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Low cost biosorbent (*Lemna gibba* L.) for the removal of phenol from aqueous media

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Abstract

Duckweed (*Lemna gibba* L.) has been evaluated as low-cost biosorbent for removal of phenol ions from aqueous solution. Effects of operational parameters such as pH of solution, biosorbent dosage, initial concentration of phenol and contact time were investigated under batch mode experiment. The obtained results showed that the optimum adsorption for the removal of phenol from aqueous solution using duckweed were 250 mg of *Lemna gibba* for 10 ml of phenol concentration at pH 6.0 after 18 min of adsorption.

1. Introduction

The world's ever increasing population and her progressive adoption of an industrial based lifestyle has inevitably led to an increased anthropogenic impact on the biosphere. Thus there have been increasing toxicological and environmental interests about organic compounds especially phenolic pollutants due to their toxicity to the aquatic environment (Shreadah *et al.*, 2006; Said et al,. 2006; Ji *et al.*, 2007; Younis and Nafea, 2012; Younis *et al.*, 2014; El-Zokm *et al.*, 2015; Okbah *et al.*, 2015; Shriadah *et al.*, 2006).

Phenols and its compounds are widely found in medicine, paint, leather and textile, oil refinery, disinfectants and lubricant production wastewater industries (Mortazavi *et al.*, 2005; Kidak and Ince, 2006; Moussavi *et al.*, 2009). Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis and death can be resulted from its overexposure (Busca *et al.*, 2008; Gholizadeh *et al.*, 2013). Therefore Phenol-containing wastewater may not be conducted in open water without treatment because of its toxicity. Phenolic compounds have been listed in priority pollutants by many Environmental Protection Agencies (Hameed, and Rahman, 2008; Jia and Lua, 2008). Consequently, the development of low cost bio sorption method for highly effective removal of phenols is increasingly attractive.

One of the most important topics of research area is the development of efficient methods to remove of hazardous pollutants from wastewater (Gandhi *et al.*, 2012; Jung *et al.*, 2015).

Up to now, various techniques have been developed to remove and degrade the phenolic compounds from aqueous solutions. These include adsorption (Frieda and Nava, 1997), biosorbents (Younis and Aly Eldeen, 2009) solvent extraction (Ruey *et al.*, 2009), activated carbon, adsorption, chemical oxidation (Wang 1992)

and bio degradation (Azin and Katayon 2002). Different polymers (Kidak and Ince, 2006; Moussavi *et al.*, 2009), carbon nanotubes (Busca *et al.*, 2008), clay (Gholizadeh *et al.*, 2013). All of these techniques suffer from serious drawbacks as high costs, incompleteness of purification, formation of harmful by-products, low efficiency and applicability to a limited concentration range (Klibanov *et al.*, 1980).

Duckweed (*Lemna gibba* L.) is a small vascular free floating flowering aquatic macrophytes belonging to family of Lemnaceae, which can be found worldwide on the surface of standing or slow flowing eutrophic fresh and brackish waters, forming a familiar green mats. Duckweeds can reproduce vegetatively by producing a daughter fronds which stay attached to the mother frond to form a colony until the maturation. At low temperature duckweed produce special fronds called turions which are rich in starch and serve as an overwintering form (Nafea, 2016; Younis and Nafea, 2015).

Duckweeds may also reproduce by forming flowers and setting fertile seeds (Hillman. 1961). It can tolerate a wide range of pH (4.5-8.5) and high salts concentrations (up to 4000 mg/liter total dissolved solids) (Zimmo, 2003). Mkandawire *et al.* (2005) stated that when levels of nitrogen in the water are high, duckweeds store nitrogen as protein and ammonium ions as a useful N source. Ammonia was found toxic to duckweed when pH of water rises to the point that allows to the formation of free ammonia. The plants can tolerate very high ionized ammonia (NH4-N) concentrations. Urea is the best fertilizer for the plant, and is rapidly converted to ammonia under normal conditions. Duckweeds tolerate concentrations of elemental N up to 375 mg/L , the nutrients taken up by duckweeds are assimilated into plant protein. Under ideal growth conditions more than 40% protein content on dry weight is determined (Skillikorn *et al.*, 1993). It is distributed naturally in water with decaying organic matter that supply the plant with growth nutrients. Duckweed species have an inherent capability to exploit favorable ecological conditions by growing more rapidly. Their wide geographic distribution indicates a high probability of sample genetic diversity and good potential to improve their agronomic characteristics through selective breeding (Skillicorn *et al.*, 1993).

