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Research Paper

Remediation of aqueous solutions contaminated by benzidine toxic dye using non-conventional adsorbent: morphological and modelling studies

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ABSTRACT

Benzidine, a class A carcinogen, poses a significant threat in textile industry wastewater as it is a key intermediate in dye production. The promising adsorption technology using agricultural waste has proven to be an effective solution for water pollution. This study explores the potential of pineapple peels (the agricultural waste of little interest) as a low-cost adsorbent. Pineapple peels, typically discarded in massive quantities annually, exhibited a remarkable 91.064% maximum adsorption efficiency in a batch-type unit. This result was achieved at a pH, agitation speed, initial concentration, adsorbent dose, contact time, temperature, and particle size of 1450 rpm, 8 ppm, 3 g, 150 min, 20C°, and 88 μm, respectively. Morphological studies elucidated a surface area of 48.627 m^2/g, retaining 11.25% post-treatment. Fourier-transform infrared (FTIR) tests highlighted various functional groups on the peel's surface, undergoing alterations upon contact with benzidine. Scanning electron microscopy (SEM) examinations confirmed structural modifications post-adsorption. The adsorption process demonstrated spontaneity, low entropy, and exothermic behavior. Kinetic modeling revealed that the intraparticle diffusion model best represented the adsorption data. The isothermal behavior of adsorption was aptly described by the Langmuir model. The pineapple peels waste was tested to be a cheap rodenticide for laboratory rats and was found to be beneficial in disposing of these toxic residues. The results show a very good ability to eliminate the rodent with half the lethal dose, identical to that recorded in the literature. Thus, the study offers an economically viable and eco-friendly approach, aligning with the ethos of achieving zero-residue levels in waste management.

1. Introduction

In the complex challenges of environmental concerns, water pollution protrudes as a serious concern, posing a threat to ecosystems, human health, and overall sustainability. The discharge of industrial effluents, agricultural runoff, and urban wastewater introduces a myriad of contaminants into different water bodies such as oceans, seas, lakes, rivers [1]. In addition to the implementation of strict pollution control measures, it is essential to implement sustainable and efficient methods for the treatment of contaminated water [2]. The comprehensive and diverse landscape of water pollutants requires a nuanced and multifaceted approach to treatment. Contaminants range from chemicals to organic dyes to heavy metals, each necessitating a modified solution [3]. Benzidine is considered as one of the most harmful impact chemical substances, whose presence in water requires stringent monitoring and remediation efforts to mitigate the health risks associated with exposure [4]. Benzidine, a known industrial chemical, of chemical formula $C_{12}H_{12}N_2$, $CAS\#92-87-5$, and grayish-yellow, white, or reddish-gray crystalline powder appearance, is a synthetic biphenyl diamine, acts as an intermediate in the production of various dyes such as azo dyes, sulfur dyes, fast color salts, naphthol, and other dye compounds. According to the EPA, Benzidine has been categorized as a human carcinogen (Class A). It causes risks through inhalation, ingestion, and dermal contact. Numerous studies, including cohort studies and case reports worldwide, link occupational exposure to benzidine with urinary-bladder cancer and related deaths. Even two decades after the last exposure, elevated risks persist for those with larger than 5 years of exposure. Animal studies further confirm the carcinogenic potential of benzidine dye, with metabolization leading to aromatic amines. Significantly, the half lethal doses (LD_{50}) for oral and intraperitoneal administration in mice and rats underline its toxicity, where they are reported as 214 mg/kg and 309 mg/kg for oral doses in mice and rats respectively; while intraperitoneal dose in mouse is 110 mg/kg, [5]. In the USA, according to the information in "$42FR2617$", published on April 27, 1977, the maximum permissible level of benzidine discharge into water bodies as part of wastewater was set at $0.1\mu g/l$, equivalent to 0.1 ppb [6]. Benzidine is acknowledged for causing bladder cancer in humans and liver cancer in laboratory animals, its toxicological impacts seem to extend to various other endpoints. This chemically significant substance serves as the foundation for more than 200 dyes, and finds extensive use in manufacturing [7].

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Nomenclature

b	Temkin isotherm constant related to adsorption heat ($J\ mol^{-1}$)	R_L	Separation factor in Langmuir model
B	Constant in Temkin Isotherm Model	S	Entropy adsorption ($kJ\ mole^{-1}K^{-1}$)
C_e	Equilibrium adsorbed concentration ($mg\ g^{-1}$)	t	Contact time (min)
G	Gibbs free energy of adsorption ($kJ\ mol^{-1}$)	T	Absolute temperature (K)
H	Enthalpy of adsorption ($kJ\ mol^{-1}$)	*Greek Symbols*	
I	Thickness of boundary layer ($mg\ g^{-1}$)	α	Initial adsorption rate in Elovich model ($mg\ g^{-1}\ min^{-1}$)
k_1	First order rate constant (min^{-1})	β	Desorption constant in Elovich model ($g\ mg^{-1}$)
k_2	Second order rate constant ($g\ mg^{-1}\ min^{-1}$)	Δ	Change
k_{ad}	Thermodynamic equilibrium coefficient of adsorption	*Subscripts*	
K_F	Constant of the Freundlich adsorption $(mg\ g^{-1}).(l\ mg^{-1})^{1/n}$	*ad*	Adsorption
K_L	Constant of Langmuir adsorption isotherm model($l\ mg^{-1}$)	*e*	Equilibrium
k_p	Rate constant in intra-particle diffusion model ($mg\ g\ min^{-0.5}$)	*F*	Freundlich
K_T	Temkin isotherm equilibrium binding constant ($l\ mg^{-1}$)	*L*	Langmuir
n	Intensity of the adsorption in the Freundlich model	*max*	Maximum
q_e	Adsorption capacity at equilibrium state ($mg\ g^{-1}$)	*p*	Intra-particle diffusion
q_{max}	Maximum adsorption capacity of Langmuir model ($mg\ g^{-1}$)	*t*	Time
q_t	Adsorption capacity at any time ($mg\ g^{-1}$)	*T*	Temkin
R	Universal gas constant (8.3144 $J\ mol^{-1}\ K^{-1}$)	1	First order
R_2	Correlation coefficient	2	Second order

Consequently, owing to the hazardous nature of this chemical, it is a priority to eliminate it from wastewater or, at the very least, reduce its concentration to the minimum level using an effective treatment technique. Conventional techniques for contaminated water treatment have included a multitude of methods, ranging from processes of physical behavior to treatments of chemical nature, furthermore, the methods of biological nature. From all these techniques, adsorption emerges as a favorable tactic due to its activity in remediating a broad range of contaminants [8]. The appearance of a promising adsorption method, with its ability to discriminatively capture pollutants, has been instrumental in addressing these obstacles. Adsorption is a paramount procedure in which molecules are linked to the surface of a solid matter, called an adsorbent [9]. It is vital in different fields, especially in water treatment, catalysis, and fluid refinement [10]. The importance of adsorption resides in its capacity to recover the impurities, poisons, and various contaminants from various milieus. Popular adsorbents encompass activated carbon, different types of zeolites, and silica gel, recognized by their considerable surface areas and ability to select and collect the pollutants on the surface of adsorbents [11]. This multilateral phenomenon is tactical in making purifier circumferences and boosting many industrial aspects. The activated carbon media, originating from several provenances, have long been the favorable adsorbent choice for adsorption implementations [12]. Activated carbon is a primary material for treating aqueous solutions, well-known for its unique adsorption properties. Known for its extensive surface area and porosity, it is extraordinarily efficient in trapping pollutants, impurities, and toxins; hence ensuring the decontamination of polluted environments. This all-reorienting foot proper answer of the year and blue ball property is a gain of plentiful water treatment challenges, for itself reflects its principle as an integral important in the sustainability revolution [13]. However, activated carbon exhibits exceptional adsorption capabilities, it also has notable limitations. The synthesis of this media comprises energy-intensive processes such as carbonization and activation, contributing to its rise cost [14]. Moreover, the prevalent application of activated carbon in different industrial activities raises concerns related to resource exhaustion and durability. However, the conventional dependence on activated carbon has propelled research into substitutional materials with the target of mitigating the environmental impact of wastewater treatment [15]. As an alternative, investigators have gradually changed their interest to manufacturing and agricultural residues and waste litterers as potential adsorbent media [10]. The use of different manufacturing and agricultural residues as vigorous adsorbent media in the treatment of polluted aqueous milieus has accumulated considerable regard in scientific research, before and after implementations as an adsorbent substance [15]. Their porous structures and inherent surface functionalities make these wastes suitable for trapping contaminants, such as heavy metals [16], valuable elements [17], dyes [18], hardness [19], phenols [20], pesticides [21], organic acids [22], and toxic pollutants [23], not from aqueous solutions only, but also from crude oil [24], and flowing rivers [25]. In contrast to conventional activated carbon, these waste-derived adsorbents, sourced from materials such as rice husks [26], eggshells [27], watermelon rinds[28], tea leaves [29], banana peels [10], lemon peels [14], orange peels [30], algae [31], pomegranate peels [32], buckthorn leave [33], water hyacinth [34], and aluminum foil [35] showcase remarkable adsorption capacities. There are multi-uses of these wastes after loaded with adsorbate like bioethanol [36], fertilizer [37], drugs [38], addition material to concrete [39], pesticides [40], promoted catalysts [41], nanomaterials [42], or converted them to benefit substances [43]. This sustainable approach not only addresses environmental concerns related to waste disposal but also offers a cost-effective alternative for efficient water remediation, underscoring the importance of agricultural waste-based adsorbents in advancing eco-friendly and accessible water treatment solutions [44]. Pineapple peels, a type of agricultural waste of low attention, which is often discarded as waste, present a compelling option for the treatment of polluted aqueous solutions due to their abundant availability and rich fibrous composition. In the year 2021, the global pineapple production totaled approximately 28.65 million metric tons. According to [45], pineapple peels make up around 28-29% (w/w) of the fruit, resulting in nearly 8 million metric tons being discarded as waste. Consequently, failing to harness this substantial waste effectively not only poses an environmental burden but also results in the neglect of a valuable resource, considering its advantageous qualities. The essential features of pineapple peels, such as their porous structure and functional groups, make them an attractive candidate for adsorption applications. The investigation of pineapple peels as an adsorbent aligns with the broader shift towards sustainable practices, emphasizing the valorization of waste materials in environmental management [46]. As a result, the main aim of this paper is to explore the ability of pineapple peels to remove benzidine from simulated aqueous solutions. To achieve this purpose, several operating parameters are investigated at different ranges for determining the optimum conditions to achieve the maximum removal efficiency, which involves assessing the zero-residue level concept.

