Original Article

Removal of Lead (II) Ions from Waste Water by Using Lebanese *Cymbopogon citratus* (Lemon Grass) Stem as Adsorbent

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ABSTRACT

The objective of this study was to investigate the possibility of using Lebanese *Cymbopogon citratus* stems as an alternative adsorbent for the removal of Pb (II) ions from aqueous solutions. The effect of different parameters such as the initial metal ion concentration, pH, adsorbent dose, contact time and temperature were studied. Maximum adsorption capacity (93%) of lead (II) ion was obtained at pH 4 and 25˚C after 1 hour for150 mg/L initial concentration. FT-IR analysis pointed out the involvement of amine and carboxyl group in the adsorption process. The adsorption isotherm was better described by Freundlich rather than Langmuir model. Based on these results, it can be concluded that the stem of *Cymbopogon citratus* is effective as an alternative adsorbent for the removal of toxic Pb (II) from waste water.

Keywords: *Cymbopogon citratus*, Adsorption, Langmuir and Freundlich isotherm models.

INTRODUCTION

Water pollution caused by heavy metals has caught increasing public attention and many techniques have been used for their removal from wastewater such as: chemical precipitation, electro dialysis, ion exchange, adsorption and others.

Heavy metals generated by industrial activities (battery manufacturing, mining activities, printed circuit board manufacturing) are disposed to water streams without proper treatment. They are non-biodegradable and therefore persist for long periods in aquatic as well as terrestrial environments. They may be transported also through soils to reach groundwater or may be taken up by plants, including agricultural crops.[1]

Lead is among these heavy metals used in such industries. It is of high toxicity and accumulates in the body after ingestion. Chronic lead poisoning may cause gastrointestinal disorders, constipation, fatigue, muscular atrophy and CNS syndrome that may result in coma and death. [2]

Many studies have been conducted to find low-cost adsorbents as a replacement for costly current methods. An adsorbent is considered of low-cost if it is naturally abundant, requires little processing or is a byproduct of waste material from waste industry according to Bailey *et al*[3]. Due to their low economic value, plant wastes are considered to be cheap adsorbents. Plants as: grape stalk wastes[4], papaya wood[5], teak leaf powder[6], rice husk ash and neem bark[7] were used as adsorbents and they have shown promising results.

In the present work, the capacity of Lebanese *Cymbopogon citratus* (Lemon Grass) stems to remove Pb (II) ions from wastewater has been studied in different experimental conditions such as initial metal ion concentration, contact time, adsorbent dose, temperature and pH.

Cymbopogon citratus staff is popularly known as citronella grass or lemon grass. This species belongs to the Gramineae family, which comprises approximately 500 genus and 8,000 herb species. Lemon grass is a tufted perennial grass growing to a height of 1 meter with numerous stiff leafy stems arising from short rhizomatous roots. It has an economic lifespan for about 5 years.[8]

MATERIALS AND METHODS

Adsorbent

The *Cymbopogon citratus* (Lemon Grass) stems were collected from a local Lebanese plantation. The stems were thoroughly rinsed with water, died at room temperature for 10 days, and then grounded into a fine powder using a grinding mill.

Adsorbate

The stock solution of 1000 mg/L of Pb (II) was prepared by dissolving Pb $(NO_3)_2$ in 1L de-ionized water. All the required solutions were prepared by diluting the stock solution with de-ionized water. Analysis of standards and simulated samples was done using an AA-140 Atomic Absorption Spectrometer.

Experimental procedure

The procedure mentioned by Al-Afy *et al*[9] were followed, where several batches were prepared to study the effect of initial Pb (II) concentration, pH, contact time, adsorbent dose and temperature on the adsorption of the Pb (II) ions from its solution. All the adsorption experiments were carried out at room temperature except where the effect of temperature was being investigated. The initial pH was adjusted with HNO_3 (1M) or NaOH (1M).

Effect of metal ion concentration

0.5g of the adsorbent was stirred with 50 ml of different concentrations of Pb (II) solution. The mixture was continuously agitated at 400 rpm, 25±2˚C and pH 4 for 1 hour. The obtained suspension was filtered in 2 steps: first by Buchner filtration then with a 0.45µm filter. After that, the final concentration of Pb (II) in the filtrate was determined using AAS.