The present work aimed to study the feasibility of using low-cost biosorbent (*Lemna gibba* L.) for removal of phenol ions from aqueous solution.The effects of experimental parameters, such as pH of solution, adsorbent dosage, contact time and initial phenol concentration on the removal efficiency of phenol were investigated.

2. Materials and methods

2.1 Materials

All the chemicals used for experimental studies were Aldrich products.

The stock standard solutions of 1000 mg L-1of phenol was prepared in bi-distilled water and stored in brown glass bottles at -4 °C in the refrigerator. The working solutions were prepared from an aqueous phenol stock standard solution by diluting with doubly distilled water to the required concentrations.

Before being dried the collected *Lemna gibba*, it was washed with fresh water and then tap water followed by washing with distilled water and then cleaned *Lemna gibba* biomass were sun dry for two days.

2.2. Batch adsorption studies

Batch adsorption experiments were carried out by soaking bio-sorbent *Lemna gibba* into wastewater containing phenol in order to study the effects of pH, contact time, adsorbent dosage and shaking speed on the efficiency removal of phenol from wastewater by low cost bio-sorbent *Lemna gibba*.

To study the effect of contact time, the suspensions were agitated at desired speeds using a mechanical shaker at room temperature. Batch experimental procedures were conducted in different shaking times of: 3, 6, 18, 24 and 30 hours at pH value of 7.0 while the other parameters such as biosorbent dosage 250 mg and concentration of phenol (100 mg/l) kept constant.

To study the effect of biosorbent dosage, batch experiments were conducted by mixing different biosorbents masses of 10, 50, 125, and 250 mg of *Lemna gibba* and the other parameters pH 7.0 and concentration of phenol kept constant.

Adsorption behaviors of phenol for the same initial concentration and equilibration time was studied as a function of pH, 250mg of a given *Lemna gibba* material was dispersed into 100mL solutions containing 100 mg/L of phenol. The initial pH values were adjusted from 3.0 to 9.0 using solutions of 0.1 mol/L of H_2SO_4 and 0.1 mol/L of NaOH. Then, the suspensions were shaken using a mechanical shaker for 30 hours at room temperature.

To study the effect of initial concentrations, adsorption experiments was conducted by shaking 250 mg of the biosorbent with different initial concentrations of phenol ranging 10, 50, 125, 250 and 500 mg/L for 30 hours. The supernatant was filtered through 0.45 µm membrane filter for measurement of the final concentration of phenol in the solutions was measured with colorimetric method using VIS/

UV Spectrophotometer-19 (SCO-Tech, Germany) (Martin, 1949).

The sorption capacity q (mg/g) was obtained using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m_s}$$

where C_0 and C_t are the initial and final concentrations (mg/L) of phenol in the aqueous solution, respectively, V is the volume of phenol solution, and m is the weight of bio-sorbent *Lemna gibba*.

3. Results and discussion

3.1. Effect of pH solution

The effect of pH is one of the most important variables that affecting adsorption due to the electrostatic attractions of ions. Figure 1 shows the effect of pH of solution on the adsorption efficiency of phenol by *Lemna gibba* at pH varied from 3 to10, while all the other parameters such as adsorbent dosage, contact time and initial concentration were kept constant at 250mg/l, 30 h, 100mg/L respectively. It is observed that the highest efficiency removal of phenol was about 85% at pH 5 and 6. However, at pH above 6 the negative charge at the surface of the *Lemna gibba* increases with increasing of pH and phenol was converted to phenoxide group that was more reactive than phenol in a solution and therefore a decrease in the adsorption efficiency was observed.