2. Methodology

2.1 Adsorbent material preparation

The virgin pineapple peels sourced from Malaysia were obtained from the residual waste of fruits procured at a local market in Baghdad, as in Fig. 1. The peels were cleaned with a series of washes by using tap water and subsequent rinses with deionized water, to ensure that the soluble dust and adhered impurities for the pristine peel surface were effectively removed. Subsequently, the pineapple peels underwent a drying process, they were first dried in sunlight for a few days, then by placing them for a period in a hot air oven at 50 C°for 24 hours. A 100 g sample of the dried pineapple peels was exposed to the processes of crushing, grinding, and sieving through metallic sieves ranging from 35 to 170 mesh. The resulting dried powder was meticulously stored in separate amber glass vials, corresponding to the size of the sieve. The sieve analysis results for the pineapple powder employed in this investigation are presented in Table 1.

2.2 Characterization of adsorbent media

Several tests were performed to determine the morphology behaviour of pineapple peels as an adsorbent medium. Fourier-transformed infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis were used to detect the functional groups of active sites, the morphology of the surface, and the specific surface area of adsorbent media, respectively. Moreover, the point of zero charge (pH_{PZC}) of the adsorbent was determined by the solid addition method.

(a) Virgin peels

(b) Dried peels

(c) Grinded peels

Figure 1**.** Pineapple peels used in this study.

Table 1**.** Sieve Analysis of pineapple peels powder used in this study.

No.	Mesh	Sieve Size, (μm)	Weight, (g)	$\%wt$
1	35	500	17.528	17.528
2	45	354	42.093	42.093
3	50	297	14.625	14.625
4	60	250	11.763	11.763
5	100	149	08.441	08.441
6	170	88	04.171	04.171
7	Pan	-	01.379	01.379
Σ	-	-	100.00	100.00

2.3 Preparation of potassium nitrate solution

A stock solution of 0.01 N potassium nitrate was prepared precisely, adhering to all required laboratory safety protocols. The process commenced by accurately weighing 1.013 g of high-purity reagent-grade KNO3 (99.8%, sourced from MERCK-Sigma-Aldrich-Germany). The measurement was executed with utmost precision using a digital analytical lab scale (Precision Balance – $USS-DBS81-110G-US$ Solid). The measured amount of potassium nitrate was then carefully and gradually dissolved in one-liter of 1.0 $\mu S/cm$ double-distilled water, obtained via a water still distillation unit of type (DS 4000, DragLab-Germany). The dissolution process was carried out under laboratory conditions with continuous manual mixing until completely dissolved all the KNO3 mass. After successful dissolution, the resulting 0.01 N KNO3 solution was carefully transferred to amber glass bottles of suitable capacity using a glass funnel. These bottles were chosen for their ability to protect the solution from light and maintain its stability. The storage bottles were securely sealed and stored in a designated dark and dry area in the laboratory, in order to maintaining optimal conditions for the stability of the solution.

2.4 Determination of the point of zero charge, pH_{PZC}

The pH_{PZC}, is consider as one of important parameter which controlling the reactivity and adsorption behavior of the adsorbent, which can be determined by using the solid addition method, which is a fundamental technique in surface chemistry and adsorption studies. This method ascertains the pH at which the surface of the adsorbent carries no net charge. A series of 100 ml $Pyrex^{TM}$ Borosilicate Glass Erlenmeyer Flasks, equipped with screw caps, were employed to prepare suspension solutions. In each flask, 100 ml of 0.01 N KNO3 solution -prepared previously-was introduced, and the pH of each solution was measured using ($HI-83141-1$ pH Meter, Hanna-USA) and accurately adjusted to span a range from 1 to 14 pH. This adjustment was achieved by judiciously employing either 0.1 N HC1 or NaOH solutions, thus establishing these pH values as the initial pH conditions. Subsequently, one gram of finely ground pineapple peel samples (45 mesh), which had been pre-dried, was added to each flask. This addition was conducted under controlled conditions, employing a hotplate magnetic stirrer ($C-MAG\ MS\ 7,\ IKA^{TM}$) operating at 200 rpm and ambient temperature. The stirring process was continued for a quarter of an hour to guarantee a uniform suspension. Upon completion of the mixing process, the flasks were promptly sealed with aluminum foil and securely fastened with rubber bands to prevent localized variations in pH measurements. To ensure consistent conditions during the experiment, the flasks, containing the suspension, were subjected to overnight agitation in an orbital water bath shaker (Marshall Scientific Barnstead MaxQ 7000). This agitation was maintained at a constant temperature of 25C°and an agitation speed of 100 rpm. Following a 24-hour equilibration period, the average pH values were determined based on five separate measurements of the liquid supernatant. These measurements were conducted to ensure the accuracy and reliability of the obtained pH_{PZC} value.

2.5 Stock solution of benzidine preparation

The benzidine stock solution (C.I. 37240) was formulated utilizing a reddish-brown powder (depicted in Fig. 2) obtained from Alpha Chemika company, India, with catalog No. AL0610 00025. For solution preparation, precisely 500 mg of the dye was dissolved in 500 cm^3 of double-distilled water, prepared via a water distillation unit (GFL-2012). Employing a magnetic stirrer under laboratory conditions, the mixing process persisted until a homogeneous solution was achieved. This precise method ensured that each milliliter of the solution contained 1 mg of benzidine dye, resulting in a solution of 1000 ppm concentration.

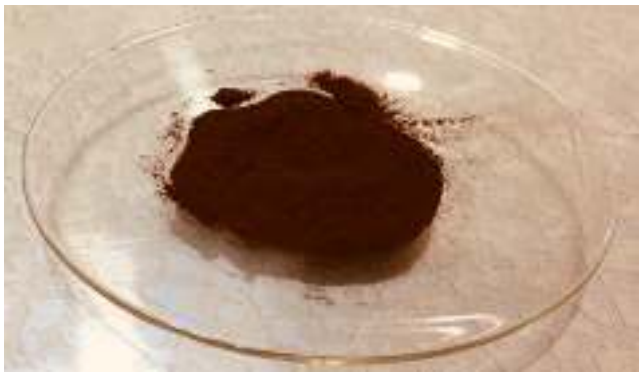


Figure 2**.** Benzidine dye used in the current study.