Effect of pH

By fixing the four other parameters (1 hour, 25±2˚C, 0.5 g of adsorbent and 150 mg/L), the effect of pH on the adsorption was investigated in the pH range 2-10 in. The pH was adjusted using a few drops of HNO_3 (1M) or NaOH (1M). Remaining Pb (II) ions were then measured using AAS.

Effect of contact time

The effect of the contact time was also performed with 50mL of 150 mg/L Pb (II) solution at a pH 4. 0.5g of adsorbent at 25±2˚C was added to an aqueous solution with respect to the following times: 30, 60, 120, 180, 210 min and mixed with a magnetic stirrer at 400 rpm. After that, the samples were filtered and the filtrate was then analyzed by AAS in order to determine the adsorption capacity.

Effect of temperature

The same procedure was followed to find the effect of temperature on the adsorption process. By fixing all other parameters, only temperature has been varied. (0˚C, 25˚C, 45˚C, and 60˚C).

Effect of the adsorbent dose

Adsorption dose experiments were also performed following the same procedure as described earlier at pH 4, 150 mg/L Pb (II), 25±2˚C, 400 rpm for 1 hour with the following adsorbent doses: 0.2, 0.5, 0.8, 1.4, 1.8 and 2.2 g, the samples were filtered and the filtrate was analyzed by AAS.

When *Cymbopogon citrates* stem powder was tested for its ability to adsorb Pb (II) from aqueous solution, initial pH 4 was used for most experiments. The effects of the following experimental parameters (pH, initial concentration, contact time, temperature and the adsorbent dose) on adsorption were studied. The percentage of the uptake or adsorption of Pb (II) was calculated using the following equation:

$$\%\,removal = \frac{Ci - Cf}{Ci} \times 100$$

Where,
C_o: initial concentration (mg/L)
C_f: final concentration (mg/L)

The adsorption capacity q_m was calculated according to the following equation:

$$qm = \frac{Co - Cf}{m} \times V$$

Where,
q_m: Adsorption capacity (mg/g)
V: volume of the reaction mixture (L)
m: mass of adsorbent used (g)
C_0: initial concentration (mg/L)
C_f: final concentration (mg/L)

RESULTS AND DISCUSSION

FT-IR analysis

The FT-IR spectrum of *Cymbopogon citratus* was used to investigate the functional groups present on the surface that may be responsible for the removal of heavy metal species. The spectrum of the adsorbent was measured within the range of 4000-400 cm^{-1} using JASCO FT/IR-6300 spectrometer. FT-IR spectra before and after the adsorption were compared. *Cymbopogon citratus* stems show a number of absorption peaks that reflect its complex nature. Three peaks between 3300 and 3500 cm^{-1} are due to the presence of N-H stretching vibration. A peak at 2930 cm^{-1} corresponds to sp^3 C-H stretching vibration. The absorption peak at 1750 cm^{-1} could be assigned to the carboxyl group, 1100 cm^{-1} to C-O stretch.

After adsorption, a broad peak at 3420 cm^{-1} corresponds to the overlapping of N-H peak, also, a broad peak at 1750 cm^{-1}. This phenomenon may be attributed to the water molecule directly interacting with amide.

After Pb (II) binding, a change of peak position occurs indicating the change in the environment of these groups. The shift in the wavelength corresponds to the change in the energy of functional groups that indicates the existence of a Pb binding process done on the surface. [10]

Effect of concentration

To study the effect of the initial concentration of Pb (II) on the adsorption capacity, several samples with different concentrations varying from 25 to 800 mg/L was taken while fixing the other parameters. Figure 2 shows that there is a rapid increase in the adsorption of Pb (II) up to 700 mg/L, which is due to the interaction between the metal ion and the active site of the adsorbent. Then, adsorption became constant due to the saturation of the active sites.

Effect of pH

The pH is another parameter that controls the adsorption of Pb (II).[11] Figure 3 shows that best adsorption occurs in the acid range. pH of solution affects the surface of the adsorbent and yet the degree of ionization of the adsorbate. At (less than 3) low pH, the amount of protons H^+ is important that prevents the formation of a bond between Pb (II) and the active site. At moderate pH (3 to 6), the number of H^+ becomes less important, and thus many of Pb (II) ions will be adsorbed on the active sites.[12] At high pH, the Pb (II) ions precipitate under the form of Pb $(OH)_2$, Pb $(OH)_3^-$, Pb_2 $(OH)^{3+}$, Pb_3 $(OH)_4^{2+}$ and Pb_4 $(OH)_4^{4+}$ which prevents adsorption of Pb (II) onto active site.[13]

Effect of contact time

There is a general increase in the % adsorption of Pb (II) with time. However, the adsorption slowed down after 2 hours. This could possibly be the time required for the equilibrium to be established. Generally equilibrium is established on the surface of adsorbent after some time or it can be instantaneous. This probably resulted from saturation of absorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation. [14] The equilibrium uptake of Pb (II) was about 95.77 % that occur after 2 hours.

