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(RESEARCH ARTICLE)

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Evaluation of low-cost adsorbent of Manilkara zapota for phenol removal in aqueous solution

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Abstract

Industrial waste water is aqueous waste that results from the dissolution or suspension of materials in water. Phenol is the substances that are utilized in the industry. The main aim of the study is to treat the wastewater for the removal of phenol by batch mode adsorption using the agricultural waste that is Manilkara zapota. The characterization of the adsorbent was determined by FTIR, SEM and XRD. The adsorption process is to evaluate the kinetics of adsorption and the pseudo second order kinetics showed good regression value of 0.995 for 60 mg/L. The Langmuir capacity was found to be 9.8 mg/g. The optimum time to reach equilibrium of adsorption is 2 hours. From the findings the Manilkara zapota prove to be a promising adsorbent for the removal of phenol from the aqueous environment.

Keywords: Phenol; Manilkara zapota; Adsorption; Langmuir; Wastewater

1. Introduction

Phenolic compounds, a class of organic and as a priority pollutants, are omnipresent in our environment, originating from both natural and anthropogenic sources. Their presence in various environmental matrices, particularly water bodies, poses significant risks to ecological health and human well-being due to their toxicity and potential for bioaccumulation. This necessitates the development of effective and sustainable remediation strategies to remove phenols from contaminated environments [1]. This introduction delves into the significance of phenols as pollutants, the potential use of Manilkara zapota leaves as a biosorbent, and the efficacy of carbonizing these leaves to enhance phenol removal. Phenols constitute a diverse group of aromatic compounds characterized by a hydroxyl group (-OH) directly bonded to a benzene ring. Naturally occurring phenols are products of plant metabolism, found in tannins, lignin breakdown products, and other biomolecules. Specific phenolic compounds commonly found in the environment include phenol, cresols, and chlorophenols, often associated with industrial activities. Anthropogenic sources of phenols are numerous, encompassing industrial discharges from petroleum refineries, coal conversion plants, pharmaceutical manufacturing, and the production of resins, plastics, and pesticides. These activities often lead to the release of phenolic compounds into wastewater streams and ultimately the broader environment [2]. The environmental persistence and toxicity of phenols present considerable challenges. Even at low concentrations, phenols can impart unpleasant tastes and odors to drinking water. Higher concentrations directly threaten aquatic life and humans [3]. Phenols can disrupt endocrine function, affect the nervous system, and have carcinogenic potential depending on the specific compound and exposure levels [4]. For instance, chronic exposure to phenol can lead to skin irritation and central nervous system disorders. In contrast, exposure to high levels of chlorophenols has been linked to liver, lung, and kidney damage. Given their environmental risks, the development of sustainable and cost-effective strategies for the remediation of phenol-contaminated waters is of crucial importance [3].

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Adsorption has emerged as a promising technique for the removal of phenols from contaminated water. The search for environmentally friendly and readily available adsorbents has led to the exploration of various biomaterials, including agricultural wastes and plant biomass. Manilkara zapota, commonly known as sapodilla or chikoo, is an evergreen tree native to tropical regions. Its leaves, abundant and often discarded as agricultural waste, represent a potentially valuable resource for biosorption applications. Manilkara zapota leaves possess many functional groups, including hydroxyl, carboxyl, and amine groups, that could facilitate the adsorption of phenolic compounds, offering a sustainable and cost-effective solution for water [5]. Carbonized biomass often exhibits increased surface area, porosity, and surface functional groups, all of which contribute to improved contaminant removal. Studies have demonstrated that carbonization can significantly increase the phenol adsorption capacity of various biomaterials, including fruit peels and agricultural residues. Carbonizing Manilkara zapota leaves could, therefore, provide a means to develop an even more effective and environmentally sustainable material for the removal of phenols from contaminated water [6]. The aim of the work is 1. To use Manilkara zapota leaf and to evaluate the efficiency of the adsorbent produced for the removal of the phenol from aqueous solution 2. To examine the equilibrium uptake capacity of the adsorption study using different isotherm models such as Langmuir, Freundlich, and Dubinin Radushkevich.