2.6 Calibration curve

The determination of the maximum wavelength (λ_{max}) of the benzidine involved conducting a series of laboratory experiments with a fixed concentration. The wavelength range explored ranged from 200nm to 700nm. These experiments were carried out using a precise spectrophotometer device, Shimadzu UV-V is 1800. At each wavelength, the absorbance of the dye was measured and recorded. These absorbance values were then plotted by the same method described in [40], resulting in Fig. 3. From the plot, it was observed that the maximum absorbance value reached 1.202. This maximum absorbance occurred at a wavelength of 282nm, which was determined to be the most

optimal wavelength for this particular dye. The chosen wavelength of 282*nm* was subsequently used to generate the calibration curve for benzidine dye, as illustrated in Fig. 3 and Fig. 4. This curve allows for accurate quantification of the dye's concentration in later experiments and analyses. Through employing the wavelength of 282*nm*, can assuredly estimate the existence and determine the concentration of benzidine dye in different specimens.

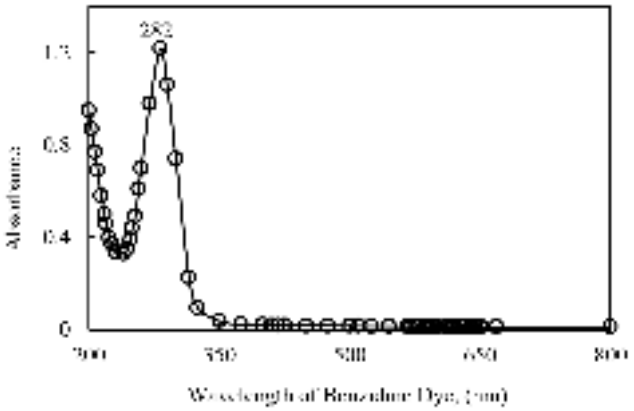


Figure 3**.** Absorbance due to Wavelength Changing of Benzidine.

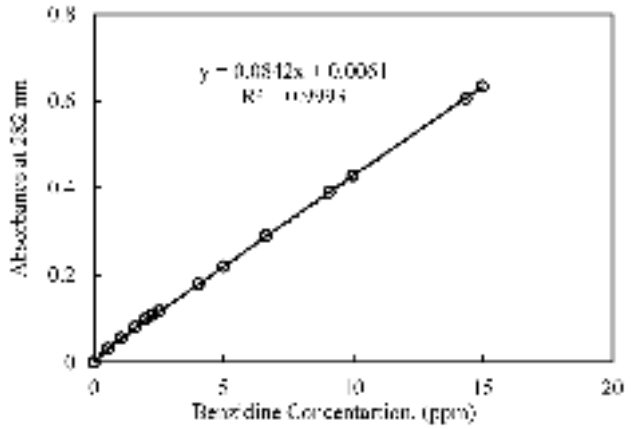


Figure 4**.** Calibration curve of benzidine dye using UV-V is Spectrophotometer.

2.7 Adsorption unit used

The experiments of adsorption of benzidine dye were utilizing peels of pineapple as a non-conventional adsorbent media were achievement in an expert batch mode unit. A determined concentration of benzidine dye was made by diluting the known amount of the stock solution. The goal was to estimate the optimal design parameters that would produce the ultimate percentage removal ratio. Different operating conditions, including acidity, shaking speed (agitation), dye initial concentration, treatment time, temperature of adsorption unit, and mass of pineapple peels (dose), were examined. The acidity of the solution of dye was controlled employing 0.1 *N* sodium hydroxide (*NaOH*) and 0.1 *N* hydrochloric acid (HCl) solutions. The range of *pH*, agitation speed, initial concentration, contact time, temperature, dose of adsorbent, and the size of particles parameters tested were varied between (1-10), (100-500 *rpm*), (0.5-10 *ppm*), (10-180 minutes), (20-50 C°), (0.1-1.3 *g*) and (35-170 mesh), respectively. Every test was started by adding 0.1 liter of the benzidine solution, with known acidity and concentrations, to a covered 250 *ml* (Pyrex Borosilicate glass supported by a glass stopper) conical flask. The flask of experiment was then laid in an electrical shaker supported by a water bath, and the test was begun by controlling the selected speed of agitation. The period of test was specified by the pre-defined contact time. After accomplishment, the treated solution was filtered through a vacuum filtration apparatus (JOANLAB VP-10L), after isolated the adsorbent peels from the mixture. The final concentration of dye (i.e., benzidine) in the addressed solution was determined spectrophotometrically. The efficiency of removal of dye was detected by Eq. 1, while the capacity of adsorption of the pineapple peels was estimated using Eq. 2. Generally, this test configuration allowed for the appraisal of the adsorption performance of pineapple peels in the remediation of benzidine dye, providing worthy vision into the performance of different designing factors.

$$\%R = \left(1 - \frac{C_f}{D_o}\right) \times 100 \tag{1}$$

$$q = \frac{V\left(C_o - C_f\right)}{m1000} \tag{2}$$

Where: %R the removal percentage of dye examined (benzidine), C_o and C_f are the initial and the final concentration of dye examined (benzidine), measured by (mg/l); q: the capacity of adsorption using pineapple peels as a non-conventional adsorbent, expressed in (mg/g), V: the volume of the aqueous solution used in the experiment of adsorption, evaluated by (ml); and m: the mass of pineapple peels employ in the experiment of adsorption measured by (g). The Eq. 1 and Eq. 2, [10], permits the quantitative speculation of the adsorption rendering, supplying worthy data on the performance of pineapple peels in recovering benzidine dye from aqueous solution.

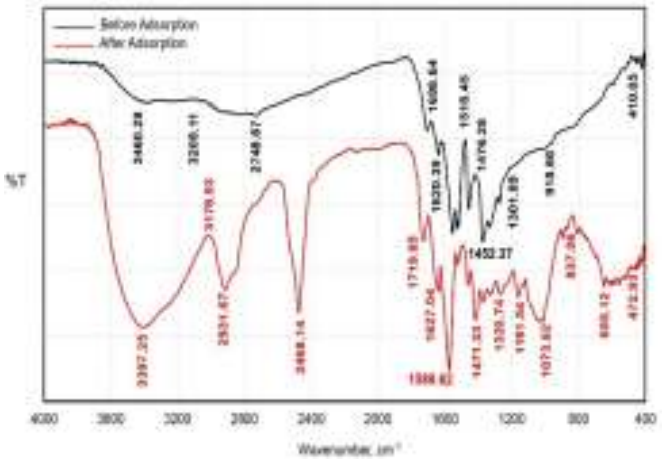


Figure 5**.** FTIR spectrum of pineapple peels before and after adsorption of benzidine.

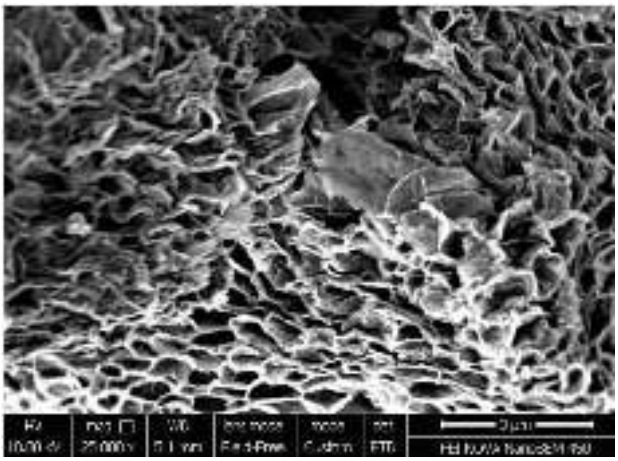
3. Results and discussion

3.1 Characterization of adsorbent media

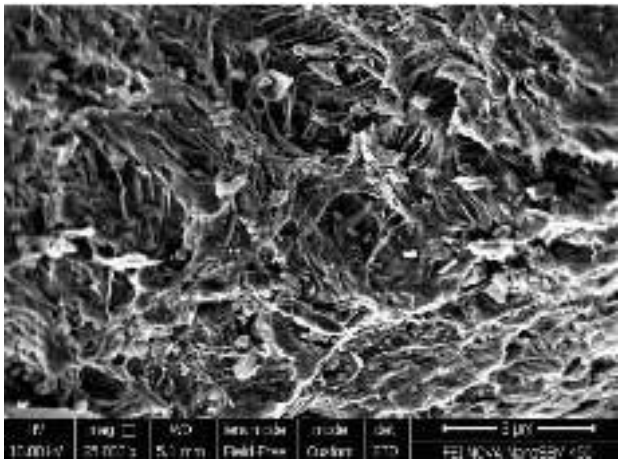
3.1.1 Specific surface area (SBET)

