalpy value exceeding 40 kJ/mol. The negative entropy change in all adsorption experiments indicates a decrease in randomness at the interface between the solid and liquid phases during the adsorption process, highlighting the strong affinity of mandarin peel surfaces for phenol adsorption. The negative entropy change is a manifestation of the transition from a more disordered state in the solution to a more ordered state on the adsorbent surfaces. This change is a consequence of the specific interactions and molecular arrangements that take place during the adsorption of phenol, emphasizing the significance of the solid–liquid interface in the thermodynamics of the process. The negative entropy value observed in the phenol adsorption indicates a shift towards greater order and uniformity in the arrangement of adsorbed ions compared to their more random state in the solution phase. This phenomenon is linked to the exchange dynamics occurring at the solid–liquid interface, specifically on the surfaces of the adsorbent material. During the adsorption process, phenol molecules are accumulated on the surface of mandarin peels and tend to arrange themselves in a more organized manner on the adsorbent surfaces. This organized arrangement leads to a reduction in entropy, reflecting a decrease in the degree of disorder or randomness in the system. Generally, if entropy is negative, the entropic contribution to the Gibbs free energy of adsorption ($-T\Delta S^\circ$) becomes positive, demonstrating that the decrease in enthalpy drives adsorbate binding onto the adsorbent surface. Furthermore, the adsorption process of phenol using this material was determined to be spontaneous under the studied experimental conditions, as evidenced by the consistently negative values for the change in free energy. This suggests that the adsorption of phenol onto the adsorption sites in mandarin peel, serving as the adsorbent material, is a self-sustaining process that does not require external energy to complete. The decreasing negative Gibbs free energy values with increasing system temperature indicate a decline in spontaneity, implying that adsorption is more favorable at lower temperatures.

5. Employment of adsorption wastes as a pesticide

After assessing the efficacy of mandarin peels as an adsorbent for toxic phenol in a simulated solution, the subsequent phase involved the environmentally friendly disposal of the phenol-loaded peels. One proposed method was the utilization of these toxic residues as rodenticide [61]. To conduct this test, a total of 110 Sprague Dawley albino rats (*Rattus rattus*), evenly divided between males and females (55 each), were employed in this experiment. The rats, aged between 6 and 10 months and weighing between 250 and 300 g, experienced a one-week acclimation period in clean cages under controlled laboratory conditions [62]. Throughout this period, they received standard rat provender to ensure overall health and acclimatization to the environment and diet before commencing the experiments [48]. Environmental conditions were upheld at a temperature of 24 ± 2 °C, with a lighting schedule of 14 h per day using a standard light bulb. Following the adaptation phase, the rats were doled out into 10 groups, each consisting of 5 animals for both (males and females) housed in separate cages [52]. These groups were fed a diet comprising regular rat provender and mandarin peel saturated with phenol. Two control groups, denoted as CG1 and CG2, were also established, each comprising five males and five females. CG1 rats were exclusively fed regular rat provender, while CG2 rats were provided with standard rat provender and uncontaminated mandarin peels (i.e., no adsorbed phenol molecules) [55]. The rats were administered toxic mandarin peels, mixed with a controlled amount of sweet material, not exceeding 5 wt% of the supplied food provision. The assessment of mandarin peels as a rodenticide resulted in notable fatalities among both male and female rats that consumed mandarin peels saturated with phenol. These fatalities manifested at varying rates and intervals, contingent upon the quantity of rodenticide ingested by the rats. Calculations for the half-lethal dose (LD_{50}), representing the amount of toxin needed to lethally affect half of the subjects in the tested animals (rats in this study), were conducted. Notably, no fatalities were observed in the control groups. The LD_{50} , expressed as the toxin amount (in mg) per body weight (in kg) of deceased animals, was determined to be 349 (mg/kg) for males and 324 (mg/kg) for females. These values are consistent with the cited literature range of 317–414 [59]. LD_{50} values within the 200–300 mg/kg range indicate a high concentration of phenol molecules in the

rodenticide, impacting crucial enzymes vital for rat physiological functions. This, in turn, results in enzyme deviation or inhibition, particularly affecting dehydrogenase enzymes, leading to myocardial infarction [59].

6. Conclusions

Considering the inherent properties of this biosorbent, there is potential for utilizing mandarin peels in treating contaminated produced water, including phenol as a pollutant, through the adsorption technique in a batch mode unit. The efficacy of adsorption is contingent upon various operational conditions. The highest removal efficiency and from aqueous solutions reached 74.43%, achieved at optimum conditions of acidity, initial phenol concentration, contact time, agitation speed, temperature, and mass of mandarin peels of 1, 38 mg/l, 180 min, 450 rpm, 20 °C, and 5 g, respectively. While the maximum adsorption capacity of phenol is 0.72 mg/g. Isothermal analyses indicate that the Langmuir model best approximates the experimental data compared to other isotherm models. Moreover, the intra-particle diffusion model outperforms other kinetic models, as evidenced by its higher correlation coefficient. The calculated enthalpy and entropy values stand at -903.12 kJ/mol and -260.34 J/mol.K, respectively, suggesting an exothermic phenol adsorption process on mandarin peels with a tendency to regulate entropy. Additionally, the Gibbs free energy values ranged from -14 to -4.88 kJ/mol, indicating a chemical type of adsorption on mandarin peels with reduced spontaneity at higher temperatures. These outcomes underscore the considerable potential of mandarin peels as a bio-adsorbent for phenol removal from simulated solutions. The resulting toxic residues could be repurposed as a rodenticide, exhibiting LD_{50} values closely aligned with those reported in the literature. This method presents a cost-effective, safe, and environmentally friendly approach to disposing of agricultural wastes and toxic compounds in produced water, aligning with the zero-residue level (ZRL) concept.

Acknowledgements

The authors would like to thank Mustansiriyah University (www.uomustansiriyah.edu.iq) Baghdad – Iraq, Kerbala University (www.uokerbala.edu.iq) Kerbala – Iraq, and University of Diyala (www.uodiyala.edu.iq) Diyala – Iraq, and Al-Nahrain University (www.nahrainuniv.edu.iq) Baghdad – Iraq for their support in the present work.

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