2. Materials and Methods

From the agricultural field the Sapota leaves were collected and were used for the treatment. It was washed in a running water three or four times to remove color and also the adhering dirt and was then dried in a hot air oven at 80^0c for 3 hours. The procure powder was ground and sieved to obtain a uniform particle size of 60 µm and then carbonized by keeping in a muffle furnace for 30 min at 600^0C.

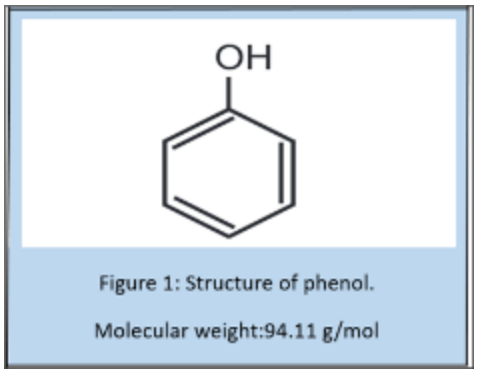


Figure 1 Phenol structure

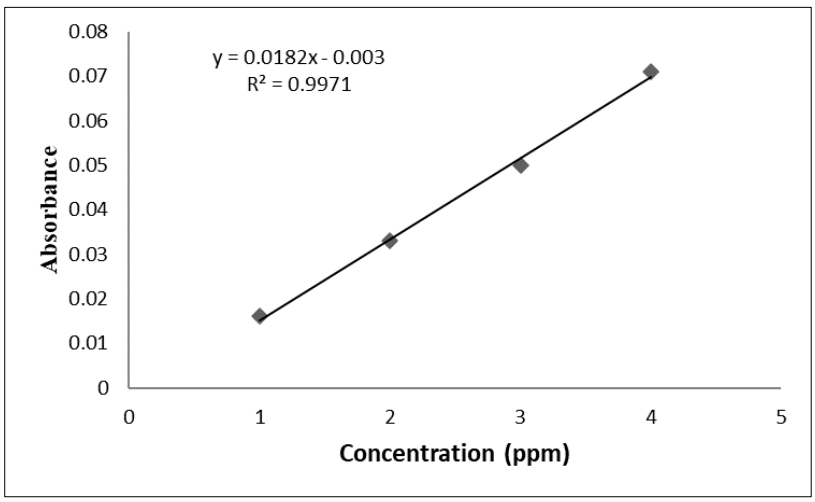


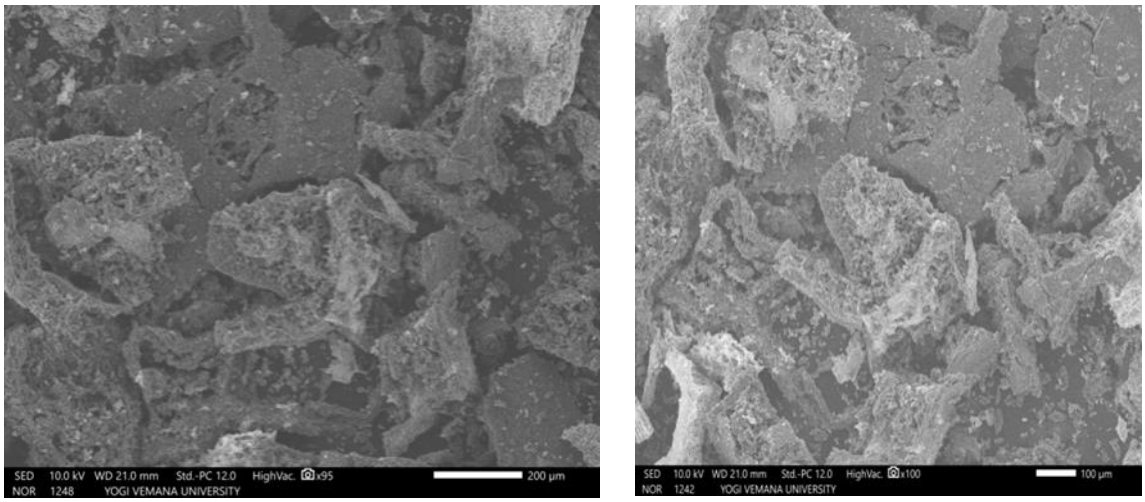
Figure 2 Calibration plot for phenol

Accurately 1000 mg of the phenol solution was separately weighed and made up to 1000 ml in a standard measuring flask to get a phenol solution of 1000 ppm. These were kept as mother solution. The solution was kept in coloured bottles to avoid degradation to light and the measurements of absorbance were carried out using a Lab India UV-Vis spectrophotometer and the maxima absorbance of phenol was used as required wavelengths for the absorbance measurements. A maximum absorbance for Phenol is 270 nm.The molecular formula of the phenol is C_6H_5OH, its molecular weight is 94.11g/mol.