The BET (Brunauer-Emmett-Teller) surface area test is an important parameter to evaluate the operational characteristics of catalysts, adsorbents, and any other porous media, and provides a valuable view into material behavior at the molecular level. The measurement process of surface area in this study, was detected for pineapple peels via physical adsorption-desorption analysis of nitrogen gas at a constant temperature equivalent to the boiling point of liquid nitrogen $(-77K)$. The adsorption process initially saturated the micro-pores of the material at $P/P = 0.34513$, followed by the filling of mesopores with multilayers of nitrogen gas. The examination of the surface area values of pineapple peels before and after benzidine adsorption was performed, and the values were determined to be 48.627 m^2/g and 5.473 m^2/g, respectively. The notable reduction in surface area of pineapple peels from 48.627 m^2/g before benzidine adsorption to 5.473 m^2/g after adsorption offers valuable information about the adsorption mechanism and relates well with the observations made during the FTIR and SEM analyses. The initial moderate surface area of pineapple peels (48.627 m^2/g) suggests the presence of a porous and rough structure, in line with the SEM analysis that revealed distinct pores on the surface of peels. This natural texture provides numerous functional groups on the active sites for potential adsorption and is consistent with the roughness identified through SEM analysis. The surface area of pineapple after adsorption of benzidine was reduced to about 11.25% of the original value. This intense decline indicates that a great portion of the surface area of the peels has been occupied by benzidine molecules. This upholds the SEM test, which manifest a more regular and lower porous surface after treatment, which is meaning padding the active pores by dye testing (i.e., benzidine). The FTIR analysis further prove these gained results by exhibited chemical reactions between the dye and the functional groups on the active sites prevalent on the peels' surface.

These relations likely played an important role in relating the dye molecules to the pineapple peel, which trigger combine the pores simultaneously and lowering the surface area value.



(a) SEM before



(b) SEM after

Figure 6. SEM of pineapple peels before and after adsorption of benzidine.

3.1.2 FTIR test

Furious Transform Infra-red (FTIR) description is significant for determining the functional groups in different materials, chemically clarifying the compositions, and estimating their appropriateness for multiple applications. Using an FTIR spectrophotometer (IRPrestige-2, Shimadzu, Japan), the FTIR spectra of pineapple peels before and after adsorption of benzidine are shown in Fig. 5. These spectra display an important view into the constitutional modifications and chemical relations within the peels' surface. Before benzidine adsorption, the FTIR spectrum offered special peaks at diverse wavenumbers, influencing the composition of the adsorbent media (i.e., pineapple peels). Peaks at 410.05 cm^{-1}, 918.66 cm^{-1}, and 1031.89 cm^{-1} indicated the existence of cellulose and lignin, popular components of plant-based materials. Moreover, the peaks at 1452.37 cm^{-1}, 1476.28 cm^{-1}, and 1518.45 cm^{-1} were suggestive of C-H bending vibrations, hinting at the existence of aromatic compounds, possibly producing from the natural phenolic content in agricultural peels. The peaks at 1620.39 cm^{-1} and 1698.64 cm^{-1} matched to carbonyl groups (C=O), indicating the presence of hemicellulose and pectin. The peak at 3460.28 cm^{-1} indicated O-H stretching vibrations, conceivably related to water molecules within or on the surface of peels. After benzidine adsorption, notable changes in the FTIR spectrum were observed. New peaks at 472.93 cm^{-1} and 655.12 cm^{-1} emerged, indicating the formation of benzidine-pineapple peel complexes. The appearance of a peak at 837.06 cm^{-1} suggested potential modifications in cellulose and lignin structures due to interactions with benzidine molecules. The presence of a peak at 1073.62 cm^{-1} confirmed the successful adsorption of benzidine onto the surface of peels, indicating chemical interactions between benzidine and functional groups present in the pineapple peel. Shifts in peaks at 2468.14 cm^{-1}, 2931.67 cm^{-1}, 3178.93 cm^{-1}, and 3397.25 cm^{-1} pointed to alterations in hydrogen bonding and functional groups, implicating their role in the adsorption process. These results agree with [31].

3.1.3 SEM test

The surface morphology of the adsorbent can be demonstrated by a scanning electron microscopy image. In the present study, the micrograph of pineapple peels before benzidine adsorption showed a heterogeneous, rough, and porous nature. However, after adsorption of benzidine dye, the surface is almost smooth and homogeneous in nature, Fig. 6a and b. The transformation of pineapple surfaces, transitioning from their initial heterogeneous, rough, and porous characteristics to a smooth and homogeneous nature, can be attributed to the process of adsorbing benzidine dye. As the dye molecules interact with the pineapple surface, they adhere to its irregularities and porous structures. This interaction leads to a coating effect, where the dye molecules fill in the gaps and unevenness present on the surface. Consequently, the previously rough and porous surface becomes coated with a layer of dye, resulting in a smoother and more uniform appearance. This phenomenon is a manifestation of the molecular-level interactions between the dye and the pineapple surface, which contribute to altering its physical characteristics. However, after dye adsorption, the surface of pineapple peel is smoother in nature [47, 48].

3.1.4 Point zero charge

Alkaline metal nitrate, especially potassium nitrate (0.01 N), is usually used to estimate the point of zero charge. The point of zero charge of pineapple peels pH_{ZPC} was determined, and the results obtained are shown in Fig. 7. The pH_{pzc} values were known for determining the position where the resulting curves cut through the pH_o axis. For pineapple peels, pH_{pzc} was recorded as 4.375. This value can be useful for predicting the surface charge of the adsorbents; when adsorption occurs at pH which is below the point of zero charge of the adsorbent, the surface of the adsorbent will be positive, and when adsorption occurred above the point of zero charge pH, adsorbent surface charge will be negative. The pH versus pH_{PZC} of the pineapple peel is depicted in Fig. 7.

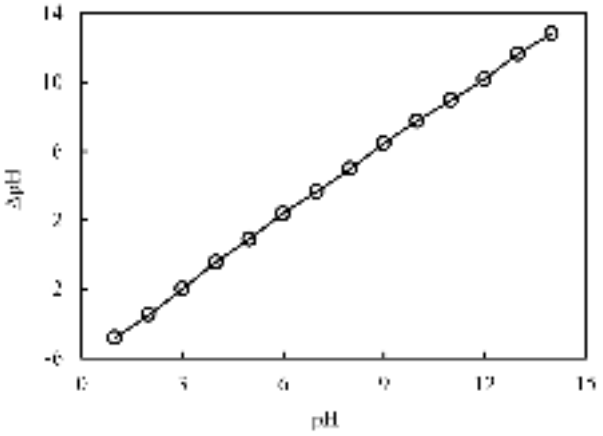


Figure 7. pH_{ZPC} analysis of pineapple peels adsorbent before treating with benzidine solution.

3.2 Adsorption experiments

3.2.1 Effect of pH

The most crucial factor for the adsorption of pollutants onto adsorbents in an aqueous solution is the concentration of hydrogen or hydroxide ions. When it comes to dye adsorption, acidic or basic pH levels have a greater impact on removal efficiency compared to moderate pH levels [3]. The final pH of the adsorption medium influences the adsorption mechanisms on the surface of the adsorbent and affects the nature of the physicochemical interactions between the species in the solution and the adsorptive sites of the adsorbent. In this study, the influence of pH was examined by adding 100 ml of benzidine dye and stirring at 500 rpm for 180 minutes at a constant temperature of 20C°. Figure 8 displays the effect of pH on the adsorption of benzidine dye by pineapple peel over a pH range of 1 to 10. The adsorption efficiency decreased from 17.585% to 5.807% as the pH of the solution varied from 1 to 10 using pineapple as the adsorbent. This indicates that pH plays a significant role in the adsorption capacity of the pineapple adsorbent for benzidine removal. Particularly, the reduction in the removal percentage of dye tested at a high value of pH may be due to two factors. One of these reasons, as

the *pH* increases, the surface charge of the adsorbent becomes more positive, resulting in electrostatic repulsion between the positively charged surface of the adsorbent and the negatively charged of molecules of dye, according to the equation ($C_{12}H_{12}N_2 + H_2O \rightleftharpoons C_{12}H_{11}N_2 + H_3O^+$), leading to lowering the efficiency of adsorption. The other factor is the benzidine's solubility, which decreases at high *pH* values, further contributing to the decrease in removal percentage. It is imperative to highlight that the optimal *pH* for benzidine removal using pineapple as an adsorbent is 1. This result agrees with studies of [35, 44, 49].

