

REMOVAL OF PHENOL FROM AQUEOUS SOLUTION BY ADSORPTION ON YEAST, *SACCHAROMYCES CEREVISIAE*

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ABSTRACT

The aim of this study is to investigate the possibility of *Saccharomyces cerevisiae* as an alternative adsorbent for phenol removal from aqueous solution. The *Saccharomyces cerevisiae* was characterised by Brunauer Emmett Teller (BET) and Fourier transform (FT-IR). Adsorption properties of *Saccharomyces cerevisiae* towards phenol were systematically investigated, including pH effect, adsorbent dosage, contact time and initial concentration. The adsorption of phenol decreased with increasing pH. The experimental data were analysed by Langmuir and Freundlich models in order to describe the equilibrium isotherms. Equilibrium data fitted well to the Langmuir model with correlating constant (R^2) higher than 0.99. The study showed that *Saccharomyces cerevisiae* could be used as a new and efficient adsorbent material for the removal of phenol from aqueous solution.

Keywords: Phenol, biosorption, *Saccharomyces cerevisiae*, equilibrium isotherms, FT-IR

1. INTRODUCTION

Phenols are organic compounds of great environmental interest. Their determination has been increasing in recent years because of their toxicity, even at low concentrations. Phenolic compounds are often derived from various manufacturing processes such as pharmaceutical, oil refineries, coke plants, and phenolic resin plants (Uddin et al., 2007; Ahmaruzzaman, 2008; Yamasaki et al., 2008; Juang and Lin, 2009; Okasha and Ibrahim, 2010). Phenolic compounds in portable water emit an unpleasant odor and flavor in concentration as low as $5 \mu\text{g L}^{-1}$ and are poisonous to aquatic life, plants and humans. Kumar et al (2009) have reported that ingestion of phenols in concentrations from 10 to 240 mg L^{-1} for long periods causes mouth irritation, vision problems, diarrhoea, and excretion of dark urine. They are considered one of the priority pollutants by the US Environmental Protection Agency (Yan et al., 2006; Uddin et al., 2007). World Health Organisation (WHO) has established the maximum permissible concentration of phenol in drinking water as 1 mg L^{-1} (Kumaran and Paruchuri, 1996). As a result, various studies have been conducted for the removal of phenolic compounds before being discharged to receiving sink.

The treatment of this type of wastewater involves recuperative techniques such as solvent extraction, adsorption, filtration, precipitation, ion exchange, biological treatment and destructive techniques such as ozonation and oxidation (Aksu, 2001; Banat et al., 2002; Rengaraj et al., 2002; Roostaei and Tezel, 2004; Hameed and Rahmann, 2008; Juang and Lin, 2009). Adsorption technology using activated carbon is currently being used extensively for the removal of pollutants from gaseous and liquid phases. The main disadvantages associated with this adsorbent are the high regeneration cost, intraparticle resistance in adsorption process and poor mechanical strength (Aravindhan et al., 2009; Kumar, 2009).

Recently, adsorption has attracted considerable interest especially from low-cost industrial wastes, natural resources for the removal of phenol and phenolic compounds. These wastes require little processing to increase their sorption capacity. Various industrial wastes and agricultural materials such as paper mill sludge, coal, dried sewage waste, water hyacinth ash, green macro alga and rice husk ash have been explored for their technical visibility to remove phenols (Calace, 2002; Mahvi et al., 2004; Uddin, 2007; Aravindhan et al., 2009).

In this study, we report the removal of phenol from aqueous solution using yeast *Saccharomyces cerevisiae*. The yeast was characterised using BET and FT-IR spectroscopy studies. The effect of various factors such as initial pH of solution, amount of adsorbent, time of contact and concentration of adsorbates was investigated under batch equilibrium technique. Equilibrium adsorption data were fitted to Freundlich and Langmuir adsorption isotherm models.