3. Results and Discussion

FTIR , XRD and SEM characterization techniques was used to know the surface functional and structural features of the adsorbent. SEM study showed the porous and surface chemistry of the carbonized carbon with their role in the phenol adsorption (Fig 3). The figure showed that the phenol molecules filled the cavities of the adsorbent surfaces.

Before Adsorption



After adsorption

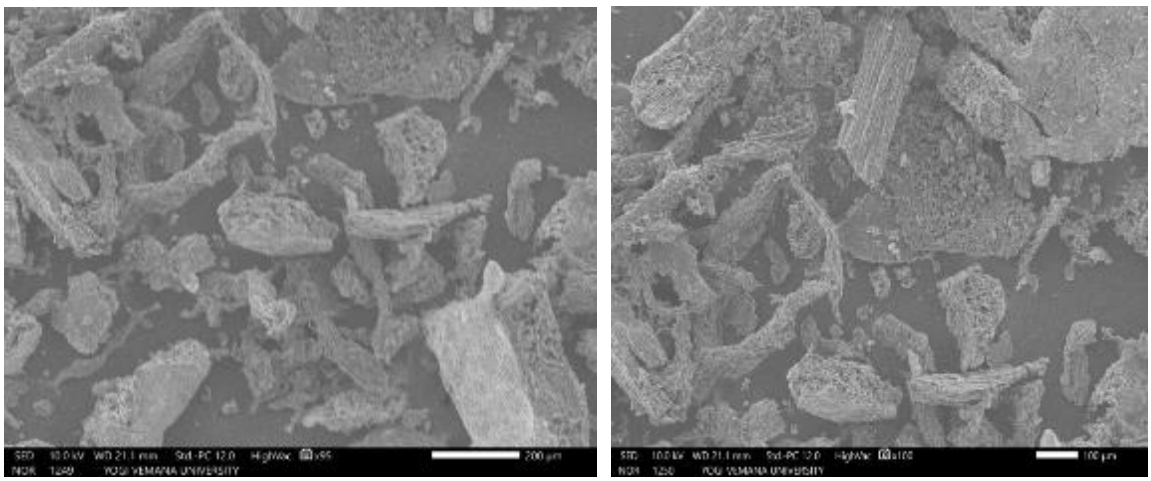


Figure 3 SEM photographs

The FTIR is a main technique to know the characteristic functional groups of the adsorbent, which are capable of adsorbing metal ions. It provides structural and compositional information on the functional groups present in the sample. The functional groups present in the carbonized Manilkara zapota leaves were investigated by FTIR spectra within the range of 400-4000 cm-1 wave number. The band at 1181cm^{-1} showed a shift due to phenol interaction with the carbonyl group which caused the band stretch of the aromatic ring. The presence of peak is a characteristic feature of the adsorbent (Fig. 4).