The surface of *Lemna gibba* would be protonated at low pH values due to increase of H^+ ions on the solution while phenol have OH^- hence strong electrostatic forces of attraction with the negatively charged biosorbate *Lemna gibba*. On the other hand, the increasing of pH lead to increase of solution and the number of negatively charged sites increases due to remove of H^+ and creation of negative charge on hydroxyl group of phenol (Delnavaz *et al.*, 2015), which must be less favorable to the adsorption of phenolate ions due to electrostatic repulsion. These observations is in agreement with previous studies. (Mirian and Nezamzadeh-Ejhieh, 2015; Yang *et al.*, 2015).

3.2. Effect of biosorbent dosage

The effect of biosorbent dosage determines the capacity of adsorbent for a given phenol concentration and adsorbate-adsorbent equilibrium of the system. Figure 2 shows the effect of adsorbents dosages on the removal efficiency of phenol using *Lemna gibba* while keeping all other experimental parameters constant at 100 mg/L of phenol concentration, pH 6, speed of shaking 100 rpm and contact time of 24 hours. The adsorbents dosages of *Lemna gibba* were varied

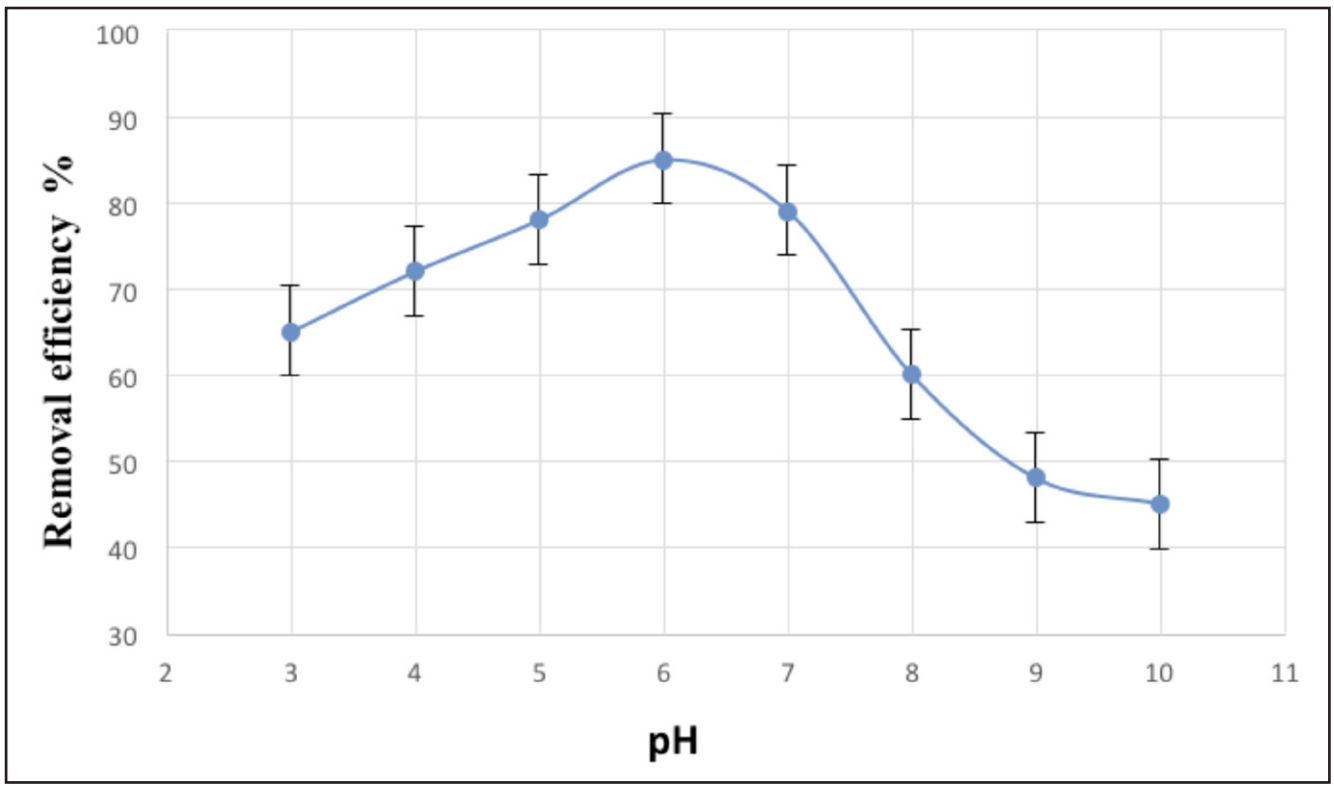


Fig. 1. Effect of pH on the removal efficiency (%) of phenol from aqueous solution using *Lemna gibba* (experimental conditions: phenol concentration 100mg/L, contact time 30 h, adsorbent dosage 250mg at room temperature).

from 10 to 250 mg. It is seen that the percentage of removal efficiency of phenol from aqueous solution was increased sharply from (49 to 90) by increasing the mass of the biosorbent dosage from 10 to 250 mg. This observation can be explained on the increasing in the available active sites on the *Lemna gibba* surface which lead to increasing number of binding sites of phenol (Younis *et al.*, 2014).