2. MATERIALS AND METHODS

2.1 Preparation and application of Adsorbent

Yeast *Saccharomyces cerevisiae* was supplied as a waste by local company. The yeast was pre-treated with 0.1 N Hydrochloric acid for an hour. The pre-treatment aids in stabilising the yeast and retaining the reactive sites intact. The acid protonated yeast was then washed with double distilled water. Finally, the washed materials were air-dried, ground in a mortar, and passed through a screener with order of 150 μm pore diameter. Then the yeast cells were stored in a desiccator for future use.

2.1.1 Characterisation of Yeast *Saccharomyces cerevisiae*

Characterisation of the adsorbent was carried out by BET (Micromeritics ASAP 2020) and FT-IR study. In FT-IR, dilution and homogenisation to 0.01% (w/w) with KBr (spectroscopic grade) were carried out with yeast additional grinding (Aravindhan et al., 2009). The disks were pressed in a hydraulic KBr press. The transmission FT-IR spectra were then recorded between 400 and 4 000 cm^{-1} using a Perkin -Elmer Spectrum system to determine the type of functional groups in the cell walls.

2.1.2 Adsorbate

Stock solutions were prepared by dissolving 1 g of phenol in 1 L of double distilled water. The stock solutions were then suitably diluted and used for biosorption experiments. Calibration curve with the concentrations ranging from 0 to 150 mg L^{-1} was obtained. The concentration of phenol was determined using a Perkin -Elmer Lambda 35 UV-VIS spectrophotometer (Shimadzu Model UV-1601) at wavelength of 270 nm.

2.2. Sorption experiments

2.2.1 Effect of pH

The effect of pH on the amount of phenol removal was analysed over the pH range from 1 to 12. In this study, 50 ml of phenol solution 100 mg L^{-1} was taken in stoppered conical flask and agitated with 0.3 g of yeast using a shaker at room temperature ($27 \pm 2^{\circ}\text{C}$). Agitation was made for 4 h at constant oscillation of 75 strokes/min. The samples were centrifuged, and the left out concentration in the supernatant solution were analysed using a UV-VIS spectrophotometer by monitoring the absorbance changes at a maximum wavelength of 270 nm.

2.2.2 Effect of adsorbent dosage

The effect of yeast mass on the amount of removal of phenol solution was obtained by contacting 50 ml of phenol solution of initial concentration of 100 mg L^{-1} with different weighed amount ranging from 0.3 g to 10 g. Each sample was then agitated for 4 h at constant oscillation of 75 strokes/min. The samples were then centrifuged and the concentrations were then analysed as before.

2.2.3 Effect of contact time

The effect of contact time on the removal of phenol was carried out at different intervals ranging from 1-6 hours. In each case 50 ml of phenol solution of initial concentration 100 mg L^{-1} was added to each of the conical flasks. Corresponding masses of approximately 0.3 g of 150 μm diameter biosorbent were added to each of the flasks and the mixture agitated at constant oscillation of 75 strokes/min. After the stated time the samples were removed from the rotary shaker and centrifuged. The supernatant solution was then analysed using the UV-VIS spectrophotometer.

2.3. Adsorption equilibriums

Equilibrium studies were carried out by contacting 0.3 g of yeast powder with 100 ml of phenol solution of different initial concentrations in the range of 10 to 160 mg L^{-1} in 250 ml stopper conical flasks. The samples were then shaken at a constant oscillation for 4 h. After equilibrium, the concentrations in the samples were analysed as before. The phenol concentration retained in the adsorbent phase was calculated according to mass balance of the equation as given below:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration (mg L^{-1}) respectively of phenol in solution, V is the volume of phenol in solution (L), and W is the mass (g) of the adsorbent. Two replicate per sample were done and the average results are presented.

3. RESULTS AND DISCUSSION

3.1 Characterisation of Adsorbent

The FT-IR technique is an important tool to identify the characteristic functional groups on the adsorbent surface. The FT-IR spectra of the chemically modified *Saccharomyces cerevisiae* before and after adsorption are shown in Figs. 1 and 2.