Effect of temperature

The adsorption of Pb (II) from its solutions at different temperatures was investigated. Samples were subjected to temperatures which ranged from 0 to 60˚C. The adsorption capacity increased to a maximum which was reached at 45˚C and thereafter it decreased gradually.

The temperature has important effects on the adsorption process. Thermodynamic parameters like heat of adsorption and energy of activation play an important role in predicting the adsorption behavior and both are strongly dependent on temperature. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate.[15]

Effect of adsorbent dose

Adsorption is also affected by the dose of the adsorbent responsible for the uptake of the metal. The percentage removal of Pb (II) increases with increasing the mass of the adsorbent from 93.82% at 0.5 g to 98% at 1.8 g. A further increase in the adsorbent mass to 2.2 g does not increase the removal of the metal ion due to the overcrowding of the solution with the adsorbent particles.

Bio-sorption isotherms

The adsorption is generally described by isothermal, that are functions relating the amount of adsorbate on the adsorbent, with the pressure (if gas) or the concentration (if liquid). Langmuir and Freundlich models are used to describe the adsorption process.

Freundlich isotherm

Freundlich isotherm model is the well-known earliest relationship which describes the adsorption process. It can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption[9]; its linear form is expressed by:

$$\log qe = \log kF + \frac{1}{n} \log Ce$$

Where,
q_e: equilibrium adsorption capacity (mg/g)
C_e: equilibrium concentration (mg/L)
K_F: Freundlich constant related to adsorption capacity (L/mg).
n: constant related to the adsorption intensity (g/L).

The value of n indicates the degree of non-linearity between solution concentration and adsorption as follows:
Linear adsorption if n=1
Chemical adsorption if n< 1
Physical adsorption if n>1

Langmuir isotherm

It is based on the assumption that:[16]

- Uniform surface
- Monolayer coverage of the adsorbate on the outer surface.
- No lateral interaction between the sorbed molecules.

The linear form of the Langmuir adsorption isotherm can be written as follows:

$$\frac{Ce}{qe} = \frac{1}{qm\ Kl} + \frac{Ce}{qm}$$

C_e: equilibrium concentration (mg/L).
q_m: saturation capacity of the theoretical maximum monolayer adsorption or (mg/g).
K_L: Langmuir constant related to energy of sorption (L/g).

The initial quality of the Langmuir isotherm can be measured by calculating R_L, a dimensionless constant referred to as the separation factor, or equilibrium parameter:

$$RL = \frac{1}{1+ Kl\ Co}$$

Where,
C_0: initial concentration of adsorbate (mg/L)
K_L: Langmuir constant (L/mg)

There are four possibilities for the value of R_L:
Irreversible sorption if R_L=0
Linear sorption if R_L =1
Unfavorable sorption if R_L>1
Favorable sorption if 0<R_L<1
R_L is between 0 and 1, so, favorable sorption.

But the q_m (theoretical)> q_m (experimental).

Langmuir isotherm is not favorable for the adsorption of Pb (II) on *Cymbopogon citratus* surface.

The n value in Freundlich equation was found to be 0.76 for the *Cymbopogon citratus*. Since n is smaller than 1, this indicates the Chemical bio-sorption of Pb (II) onto *Cymbopogon citratus.*

CONCLUSION

This study investigated the adsorption of Pb (II) ions from aqueous solution onto *Cymbopogon citratus* stem that was found to be dependent on different parameters as initial metal ion concentration, pH, adsorbent dose, temperature and contact time. To provide the best correlation for bio-sorption of Pb (II) ions onto *Cymbopogon citratus*, Freundlich and Langmuir isotherms were demonstrated. From this study, it was observed that stems of *Cymbopogon citratus* can be used as an alternative low cost, eco-friendly and effective adsorbent for treatment of waste water containing Pb (II).