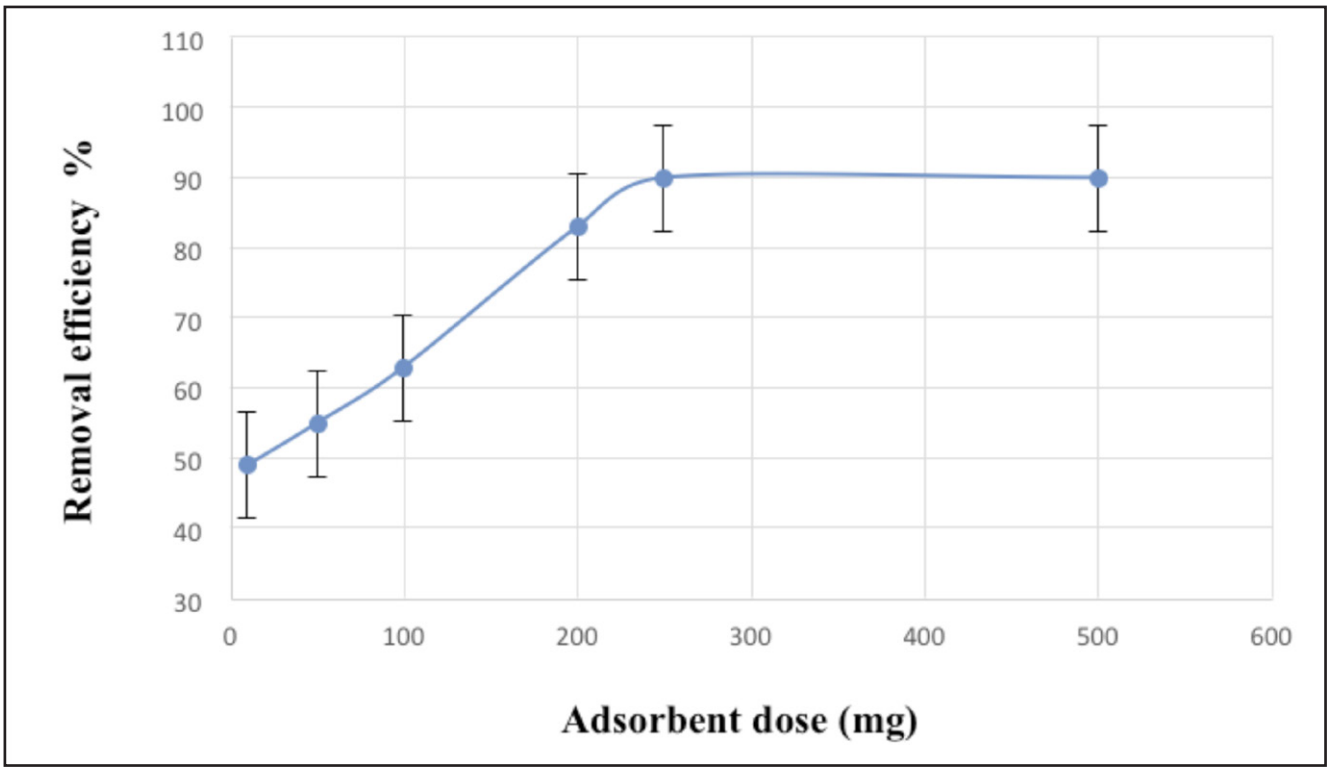


Fig. 2. Effect of adsorbent dose on the removal efficiency (%) of phenol from aqueous solution using *Lemna gibba* (experimental conditions: phenol concentration 100mg/L, contact time 30 h, pH 6 at room temperature).