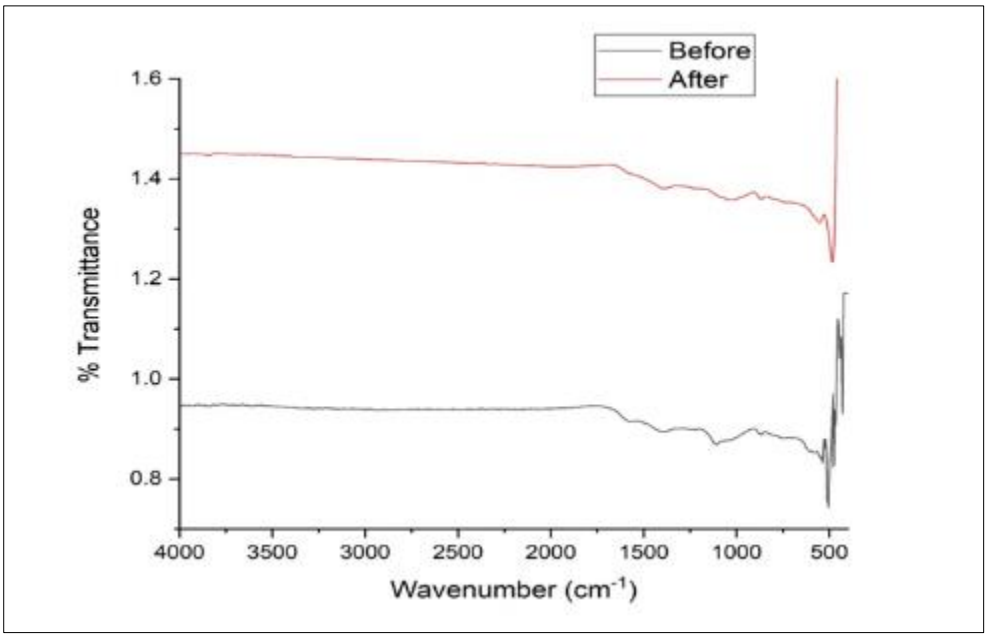


Figure 4 FTIR Spectra of before and phenol adsorbed carbonized samples.