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Table 1. Equilibrium constants for Pb (II) adsorption

Langmuir	q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2
	1000	0.0005	0.992
Freundlich	***n***	**K_F (L.mg^{-1})**	**R^2**
	0.76	0.385	0.998

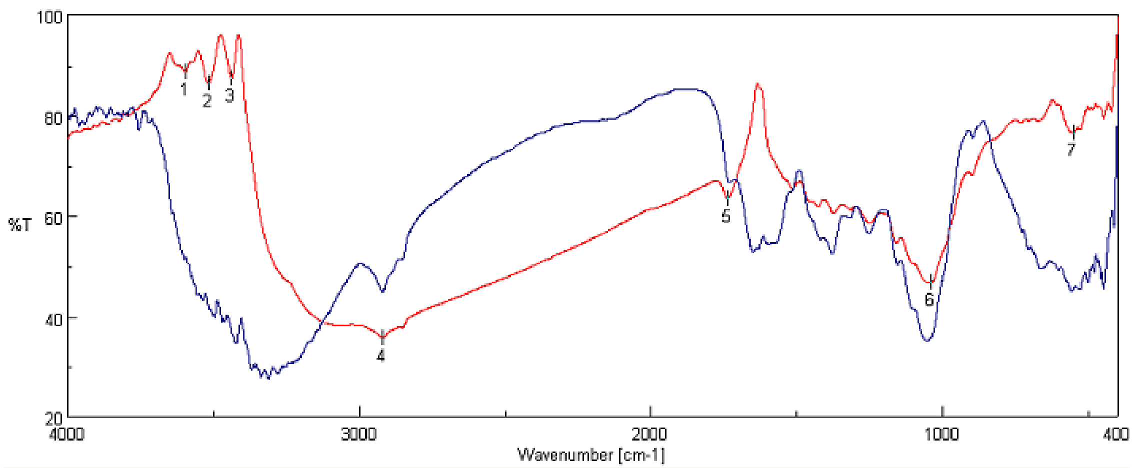

Figure 1. FT-IR of *Cymbopogon citratus* before and after adsorption

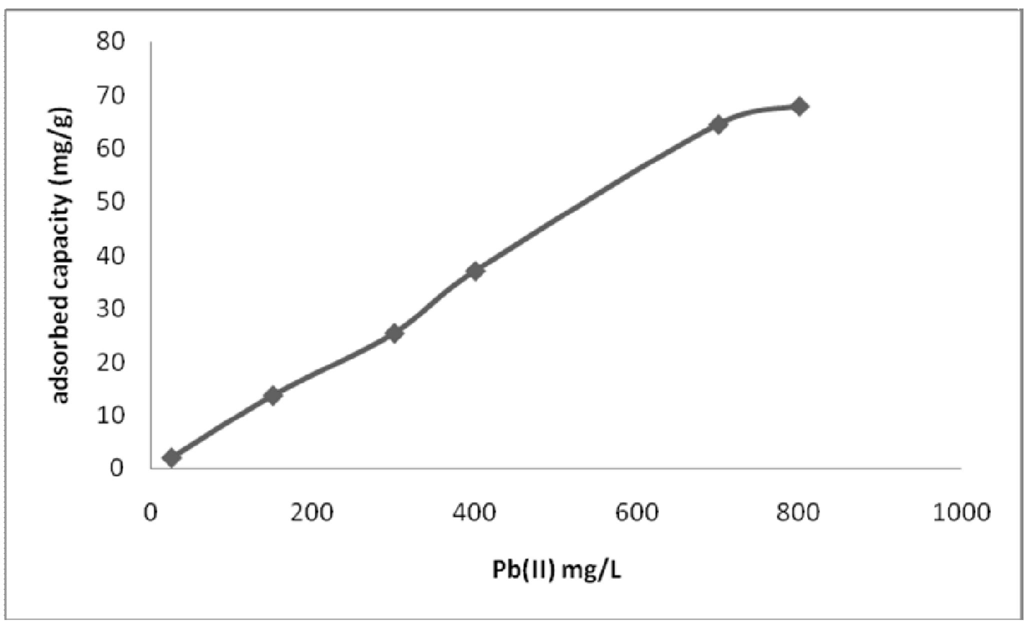

Figure 2. Effect of initial concentration of Pb (II)