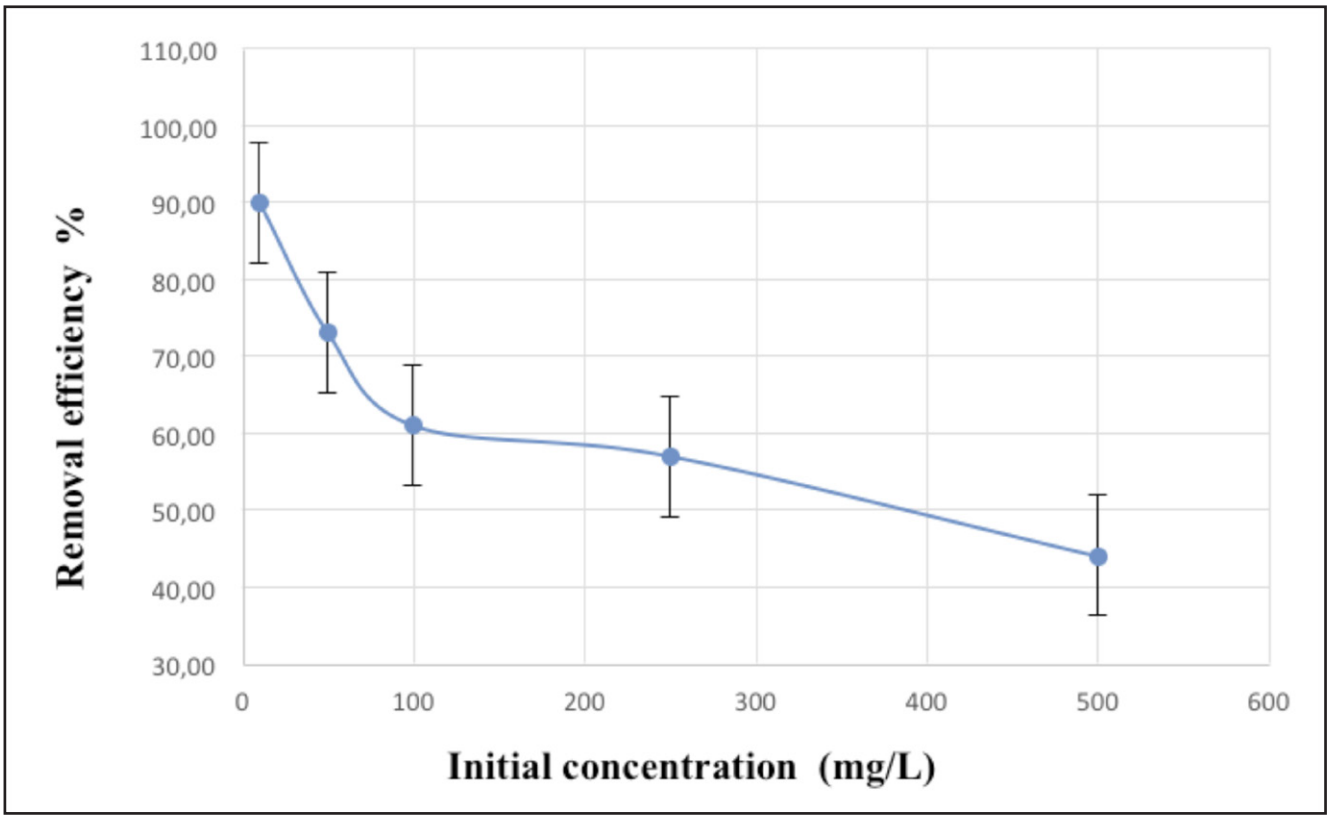


Fig. 3. Effect of initial concentration on the removal efficiency (%) of phenol from aqueous solution using *Lemna gibba* (experimental conditions: adsorbent dose 250 mg, contact time 30 h, pH 6 at room temperature).

3.3. Effect of initial concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of phenol between the aqueous and solid phase (Moyo *et al.*, 2012). The initial concentration of phenol in the aqueous solution was varied between 10 and 500 mg/L, while all the other parameters were kept constant at 250 mg/L of *Lemna gibba*, pH7, speed of shaking 100 rpm and contact time of 24 hours (Fig 3).

The percentage of phenol removal efficiency was 90% at an initial phenol concentration of 10 mg/L. While, increasing the initial phenol concentration in aqueous solution resulted in a decrease in the removal efficiency of the phenol. This observation could be attributed to saturation of the availability of active adsorption sites of *Lemna gibba* surface at higher concentration of phenol, which leads to rise in the amount of phenol ions in the aqueous solution and thus decreased the percentage of removal efficiency of phenol. (Asmaly *et al.*, 2015; Younis *et al.*, 2014).

3.4. Effect of contact time

The effect of contact time is one of the important characteristics that define the equilibrium point of phenol adsorption on the surface of *Lemna gibba*. In order to establish equilibration time for optimum removal efficiency of phenol from waste, the adsorption of phenol on the surface of *Lemna gibba* was studied as a function of contact time at different intervals ranging from 0-30 hours while keeping all other parameters constant at concentration 100 mg/L of phenol, pH7. Speed of shaking 100 rpm and 250 mg of *Lemna gibba* as shown in Figure 4. It is observed that a gradual increase in phenol removal efficiency was observed to increase in contact time during the first 18 hours and then tended to keep constant after this time.

This observation could be attributed to the contact time facilitates a proper contact between phenol ions in the aqueous solution and biosorbent binding sites and thereby presence of more active adsorption sites on the *Lemna gibba* surface and promotes effective diffusion of phenol ions toward the biosorbent surface (Zhaoqian Jing, 2013; Younis *et al.*, 2014)

3.5. The Sorption Capacity

Adsorption capacity q (mg/g) at optimum set of parameters is one of the most important factor to determine how much the pollutant can be removed from the aqueous solution by a unit mass of the adsorbent. Adsorption capacity of *Lemna gibba* surface for removal of phenol from aqueous solution was determined at different initial concentrations in the range of 10 to 250 mg/L (Fig. 5). It is observed that adsorption ca-