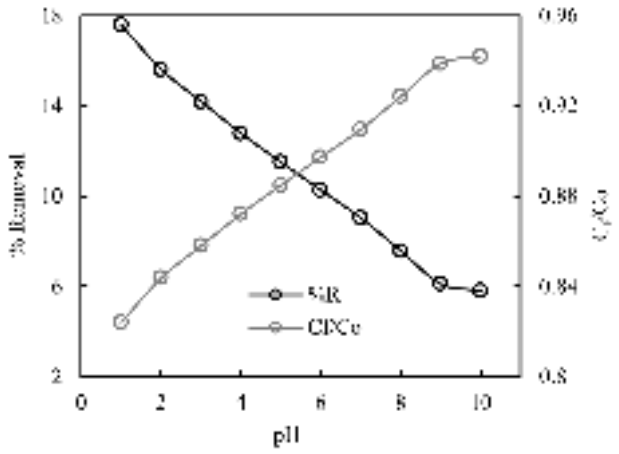


Figure 8. Effect of pH on benzidine adsorption using pineapple peels.

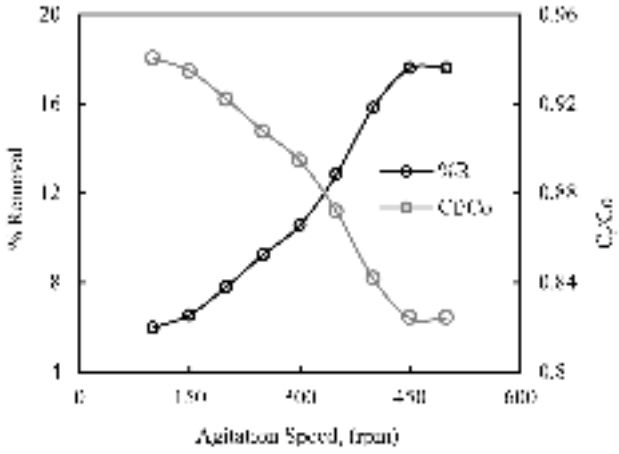


Figure 9. Effect of agitation speed on benzidine adsorption using pineapple peels.

3.2.2 Effect of agitation speed

The shaking speed at which the fluid is agitated is a vital condition in a batch mode adsorption unit, because it affects the adsorption of the adsorbate between the adsorbent and the solution. By estimating the agitation speed value, it is possible to realize maximum abilities and rapid kinetics of adsorption, leading to more dynamic and flexible of polluted solutions treatment processes. Therefore, comprehending the performance of agitation speed on the adsorption process is an important matter for the development of active adsorption systems. Figure 9 explain the effect of agitation speed on the percentage removal of dye tested (i.e., benzidine) using pineapple peels as a non-conventional adsorbent, while keeping other parameters fixed at optimal values. Due to the results shown in Fig. 9, the removal efficiency of benzidine dye escalated from 5.975% at an agitation speed of 100 *rpm* to 17.585% at 450 *rpm*. There are various reasons to illustrate these results. Firstly, the escalating agitation speed value promotes the mass transfer process between the solution and the pineapple peels' surface, leading to an escalation in the rate of adsorption. This amended mass transfer permits for more active contact between the adsorbent and the adsorbate, resulting in an escalation of the percent removal of benzidine. Secondly, the increased agitation speed helps to break up any boundary layer around the adsorbent particles, ensuring fresh solution meets the adsorbent surface. This prevents the formation of stagnant regions and promotes better adsorption. Additionally, the higher agitation speed can also dislodge adsorbate molecules initially adsorbed onto the adsorbent surface, making more adsorption sites available. However, after reaching 450 *rpm*, the removal efficiency reached a plateau and remained constant. This can be attributed to the adsorption sites on the adsorbent surface becoming filled and saturated over time, reaching their limit. Once the adsorption sites are filled, the removal efficiency remains constant regardless of the agitation speed. Therefore, increasing the agitation speed beyond this point does not significantly impact the removal efficiency in batch adsorption. This result agrees with [30, 32, 33].

3.2.3 Effect of initial concentration

The concentration of the adsorbate at the start of the adsorption process is a vital factor that determines the driving force behind adsorption. To examine the influence of the initial concentration of benzidine dye, a series of experiments were conducted using 0.1 *g* of pineapple peels as the adsorbent. The agitation speed was set at 450 rpm, the contact time was 180 minutes, and the temperature was 20C°. The range of initial concentrations tested varied from 0.5 to 10 mg/l. The results indicated an inverse relationship between the removal efficiency and the initial concentration. The maximum removal efficiency of 18.826% was achieved when the initial concentration was 0.5 mg/l.

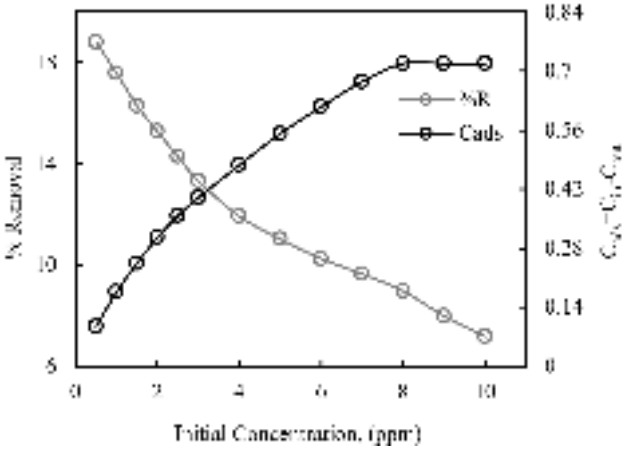


Figure 10. Effect of initial concentration on benzidine adsorption using pineapple peels.

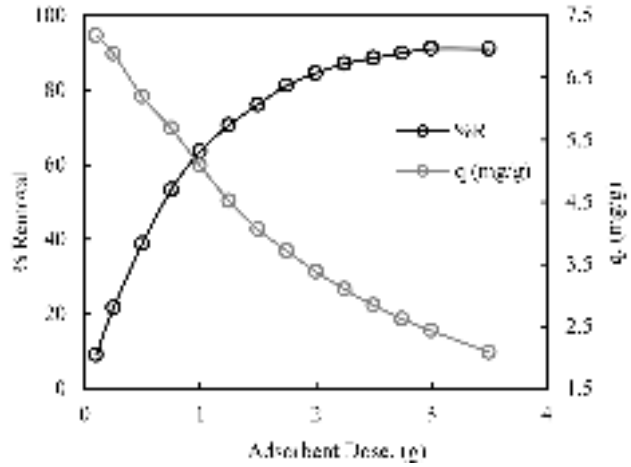


Figure 11. Effect of adsorbent dose on benzidine adsorption using pineapple peels.

Removal efficiency refers to the ability of the adsorbent to remove a specific contaminant from a solution, while the initial concentration represents the concentration of the contaminant at the beginning of the process. This inverse proportionality can be explained by the concept of adsorption equilibrium. With higher initial concentrations, there are more contaminant molecules

available for adsorption onto the adsorbent surface, leading to a faster saturation of the adsorbent's capacity to adsorb additional molecules. As a result, the removal efficiency decreases as the initial concentration increases. Figure 10 illustrates that the adsorbed concentration increased until reaching 8 mg/l and then remained constant. This indicates that the pineapple peels became saturated, as all available sites on the adsorbent surface were occupied by benzidine molecules, preventing any further adsorption. This result agrees with studies of [19, 22, 25].

3.2.4 Effect of adsorbent dosage

The effect of adsorbent dose on the adsorption of benzidine was investigated under optimum conditions, which included an initial concentration of 8 mg/l, a contact time of 180 minutes, a temperature of 20C°, an agitation speed of 450 rpm, and an acidity level of 1. As elucidated in Fig. 11, the results obtained uncovered a direct relationship between the percentage removal of benzidine and the dosage of pineapple peels employed as a non-conventional adsorbent. These outcomes propose that increasing the dosage of pineapple peels influences the capability of the adsorption process to remove benzidine from the contaminated milieu. These findings can be understood by the increasing available active sites on the adsorbent's surface, which occurs at high doses of pineapple peels. With more active sites obtainable for adsorption, there is an increasing opportunity for benzidine molecules to interact with the functional groups dispersed on the surface of the adsorbent, resulting in an increase in the remediation process. This result agrees with [50–52].