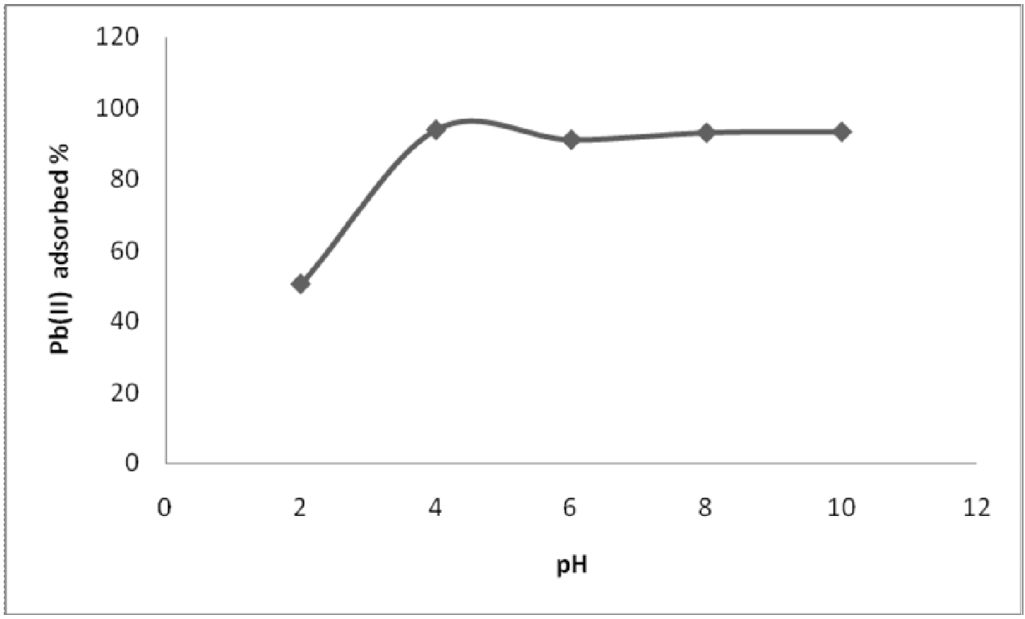

Figure 3. Effect of the pH of solution

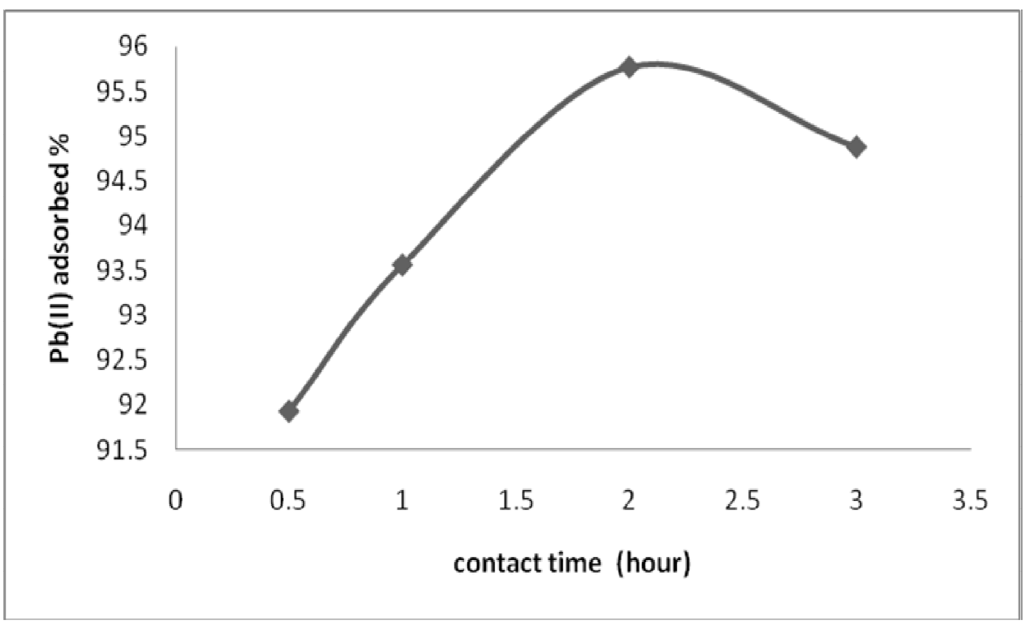

Figure 4. Effect of contact time