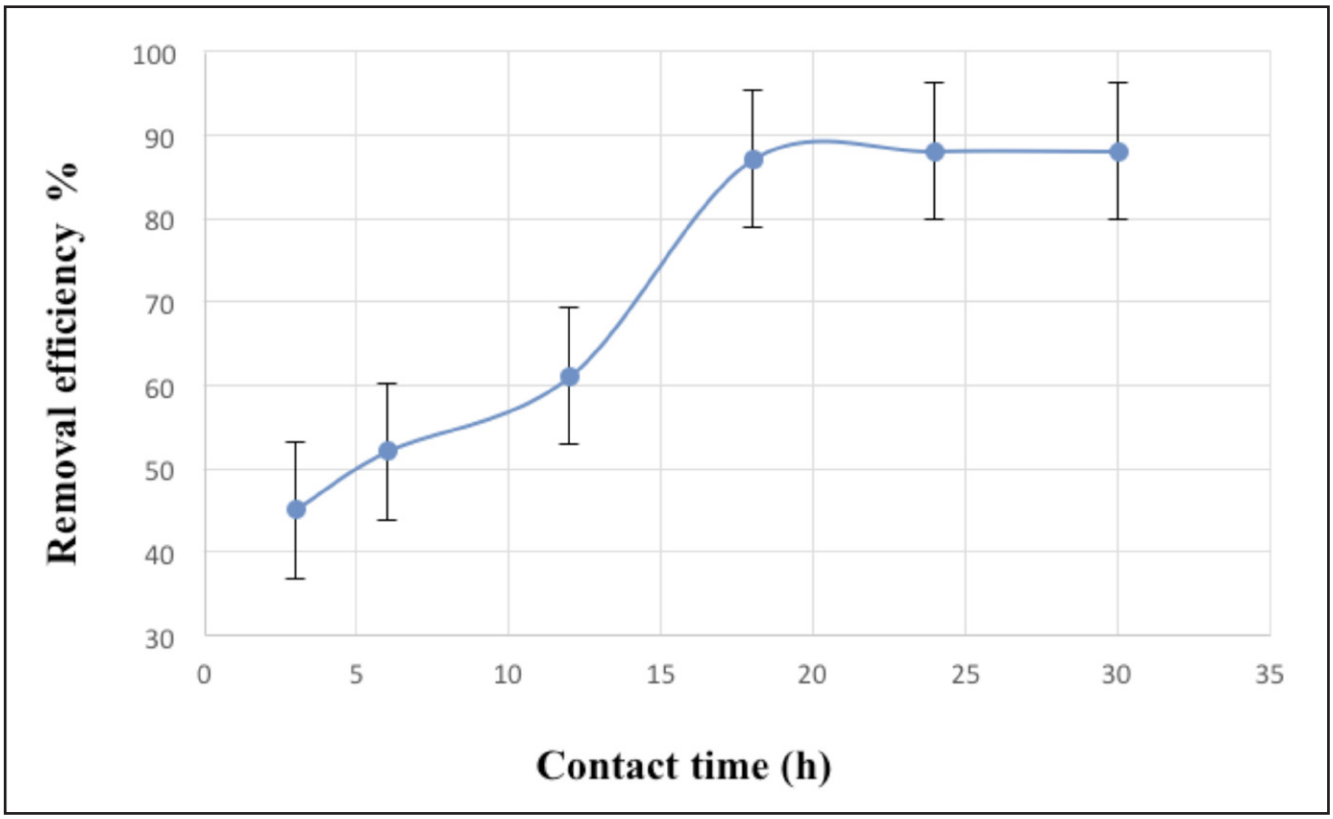