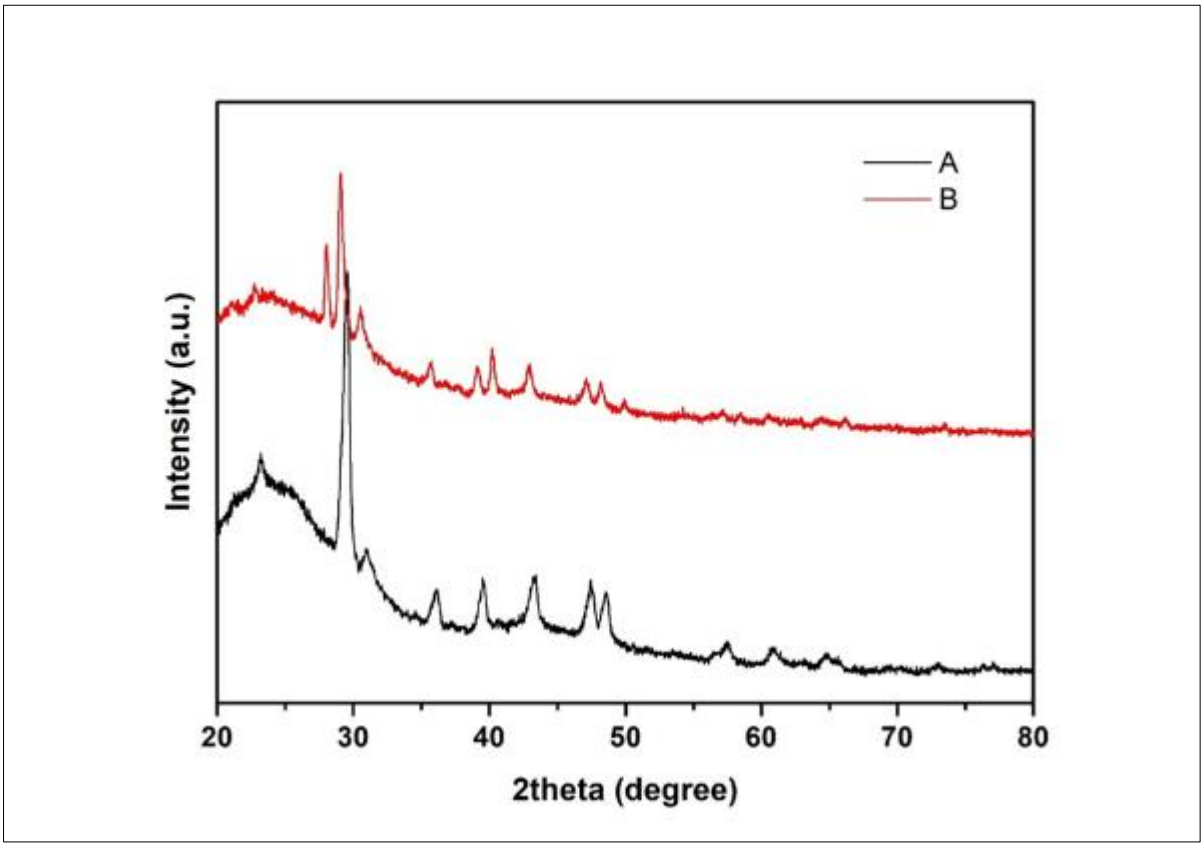


Figure 5 XRD patterns of adsorbent and phenol adsorbed sample

The results were analysed to the Langmuir, Freundlich, and DubininRadushkevich isotherm equations to calculate the adsorption parameters as well as the kinetic studies were analyzed using first and second-order models concerning phenol concentration.

3.1. Contact Time

It has been noted there is increase in removal with time and attain a constant value at some point of time, where no more phenol was removed and the process was in a state of equilibrium. Table 1 showed the stable time increased with an increase in the initial concentration of the phenol. Removal of phenol at equilibrium (q_e) was 2.923 mg/g at 32°C for an phenol concentration of 40 mg/L. For any given time, an increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of phenol uptake (q) per unit weight of adsorbent (mg/g) (Tables 1). Previous observation has been reported for the adsorption of phenol onto natural bioadsorbent neem leaves [7].

Table 1 Comparing the kinetics of first and second-order for adsorption of Phenol.

Phenolconc. (mg/L)	**q_e (exp) (mg/g)**	**Kinetics of First order**			**Kinetics of Second order**		
		k_1 (1/min)	q_e (cal) (mg/g)	R^2	k_2 (g/mg/min)	q_e (cal) (mg/g)	R^2
40	2.923	0.027	1.377	0.898	0.062	2.857	0.983
60	5.227	0.02	1.648	0.894	0.035	6.329	0.995
80	6.384	0.029	2.559	0.785	0.047	5.076	0.966
100	6.582	0.009	2.432	0.588	0.03	5.882	0.976

Table 2 Langmuir and Freundlich constants for adsorption of Phenol

Langmuir			**Freundlich**		
Q_0 (mg/g)	b (L/mg)	RL	kf (mg1-1/n L1/n g –1)	n	R^2
9.8	0.032	0.44	0.004	0.422	0.994
		0.342	0.048	0.73	0.973
		0.280	1.648	3.69	0.414
		0.238	0.014	0.789	0.701

3.2. Adsorption Kinetics

The first-order kinetic given by Lagergren [8] can be given:

$$\text{Log } (q_e\text{-}q) = \log q_e - k_1 t/2.303 \quad (1)$$

Values of q_e and k_1 were calculated from the slope and intercept of the plot of log (q_e-q) vs. t for different concentrations of phenol.

The second-order kinetic model [9] is given below:

$$t/q = 1/k_2 q_e^2 + t/q_e \quad (2)$$

Table 2 showed the results of fitting kinetic data to the first and second-order model and also comparing of the q_e values that are experimental with those of calculated from first and second-order kinetic model, showed a good agreement between the second-order equations for the adsorption of phenol by the adsorbent (Fig. 6). Indicating that the treatment process of the phenol followed a kinetic model of second-order. This is in accord to the findings of phenol removal using neem leaves [7] and phenol adsorption onto banyan root activated carbon [10].