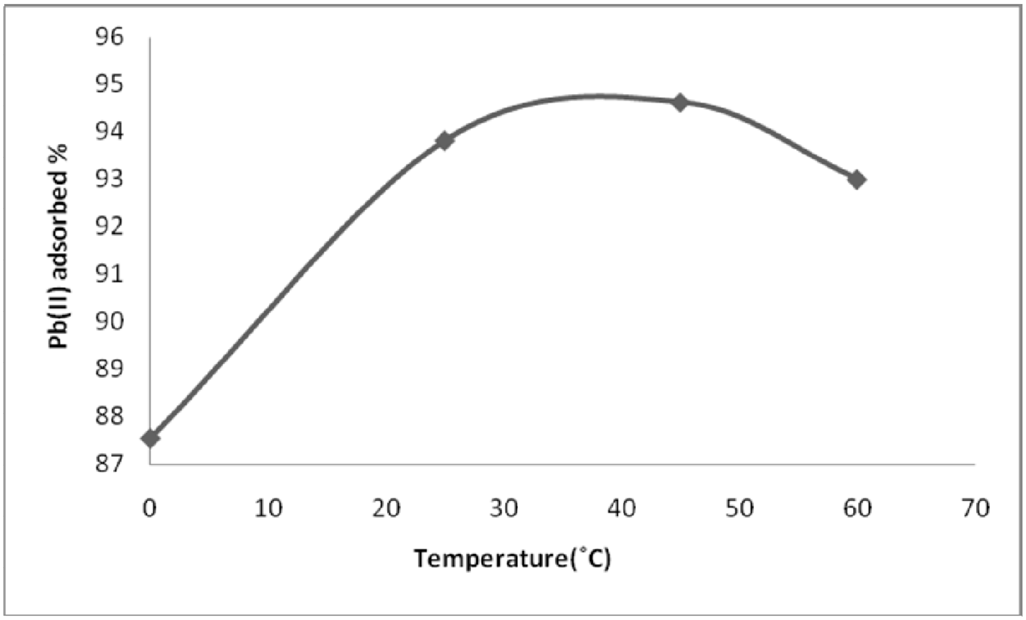

Figure 5. Effect of temperature

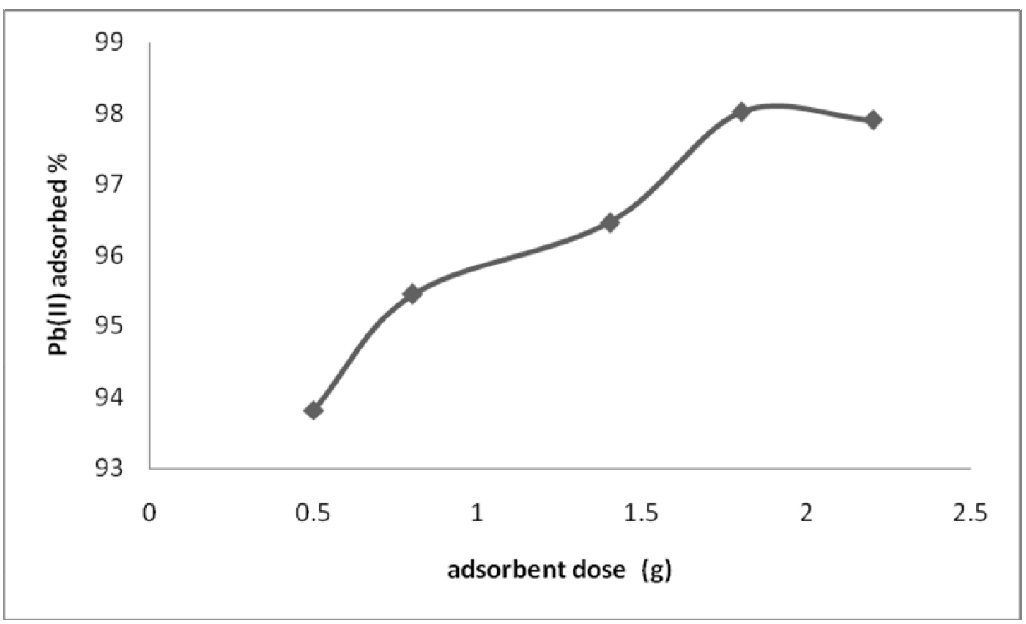

Figure 6. Effect of adsorbent dose