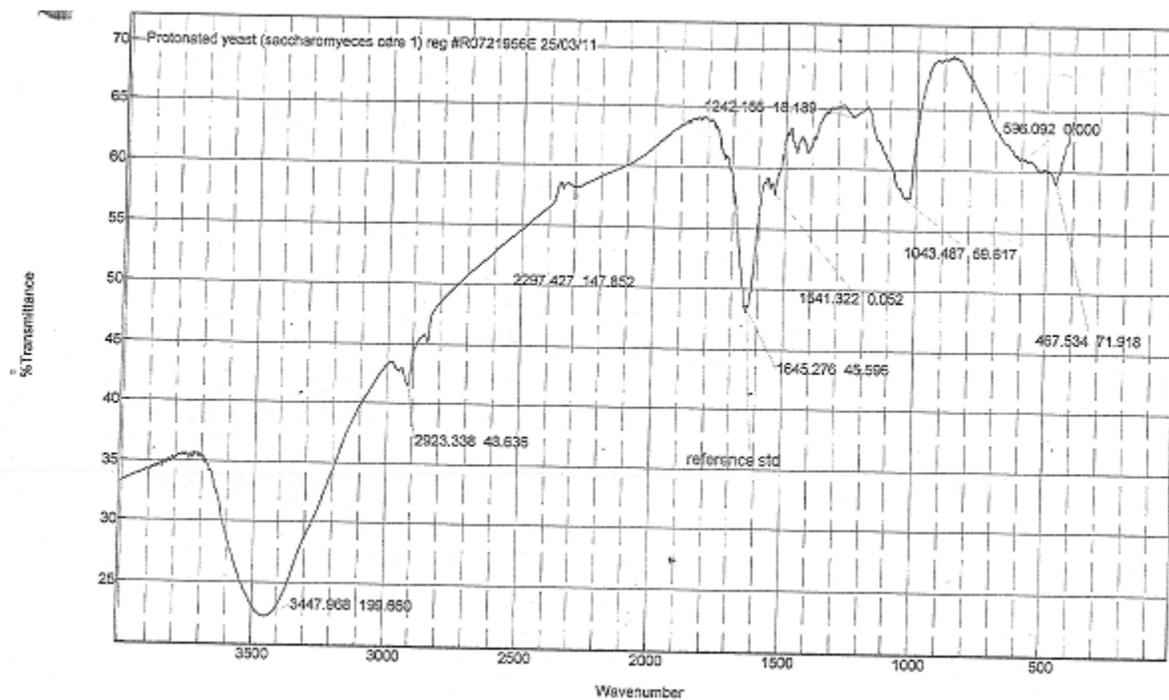


Fig. 1. FTIR spectrum of *Saccharomyces cerevisiae* before biosorption of phenol

The FT-IR spectrum of the chemically modified yeast before adsorption shows a broad absorption peak at 3448 cm^{-1} corresponding to overlapping of -OH and -NH peaks. A peak at 2923 cm^{-1} represents the C-H group. A peak at 1645 cm^{-1} is conjugated to an NH deformation mode and is indicative of an amide 1 band. The peak at 1541 cm^{-1} is indicative of amide 2 and results from NH deformation mode. There are no significant changes in the FT-IR of biosorbent after adsorption in Fig. 2. Some peaks slightly shifted to a lower frequency region, i.e. at 3415 cm^{-1} (-OH and -NH), around 1639 cm^{-1} (-NH) stretching vibrations in the spectrum after biosorption. Also it was evident from the figures that there were no significant changes in the IR spectrum of modified and phenol treated yeast, proving it to be a physiosorption.