3.2.5 Effect of contact time

The contact time effectiveness on the benzidine removal efficiency was also studied in this investigation. By keeping other parameters constant at optimum values, the contact time was varied. The results demonstrate that extending the contact time from 10 to 180 minutes leads to a significant increase in the percentage removal of benzidine. Specifically, the percentage removal of benzidine increased from an initial value of 8.372% to a final value of 91.064% as elucidated in Fig. 12. This substantial improvement in removal efficiency can be attributed to several factors. Firstly, enhancing the interaction between the adsorbent and benzidine, a longer contact time allows for more thorough interaction between the benzidine molecules and the adsorbent material. As the contact time increases, there is a greater chance for the adsorption process to occur, resulting in a higher percentage of benzidine being removed from the solution. Secondly, the attainment of equilibrium, an extended contact time enables the adsorbent material to reach equilibrium with the benzidine present in the solution. When the balance between benzidine concentration in the polluted solution and the mass of pineapple peels occurs, this state is known as equilibrium. By permitting enough time for equilibrium to be reached, a maximum removal of benzidine dye can be effectively adsorbed by the pineapple peels, resulting in an escalating removal capacity. Eventually, the resumption of surface bindings and diffusion processes, the developing percentage removal with escalating contact time, can be explained by the continuation of surface bindings and diffusion processes. These processes comprise the transfer of dye molecules from the polluted solution in the direction of the active sites on the surface of pineapple peels and then linking together. With escalating contact time, there is more chance for these surface reactions and diffusion processes to occur, resulting in a maximum benzidine removal efficiency [12–14].

3.2.6 Effect of temperature

The effect of temperature on the percentage removal of benzidine was studied, exhibiting an outstanding descending in removal ability from 91.064% to 1.91% when the temperature escalated from 20 to 50C°as illustrated in Fig. 13. There are several factors that contribute to this observed decrease in removal efficiency with increasing temperature. The first factor is weakened interactions between the adsorbent material and benzidine molecules. Higher temperatures can disrupt the physical adsorption process by causing weaker interactions between the adsorbent material and the benzidine molecules. As the temperature rises, the increased thermal energy can weaken the attractive forces between the active sites of adsorbent media and the benzidine molecules, resulting in a reduced adsorption capacity and hence a lower percentage of benzidine being removed. Another factor is the desorption of the adsorbate. The elevated temperatures can also enhance the desorption of previously adsorbed benzidine molecules from the surface of the adsorbent material. As the temperature increases, the molecules' kinetic energy increases, leading to greater movement and desorption from the active sites. Consequently, the removal efficiency decreases as a result of a higher proportion of benzidine being released back into the solution. Furthermore, higher temperatures may accelerate certain chemical reactions that could potentially interfere with the adsorption process. For example, the presence of reactive species or the occurrence of competing reactions in the solution may be encouraged at elevated temperatures, hindering the effective adsorption of benzidine onto the adsorbent material. This interference can further contribute to the reduction in removal efficiency observed with increasing temperature [30].

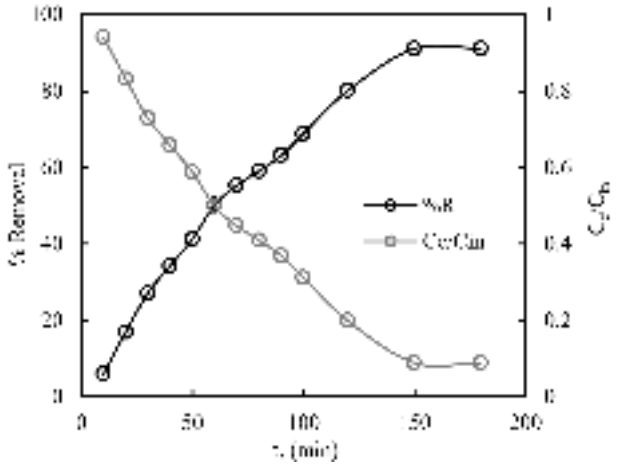


Figure 12**.** Effect of contact time on benzidine adsorption using pineapple peels.

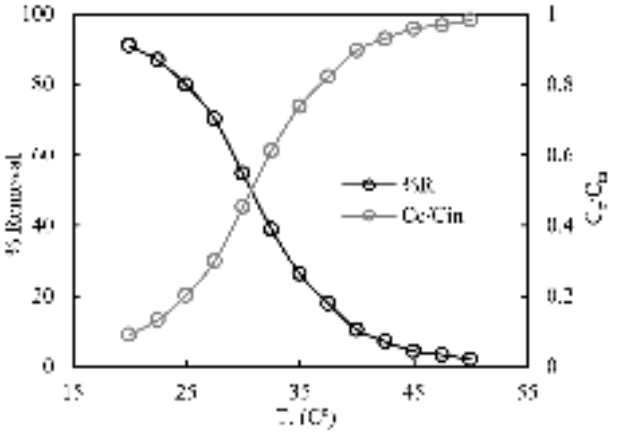


Figure 13**.** Effect of temperature on benzidine adsorption using pineapple peels.

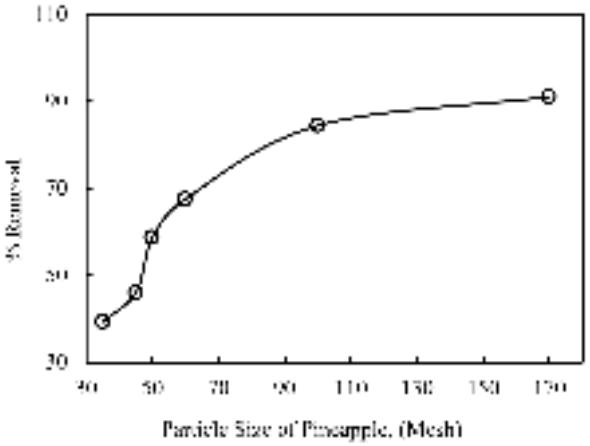


Figure 14**.** Effect of particle size on benzidine adsorption using pineapple peels.

3.2.7 Effect of particle size of adsorbent

The effect of particle size on the adsorption capacity of pineapple adsorbent was investigated under constant conditions of 1, 3 *g*, 450 *rpm*, 20C°, 150 min. and 8 *mg*/*l* of *pH*, adsorbent dosage, agitation speed, temperature, and initial concentration of benzidine, respectively. The results obtained revealing a significant increase in percentage removal as the particle size increased from 500 to 88 microns, (i.e., from 35 to 170 mesh), the percentage removal of the target substance increased from an initial value of 39.276% to 91.064% as illustrated in Fig. 14.

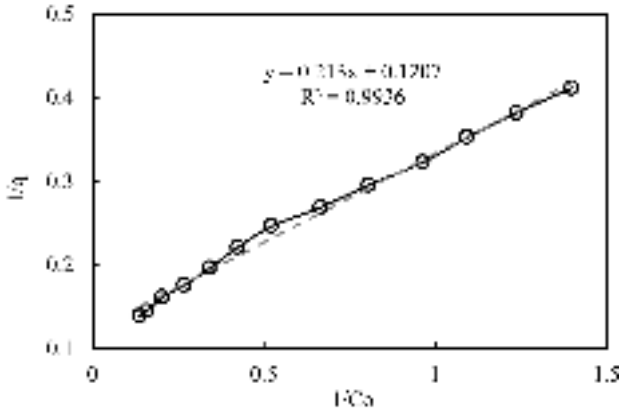


Figure 15**.** Langmuir isotherm model of benzidine adsorption using pineapple peels.

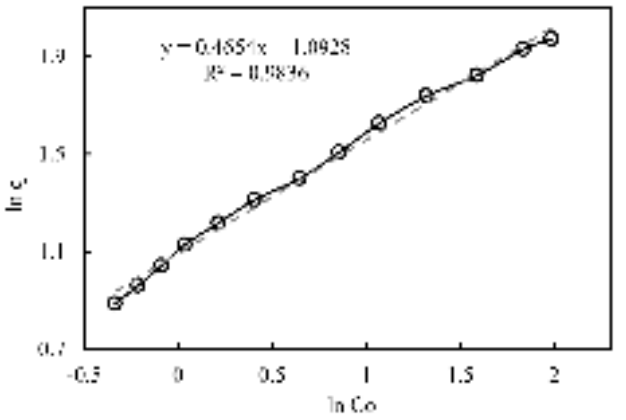


Figure 16**.** Freundlich isotherm model of benzidine adsorption using pineapple peels.

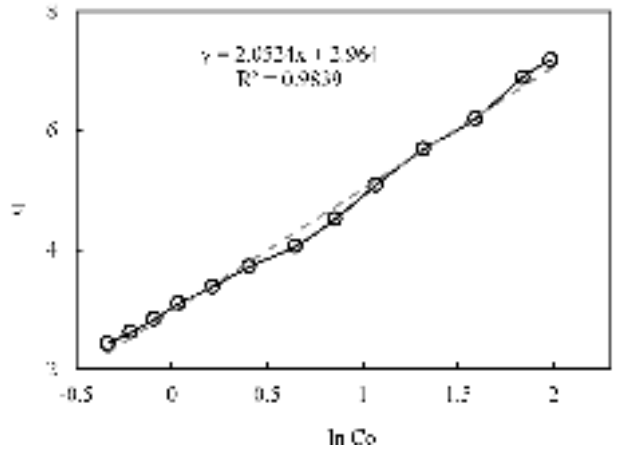


Figure 17**.** Temkin isotherm model of benzidine adsorption using pineapple peels.