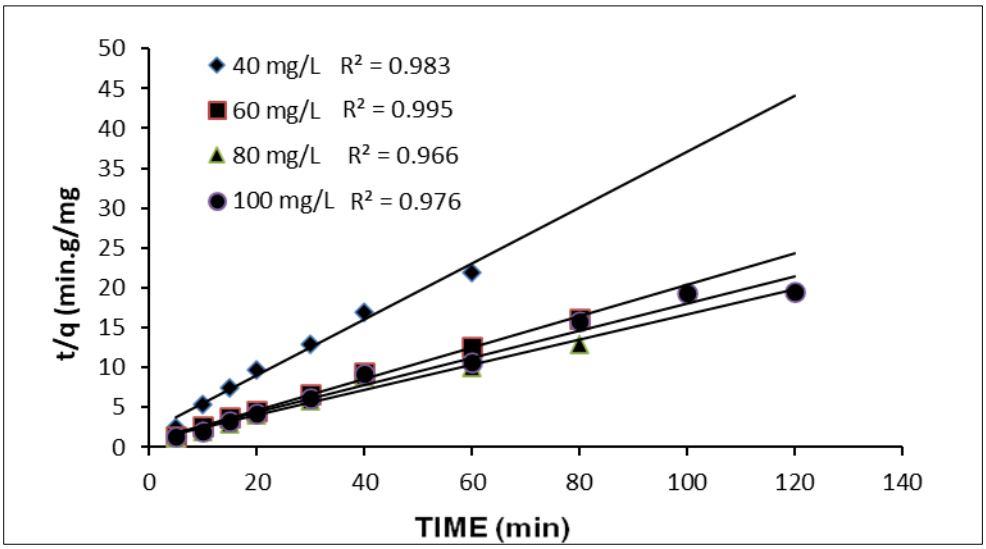


Figure 6 Second-order kinetics for adsorption of Phenol

3.3. Adsorbent dosage

To examine the effect of the adsorbent dosage on the removal efficiency of phenol, adsorption experiments were put up with different amounts of Manilkara zapota Leaves (100, 200, 300, 400, and 500mg/50 ml) and phenol concentrations (40, 60, 80, and 100 ppm). The percent removal of phenol increased with the increase in dose of the adsorbent and attains a constant value after a particular adsorbent dose. The more amount of adsorbent could adsorb larger quantity of adsorbate due to the obtainability of increased surface area of the material, greatest removal of phenol observed be nearby 62.97% for the material for the initial concentration of 40 mg/L.

Isotherm of Langmuir [11] can be described as

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (3)$$

The Q_o constant signifies the monolayer adsorption capacity (mg/g) and b is linked to the energy of adsorption (L/mg). For the room temperature 32^0C, the obtained Q_o value, is index of adsorption efficiency of the adsorbate on the material was found to be 9.8 mg/g. Some of the Langmuir capacity onto various adsorbent reported in the literature are for sugarcane bagasse as 4.57mg/g [12], Acacia tortlis pod shell as 21.32 mg/g [13].

Freundlich isotherm [14]

$$\text{Log } q_e = \log k_f + 1/n \log C_e \quad (4)$$

Figure 6 showed better agreement to experimental data of Freundlich isotherm (plot q_e vs. C_e) of phenol studied.

Dubinin-Radushkevich isotherm

Another equation used in the analysis of isotherms was proposed by Dubinin-Radushkevich [15].

$$q_e = q_m \exp(-B\varepsilon^2) \quad (5)$$

where $q_m$is the D-R constant and ε can be correlated as

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \quad (6)$$

Where R is the universal gas constant (8.314 J/mol/K), C_e is the equilibrium concentration of adsorbate in solution (mol/L) and T(K) is the absolute temperature.