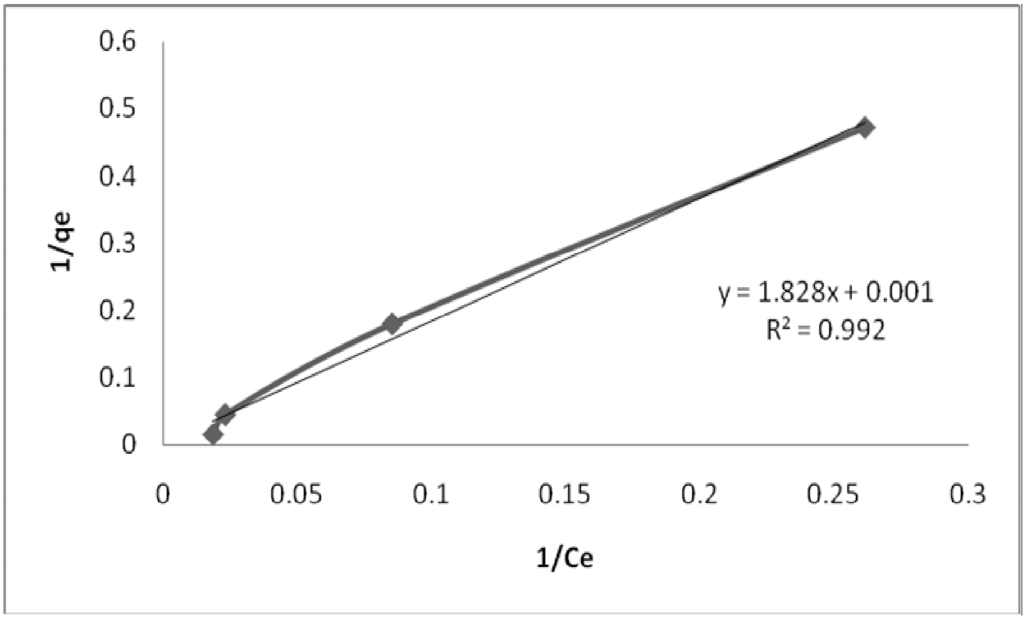

Figure 7. Langmuir isotherm

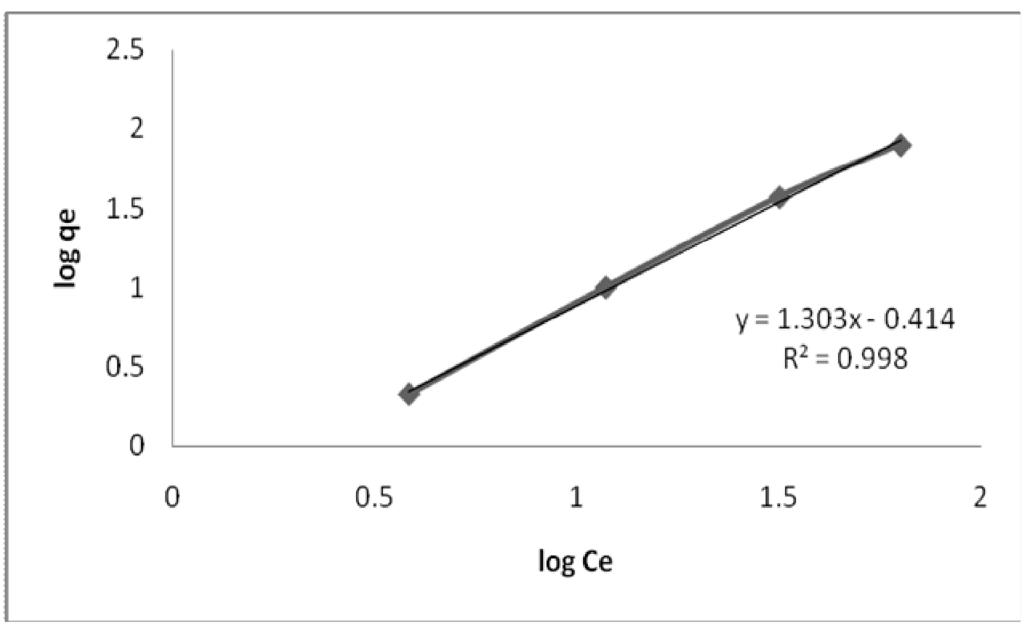

Figure 8. Freundlich isotherm

Figure 9. Lemon grass