The observed increase in removal efficiency with decreasing particle size can be attributed to several factors. First and foremost, as the particle size decreases, the surface area available for adsorption increases significantly. A smaller particle size leads to a larger surface area-to-volume ratio, allowing for more active sites to come into contact with the target substance. This creates more opportunities for adsorption interactions, resulting in a higher percentage of removal. Furthermore, lowering the particle size promotes the mass transfer within the adsorption unit. Particles show stumpy diffusion ways, providing the goal material to prevalent more rapidly via the porous framework of the pineapple peels. This expedites quick adsorption kinetics, resulting in maximum percentage removal. Moreover, the small type of particles resort to show superior approachability to the benzidine dye molecules. The small size permits for the development breakthroughs of the peels into the solution, guaranteeing a major contact between the benzidine and the pineapple peels. Thus, more dynamic and efficacious adsorption can happen, resulting in a maximum removal efficiency. It should be emphasized that the fundamental characteristics of the adsorbent material (i.e, pineapple peels) itself may have played a vital function in these findings. Pineapple peels adsorbent might have particular properties (e.g., high surface reactivity, favorable surface functional groups) that lead to its influencing performance at a lower particle size. These properties can help ensure efficient adsorption occurs between the pineapple peels and the benzidine, consequently escalating the percentage removal [33].

Table 2. Details of the isotherm models used in the current study.

Model	General Form	Linear Form	Slop	Intercept	Augmented Parameter
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{max} K_L}$	$\frac{1}{q_{max}}$	$R_L = \frac{1}{1+K_L C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\frac{1}{n}$	$\ln K_F$	– – –
Temkin	$q_e = \frac{RT}{b} \ln K_T C_e$	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	$\frac{RT}{b}$	$\frac{RT}{b} \ln K_T$	– – –

Table 3**.** The values of the constants of isotherm models.

Model	Constant	Value
Langmuir	q_{max}	8.2850
	K_l	0.5666
	R_L	0.1807
	R^2	0.9936
Freundlich	K_F	2.9826
	n	2.1487
	R^2	0.9836
Timkin	b	1187.5
	K_T	3.2360
	R^2	0.9893

3.3 Adsorption behavior studies

3.3.1 Isothermal study

Isothermal study embraces exploring the behaviour of the adsorption process when the temperature of the system remains constant. Langmuir, Freundlich, and Temkin adsorption isotherm models are considered famous models used to describe adsorption characteristics and equilibrium relationships between the two sides of the adsorption process, (i.e., adsorbate and adsorbent) [53]. The algebraic formulas that dub the various mathematical equations of the

isothermal models used in this study are listed in Table 2. These models assist in knowing and estimating the behaviour of adsorption in different scientific and industrial implementations. Following detailed scrutiny, explained through Fig. 15, Fig. 16, and Fig. 17, and Table 3, it was ascertained that the Langmuir model displayed the optimal precision. The correlation coefficient (R^2) value resulting from the Langmuir model was 0.9936, signifying a strong match between the predicted values and the real data from the experimental part. On the other hand, the other isothermal formulas (i.e., Temkin and Freundlich models) exhibited R^2 values of 0.9893 and 0.9836, respectively [47]. This result suggests that these models may not sufficiently represent the adsorption behaviour investigated, in contrast to the Langmuir model. The main assumptions of the Langmuir model are that adsorption happens on a regular surface where every adsorption position possesses an equal affinity for the adsorbate. It also supposes that when the adsorption site is occupied, no more adsorption can take place at that adsorption position. These hypotheses make the Langmuir model predominantly appropriate for characterizing the conduct of monolayer adsorption on a surface. Its high accuracy implies that it can effectively predict and explain the adsorption behaviour of the system under investigation [54, 55].

Table 4. Details of the kinetic models used in the current study.

Kinetic Model	Differential Form	Linear Form	Slop	Intercept
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$-k_t$	$\ln q_e$
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{1}{q_e}$	$\frac{1}{k_2 q_e^2}$
Elovich model	$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$	$q_e = \frac{1}{\beta}\ln t + \frac{1}{\beta}\ln \alpha\beta$	$\frac{1}{\beta}$	$\frac{1}{\beta}\ln \alpha\beta$
Intra-particle diffusion	– –	$q_t = k_p t^{0.5} + I$	k_p	I

Table 5. The values of constants of kinetic models.

Model	Constant	Value
Pseudo first order	k_1	0.0079
	q_e	3.5708
	R^2	0.9966
Pseudo second order	k_2	1.650310^{-4}
	q_e	11.6414
	R^2	0.2529
Elovich model	α	0.0743
	β	1.1899
	R^2	0.9549
Intra-particle diffusion	k_p	0.2515
	I	-0.6575
	R^2	0.9982

3.3.2 Kinetic study

Kinetic studies in adsorption processes aim to understand the rate at which adsorbate molecules are taken up by an adsorbent material. Several models are commonly used to describe these processes, including pseudo-first-order, pseudo-second-order, Elovich, and intra particle diffusion models. These models provide mathematical equations that describe the relationship between the amount of material adsorbed and time taken, allowing for a better understanding and prediction of the adsorption kinetics.Table 4 explains the models used to describe the kinetic study in the current research. The results of the kinetic study are represented by Fig. 18, Fig. 19, Fig. 20, and Fig. 21 and Table 5 indicate that the intra-particle diffusion model yielded the best fit to the experimental data compared to the other aforementioned models [49].

Table 6. The values of thermodynamic properties constants.

$T, C°$	$\Delta H(KJ/mol)$	$\Delta S(J/mol.K)$	$\Delta G(KJ/mol)$
20.0	-169.8229	-491.3600	-25.7808
22.5			-24.5524
25.0			-23.3240
27.5			-22.0956
30.0			-20.8672
32.5			-19.6388
35.0			-18.4104
37.5			-17.1820
40.0			-15.9536
42.5			-14.7252
45.0			-13.4968
47.5			-12.2684
50.0			-11.0399

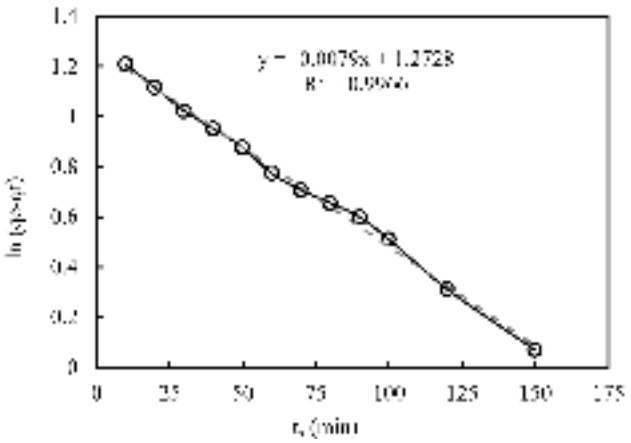


Figure 18. Pseudo first order model of benzidine adsorption using pineapple peels.

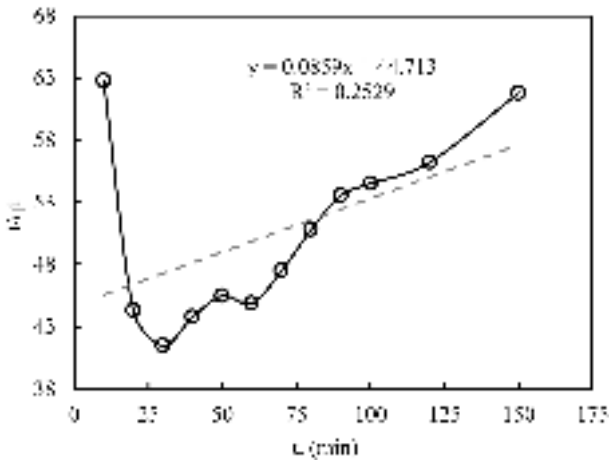


Figure 19. Pseudo second order model of benzidine adsorption using pineapple peels.