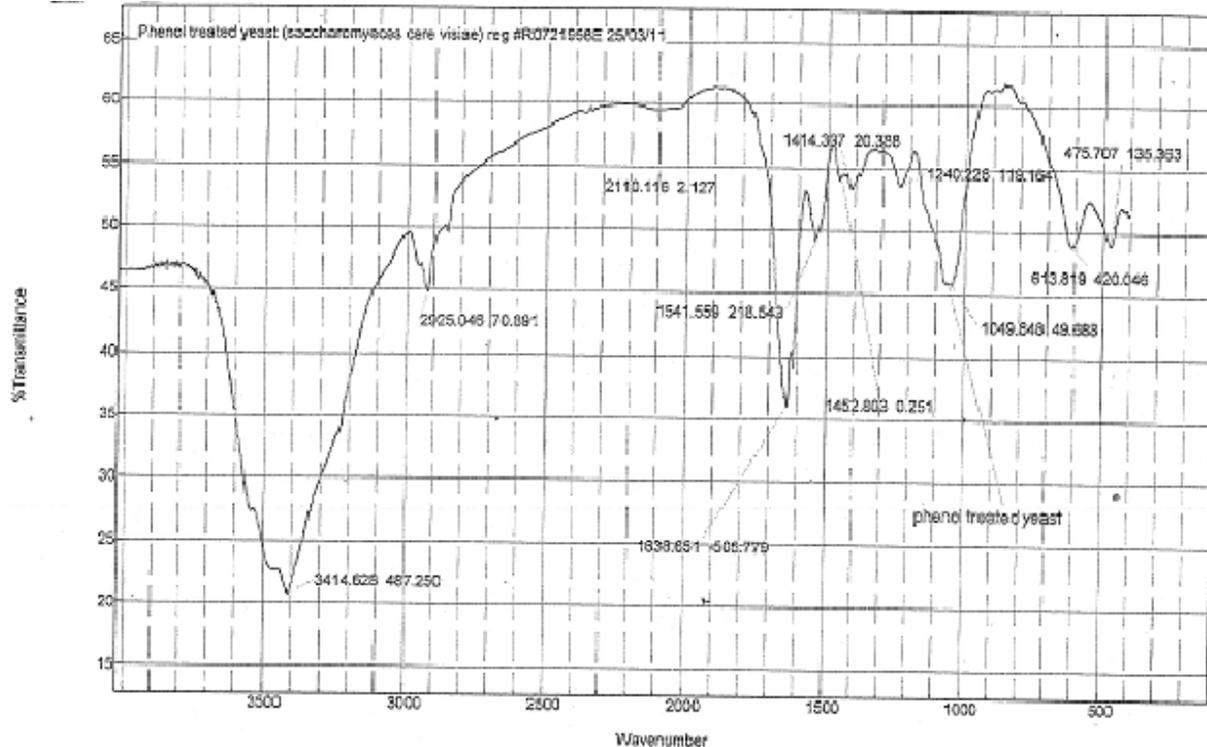


Fig. 2. FTIR spectrum of *Saccharomyces cerevisiae* after biosorption of phenol

3.2 Surface area analysis

Table 1 shows the summary of the physical properties of the *Saccharomyces cerevisiae* which were determined by BET. The N_2 adsorption gave the specific surface area (S_{BET}) of $188.6 \text{ m}^2/\text{g}$ and the value is close to other values reported in literature for other low cost sorbents (Aravindhana et al., 2009; Kumar et al., 2009).

Table 1. Physical properties of *Saccharomyces Cerevisiae*

Property	Magnitude
Surface area(m^2/g^{-1})	188.6
Total pore volume($\text{cm}^3/\text{g}^{-1}$)	0.554
Pore diameter(Angstrom)	92.45
pH_{zpc}	4.80

3.3 Effect of pH on phenol adsorption

The biosorption capacity is influenced most by the pH of the solution. The pH of the solution affects the surface charge of the adsorbent, degree of ionisation and speciation of the adsorbate species, which may lead to change in kinetics and equilibrium characteristics of the adsorption process. Fig. 3 shows the effect of pH on the adsorption of phenol.