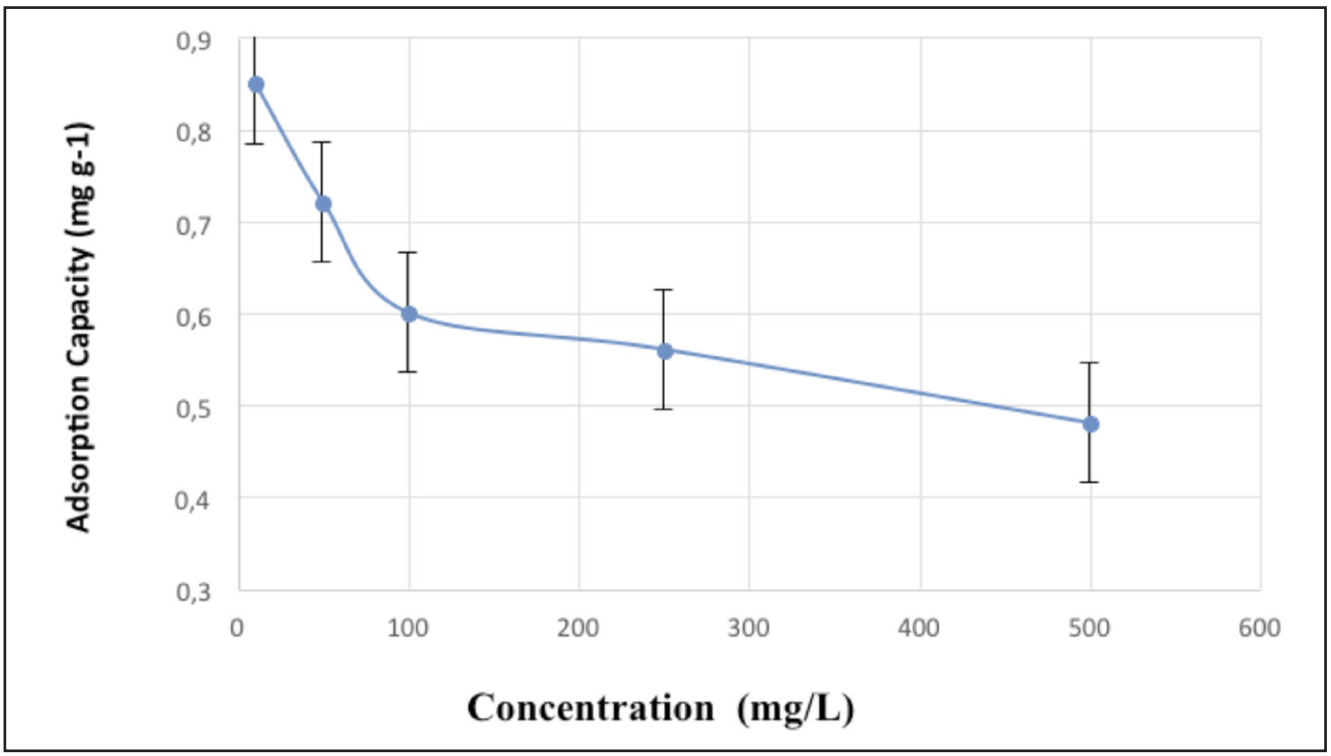