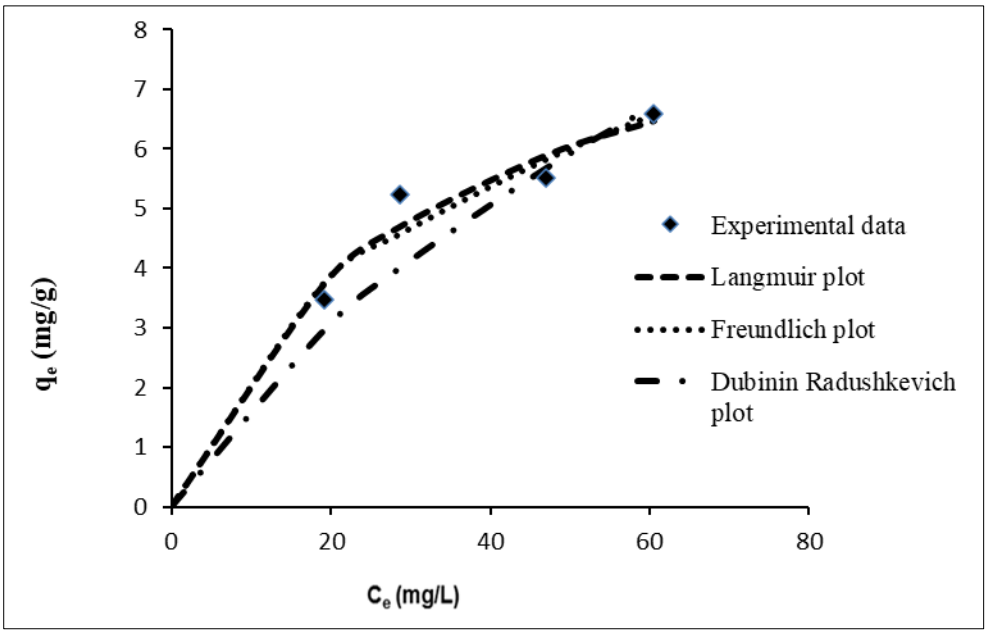


Figure 7 Isotherms study of Phenol

3.4. Impact of pH on the phenol removal

The pH is highly relevant because it can change the particle's surface charge, favoring the adsorption process. The pH was found out with the variation of pH value from 2 to 11 and initial phenol concentration of 60 and 80 mg/L. The percent removal decreased from 61.39 to 26.4 % for 60 mg/L of phenol concentration for adsorbent. From the different values of pH, the pH 2 showed a big removal percentage of phenol as seen to other pH values (Fig. 8). In an acidic environment, the amount of H^+ ions would be higher and they are likely to neutralize some of the anionic functional groups present on the surface of the adsorbent. As the pH increased, the adsorbate molecules shifted towards ionization, enabling the adsorbent to effectively capture the phenoxide ions. Previous study was observed in the phenol removal from green tea leaves [16].

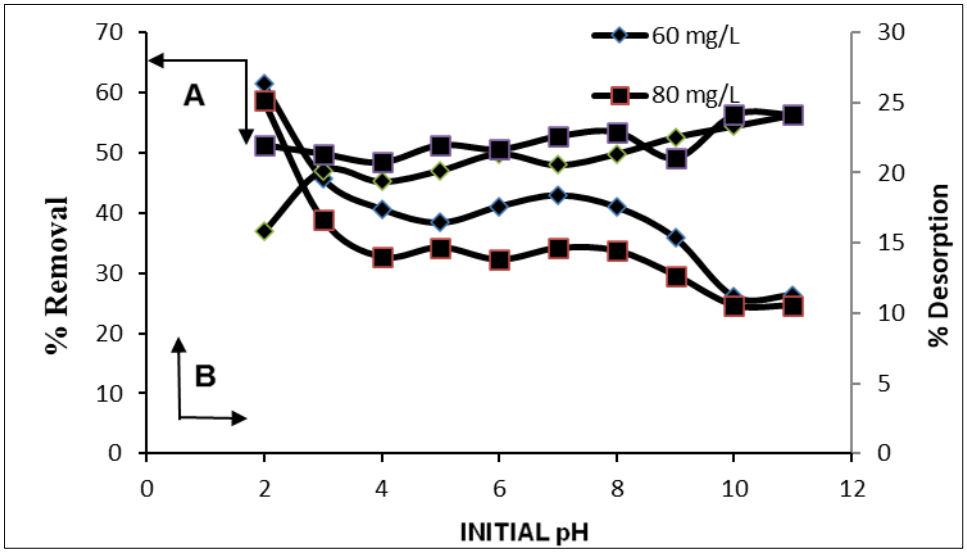


Figure 8 Impact of pH on adsorption of Phenol

4. Conclusion

The percentage removal of phenol exponentially increases with the increase in the material dosage. The photograph of the SEM reported total covered pores by after adsorption of the phenol solution molecule supporting the adsorption

method. It was reported that the Freundlich isotherm model suited better for phenol adsorption and the kinetic study followed the pseudo–second order kinetics. The maximum phenol uptake was observed at pH 2.0. With the above work we draw the conclusion that Manilkara zapota leaves can remove the phenol from aqueous solution. However, proper optimization of the removal process is recommended before any industrial application.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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