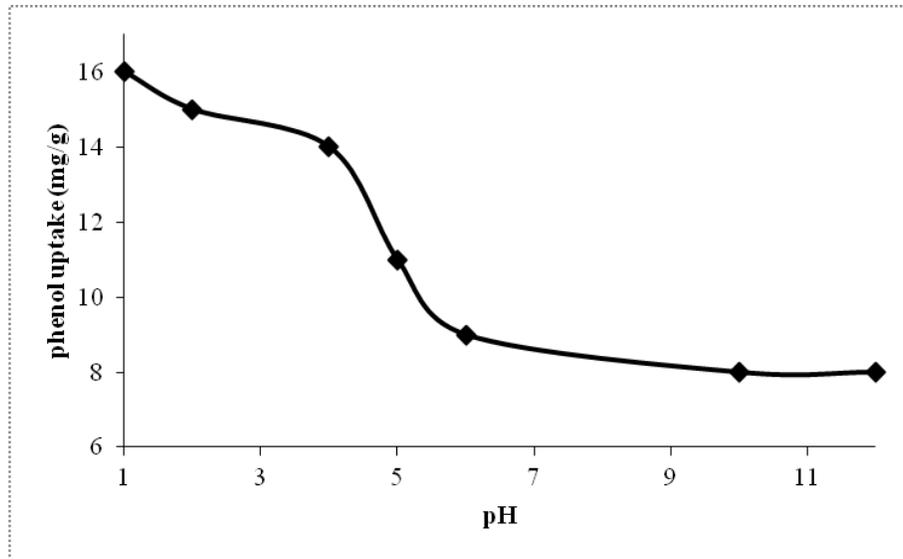


Fig. 3. Effects of initial pH on phenol uptake

Generally, the adsorbed amount decreases with increasing pH value. Phenol ionisation depends on the pH value and the ionic fraction of the phenolate ion (α_{ions}) can be calculated using the following equation (Banat et al., 2002; Uddin et al., 2007):

$$\alpha_{ions} = \frac{1}{1 + 10^{pK_a - pH}} \quad (2)$$

The surface of yeast would be protonated at low pH values hence strong electrostatic forces of attraction with the negatively charged sorbate. Phenol has pK_a value of 10, hence at high pH values it behaves as an anion (Rubin et al., 2006). Adsorption at higher pH would be less due to repulsion (Rengaraj et al., 2002). Competition occurs between the OH^- ions and the phenol molecules for sorption sites. Similar trends have been reported for the biosorption of phenol by activated carbon, water hyacinth ash, bagasse ash, wood charcoal, activated carbon from tobacco residues (Halouli and Drawish, 1995; Rengaraj et al., 2002; Mukherjee et al., 2007; Uddin et al., 2007; Kilic et al., 2011).

3.4 Effect of Adsorbent dosage

This parameter determines the capacity of adsorbent for a given phenol concentration and adsorbate-adsorbent equilibrium of the system is determined. Fig. 4 shows the plot of the phenol uptake against the quantity of yeast *Saccharomyces cerevisiae*.

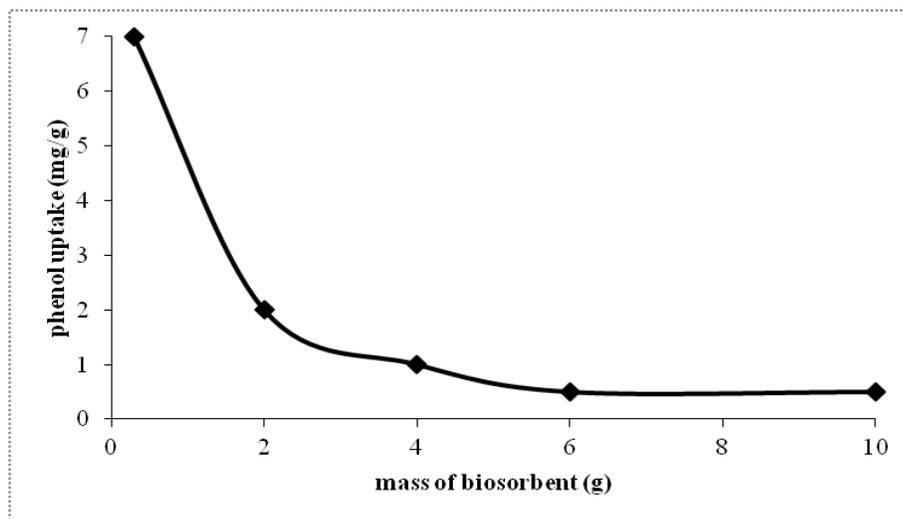


Fig. 4. Effect of biosorbent dosage on phenol uptake

The phenol uptake per unit mass decreased with the increase in adsorbent dosage. The reason for this trend may be attributed to the fact that at high sorbent dosages, the available phenol molecules are not able to cover all the exchangeable sites on the biosorbent, resulting in low phenol uptake.