Fig. 4. Effect of contact time on the removal efficiency (%) of phenol from aqueous solution using *Lemna gibba* (experimental conditions: adsorbent dose 250 mg, phenol concentration 100mg/L, pH 6 at room temperature).



Fig, 5. Adsorption capacity of phenol onto *Lemna gibba* (experimental conditions: adsorbent dose 250 mg, contact time 30 h, pH 6 at room temperature).

pacity of *Lemna gibba* surface was 0.85 mg/g at low initial phenol concentration (10 mg/L), with increase of the initial phenol concentration in aqueous solution lead to a decrease in the adsorption capacity of *Lemna gibba* due to the saturation of the available active sites on the surface of *Lemna gibba* at higher concentration of phenol.

Conclusion

The results of this work report batch mode experiment for the removal of phenol from aqueous using Duckweed (*Lemna gibba* L.). The results showed that adsorption efficiency of phenol was dependent on adsorbent dosage of *Lemna gibba*, pH of solution, contact time and initial phenol concentration and the adsorption capacity increased with decreasing the initial phenol concentration in aqueous solution, indicating the saturation of the available active sites on the surface of *Lemna gibba* at higher initial concentration of phenol. It can be concluded that low cost biosorbent (*Lemna gibba* L.) can be used for the removal of phenol from industrial waste water.

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