The correlation coefficient (R^2) for this model was found to be 0.9982, which suggests a very strong agreement between the predicted values and the actual experimental observations [48]. The intra-particle diffusion model is based on

the assumption that the rate-limiting step in the adsorption process is primarily governed by the diffusion of the adsorbate within the adsorbent particles. The model explains the relevance related to the amount that is adsorbed (q) and the square root of time, which demonstrates the diffusion process. The high correlation coefficient of this model indicates that the diffusion formula exceedingly describes the benzidine adsorption behavior. This suggests that the rate of benzidine dye diffusion within the porous structure of pineapple peels meaningfully impresses the adsorption process. The strong agreement between the predicted and experimental values supports the suitability of the intra-particle diffusion model for this particular adsorption system. On the other hand, the pseudo first order, pseudo second order, and Elovich models exhibited lower correlation coefficients of 0.9966, 0.2529, and 0.9549, respectively. These lower correlation coefficients suggest that these models were relatively less effective at capturing the kinetics of benzidine dye adsorption onto pineapple peels.

3.3.3 Thermodynamic study

Thermodynamic studies in adsorption processes focus on understanding the energy changes that occur during the adsorption process. This includes examining the effects of temperature on the adsorption behavior. The functions used to describe the thermodynamics of an adsorption system are Enthalpy (H), Entropy (S), and Gibbs free energy (G). The relationship between these thermodynamic functions is given by the equation: $\Delta G = \Delta H - T\Delta S$, where ΔG is the change in Gibbs free energy, ΔH is the change in enthalpy, T is the temperature in Kelvin, and ΔS is the change in entropy. Determining these thermodynamic functions for any adsorption process provides insights into the physical and chemical nature of the process [53]. Also, it helps to optimize the efficiency of the adsorbent material by understanding the mechanism of adsorption, estimating the heat exchange, evaluating the spontaneity of the process, and characterizing the disorder level. From Fig. 22 and Table 6, it can be seen that the adsorption is of chemical type, spontaneous, exothermic and of decreased entropy, according to the value of enthalpy and the sign of ΔG, ΔH, and ΔS, respectively.

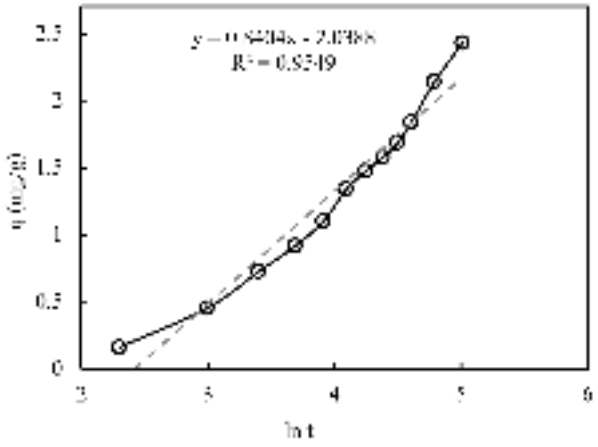


Figure 20**.** Elovich model of benzidine adsorption using pineapple peels.

4. Using the adsorption residues as a rodenticide

After assessing the efficacy of pineapple peels as an adsorbent for toxic benzidine in a simulated solution, the subsequent step involved the environmentally friendly disposal of the toxic-loaded peels. One proposed method was the utilization of these toxic residues as rodenticide [51]. To conduct this purpose, a total of 50 Sprague Dawley albino rats (Rattus rattus), evenly divided between males and females (25 each), were employed in this experiment. The rats, aged between 5 and 6 months and weighing between 200 and 350 g, experienced a one-week acclimation period in clean cages under controlled laboratory conditions. Throughout this period, they received ordinary provender of rats to ensure overall health and acclimatization to the environment and diet before commencing the experiments [56]. Environmental conditions were upheld at a temperature of $22 \pm 2C°$, with a lighting schedule of 12-14 hours per day using a standard light bulb. Following the adaptation, the rats were divided into 5 groups, each consisting of 5 animals for both (males and females) housed in separate cages [55]. These groups were fed a diet comprising regular rat provender and pineapple peel loaded with benzidine. 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 pineapple peels. The rats were administered toxic pineapple peels, mixed with a controlled amount of sweet material, less than 5 wt% of the supplied food provision [57]. The assessment of pineapple peels as a rodenticide resulted in notable fatalities among both male and female rats that consumed pineapple peels loaded with binzidine. These fatalities manifested at varying percentages and intervals, contingent upon the quantity of rodenticide ingested by the rats [58]. 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 (mg) per body weight (kg) of deceased animals, was determined to be 315 (mg/kg) for males and 300 (mg/kg) for females. These values are consistent with the cited literature range of 309 [59]. LD_{50} values within the 300 to 315 mg/kg range indicate a high concentration of binzidine in the rodenticide, impacting necessary enzymes vital for rat physiological functions. This, in turn, results in enzyme deviation or inhibition, particularly affecting dehydrogenase enzymes, leading to myocardial infarction [60]. Similar results are recorded by [49] polluted using mandarin with adsorbed phenol.

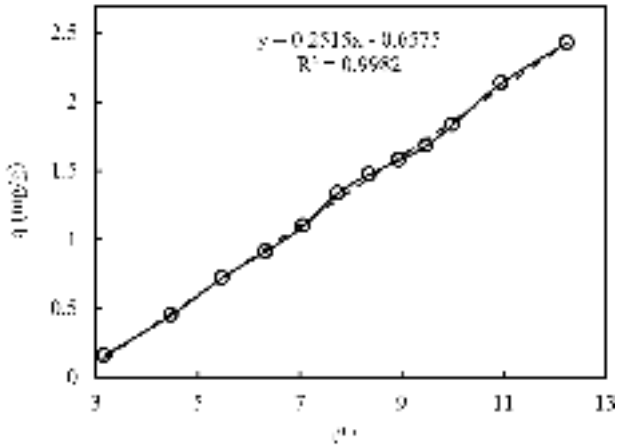


Figure 21**.** Intra-particle diffusion model of benzidine adsorption using pineapple peels.

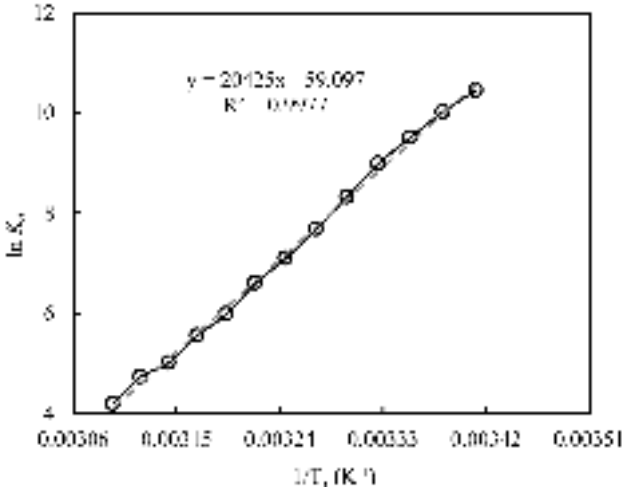


Figure 22**.** Thermodynamic properties of benzidine adsorption using pineapple peels.

5. Conclusions

Agricultural waste persists as an ongoing environmental challenge, a consequence of essential farming activities. This study introduces an inventive approach to repurpose a substantial agricultural byproduct: pineapple peels. Discarded in millions of tons annually, these peels could be a sustainable resource for water treatment. Results reveal a surface area of nearly $48.6 m^2/g$,

suggesting significant potential for recovering benzidine, a carcinogenic substance, from aqueous solutions under diverse operational conditions. The removal efficiency directly correlates with key factors—pineapple peels dose, contact time, and agitation speed—while inversely relating to pH, temperature, particle size, and the initial concentration of benzidine. Under specific conditions—pH 1, a contact time of 150 minutes, a temperature of 20C°, 3 g of pineapple peels, an initial benzidine concentration of 8 ppm, an agitation speed of 450 rpm, and a particle size of 88μm the highest removal percentage, reaching 91.064%, is achieved. Isotherm studies confirm the Langmuir model as an apt representation of the adsorption process, further corroborated by the high correlation coefficients (R^2) of 0.9936 and 0.9982 for the intra-particle diffusion model. Thermodynamically, the adsorption is exothermic, accompanied by a reduction in entropy, as evident from enthalpy and entropy values of $-169.8229\ kJ/mol$ and $-0.4914\ kJ/molK$, respectively. This signifies spontaneous adsorption, supported by negative Gibbs free energy values across various temperatures. Morphological investigations, including BET, FTIR, and SEM analyses on both pristine and exhausted pineapple peels, illustrate the impact of benzidine adsorption on pore closure. BET analysis indicates that the adsorption process occupies less than 89% of the surface area post-treatment, and FTIR results highlight the disappearance and shift of numerous peaks, emphasizing the significant role of adsorption. SEM observations elucidate the closure of pores within pineapple peels due to benzidine adsorption.

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

Funding source

This study didn't receive any specific funds.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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