3.5 Effect of contact time on phenol adsorption

Contact time is an important parameter to determine the equilibrium time of adsorption process (Kilic et al., 2011). The characteristics of *Saccharomyces cerevisiae* and its available sites affected the time needed to reach equilibrium. The experimental results for determination of equilibrium time are given in Fig. 5 and it is obviously seen that adsorption capacity increased with increasing contact time. Large amounts of phenol were removed in the first 3 h and equilibrium was reached in 4 h. After the equilibrium, adsorption uptake was not increased significantly.

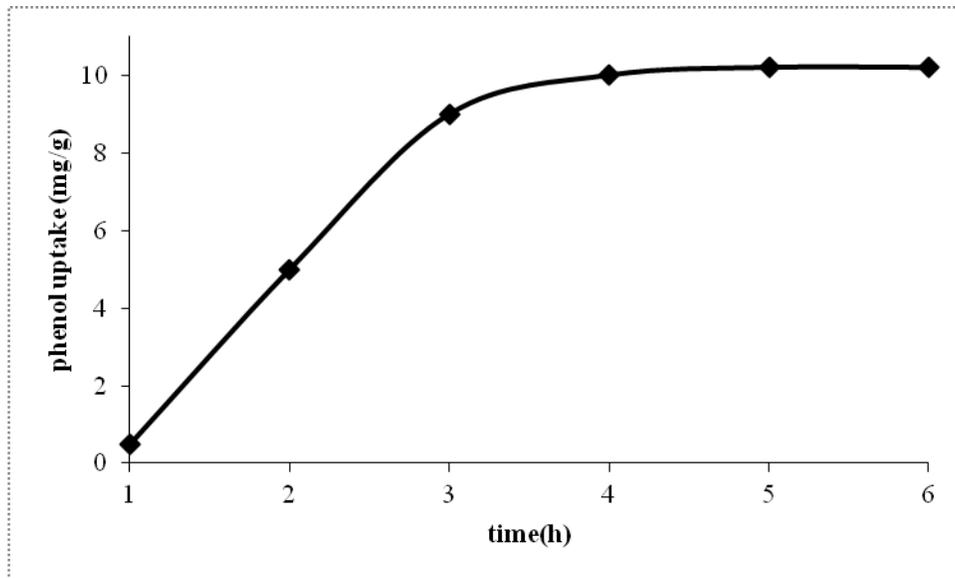


Fig. 5. Effect of contact time on phenol uptake

3.6 Effect of initial concentration of phenol

The initial concentration provides an important driving force to overcome all mass transfer resistance of phenol between the aqueous and solid phase. Fig. 6 represents the results of initial concentration effect of phenol within the range of 10-150 mg L⁻¹.

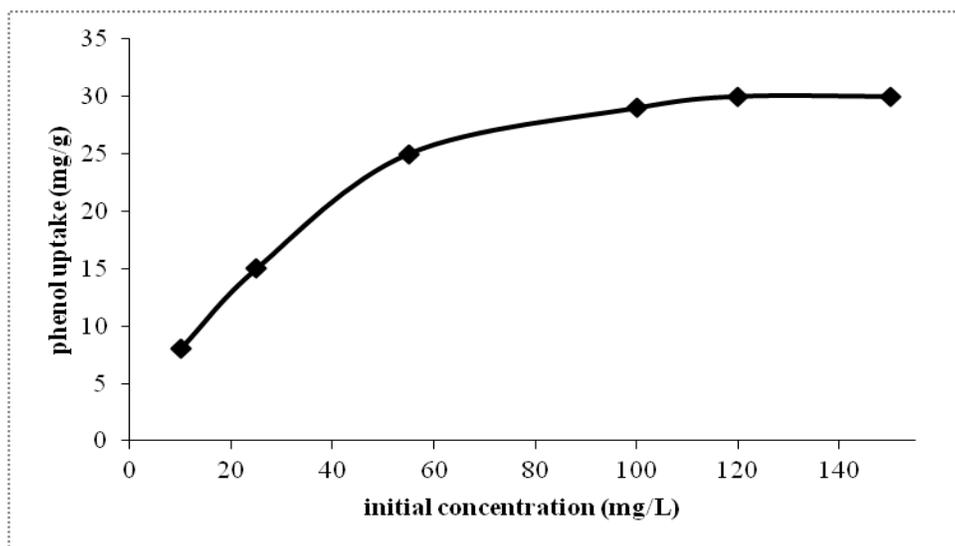


Fig. 6. Effect of initial concentration on phenol uptake

The uptake of phenol increased with the initial concentration up to 120 mg L⁻¹. Then uptake decreased as the initial phenol concentration was increased. The higher uptake at lower concentrations may be due to the presence of more available sites on the adsorbent than the number of phenol ions which are available in solution. The maximum uptake was determined at 120 mg L⁻¹ as 30 mg g⁻¹.

3.7. Adsorption Isotherms

There are several models that have been reported in literature to show equilibrium relationships between sorbent and sorbate. The Freundlich and Langmuir models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of phenol and its equilibrium concentrations. The linear form of the Freundlich isotherm is given by the relation:

$$\text{Log}(q_e) = \text{Log}(k) + \frac{1}{n} \text{Log}(C_e) \quad (3)$$

where, q_e is the amount adsorbed at equilibrium (mg g⁻¹), C_e is the equilibrium concentration of the adsorbate (mg l⁻¹), k and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity respectively of the adsorbent. Freundlich isotherm constants were determined from the plot of $\log q_e$ versus $\log C_e$ (Fig.7).

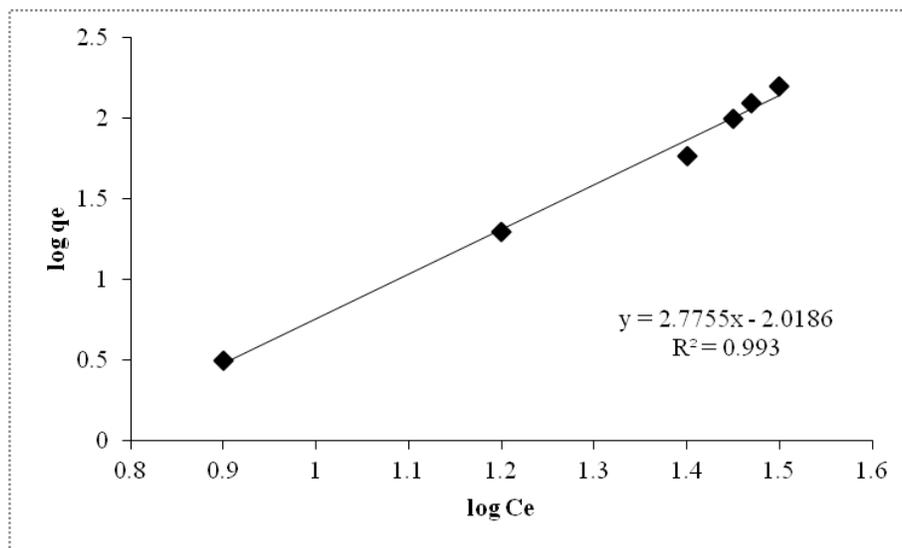


Fig. 7. Freundlich adsorption isotherm of phenol by *Saccharomyces cerevisiae*

The linear form of the Langmuir isotherm model can be represented by the relation:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \cdot \frac{1}{C_e} \quad (4)$$

where, q_e is the amount adsorbed at equilibrium (mg g⁻¹), Q (mg g⁻¹) and b (L mg⁻¹) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively. Langmuir isotherm constants were determined from plots of C_e/q_e versus C_e as shown in Fig. 8.

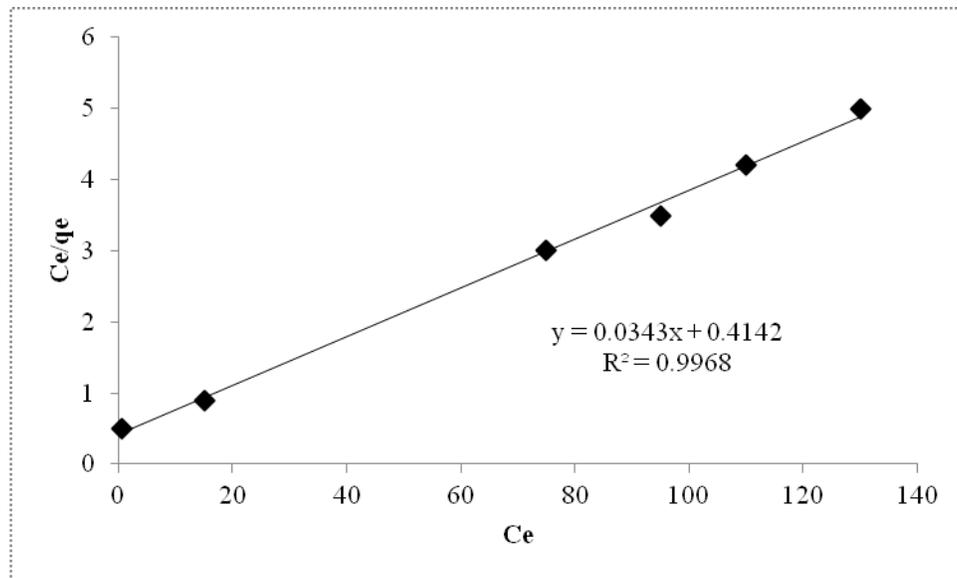


Fig. 8. Langmuir adsorption isotherm of phenol by *Saccharomyces cerevisiae*

The isotherm parameters and correlation coefficient are shown in Table 2 below. The sorption equilibrium data fitted Langmuir and Freundlich equations with correlation coefficients values of 0.9968 and 0.9930, respectively. The best fit of equilibrium data in the Langmuir isotherm predicted the monolayer coverage of phenol onto yeast. From Table 2, it was observed that the maximum sorption capacity of yeast for phenol was found to be 26.95 mg g⁻¹.

Table 2. Isotherm parameters of Langmuir and Freundlich isotherms for biosorption of phenol on *Saccharomyces cerevisiae*

Isotherm type	parameters	<i>Saccharomyces Cerevisiae</i>
Langmuir	q_{\max} (mg g ⁻¹)	26.95
	B	0.1790
	R ²	0.9968
Freundlich	K _F	0.268
	N	0.1180
	R ²	0.9930

3.8 Comparison of *Saccharomyces cerevisiae* and other sorbents

The performance of *Saccharomyces cerevisiae* as an adsorbent for phenol is compared with other biomass sorbents in Table 3. *Saccharomyces cerevisiae* displayed a good adsorption capacity when compared to other biosorbents listed in Table 3.

Table 3. Overview summary of selected studies on phenol sorption by biosorbents

Biosorbent	q_{\max} (mg g ⁻¹)	Reference
Dried sewage sludge	16	Thowornchaisit and Pakulanon, 2007
Rice husk carbon	22	Kennedy et al., 2007
Organobentonite	38	Rawajhh and Nsour, 2006
<i>Saccharomyces Cerevisiae</i>	27	Present study

4. CONCLUSIONS

The present study reports batch studies for the removal of phenol from aqueous using yeast, *Saccharomyces cerevisiae*. Adsorption of phenol was dependent on initial pH, adsorbent dosage, contact time and initial phenol concentration. The results indicated that adsorption of phenol decreased with increasing pH. Equilibrium data fitted very well to Langmuir confirming monolayer coverage of phenol onto yeast. It can be concluded that some industrial waste by-products can be used as effective and alternative adsorbents for the sorption of organics such as phenol from aqueous solution, because of they are readily available, low cost hence reducing pollution.

5. ACKNOWLEDGEMENTS

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