Utilization of Poly(Acrylic Acid)/Cellulose Graft Copolymer for Dye and Heavy Metal Removal

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A cellulosic component was extracted from low-value palm tree wastes, empty fruit bunches, and functionalized through grafting with acrylic acid in a previous study. The as-synthesized poly(acrylic acid)/cellulose graft copolymer was applied in the current study as an adsorbent for the removal of the cationic dye methylene blue and the heavy metal lead from industrial wastewater. Factors and parameters that govern the adsorption process were studied during the experimental portion of this study. These factors included the effect of agitation duration, adsorbate medium pH, adsorbent dose, adsorbent graft yield, and initial adsorbate concentration on the efficiency of the said adsorption processes. The data obtained from the adsorption of either methylene blue or lead ions onto the graft copolymer were well fitted to both Langmuir and Freundlich adsorption models.

Keywords: Adsorption; Methylene blue; Heavy metal; Graft copolymer

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INTRODUCTION

Environmental pollution due to rapid industrial progress has become a serious problem not only nationally but also globally. Among the very complicated environmental pollution problems, the pollution of water resources with different agricultural and industrial effluents is a matter of great importance. Pollution of water bodies occurs due to the accumulation of pollutants such as heavy metals and synthetic dyes. The introduction of these harmful pollutants into aquatic systems is due to various industrial operations, which increase annually to cover the continuous needs from the rapid increase in the global population. Heavy metal pollutants are frequently released from industries such as plastic processing, fertilizers, electroplating, pigment and dye industries, and metallurgical and mining activities. On the other hand, synthetic dye pollutants are usually discharged to aquatic life with the waste effluents resulting from the textile mills, which are widely spread worldwide.

The major problem in heavy metal pollution is that these metals are not degradable biologically, and accordingly, they can accumulate in the bodies of living organisms, causing dangerous diseases and serious cell disorders (George 1983). On the other hand, upon discharging synthetic dye effluents into water resources, these dyes remain for a long time and cause several aquatic problems; these include undergoing chemical changes to more toxic substances and consuming huge amounts of water-dissolved oxygen, which leads to mortality of aquatic creatures. Moreover, water contaminated with such synthetic dyes can cause genotoxic effects (Freeman *et al*. 2013).

There are huge amounts of natural materials and industrial processing wastes resulting from certain industries. Rather than just being regarded as waste, such biomass can have valuable uses. For instance, biomass generally has a high capacity to adsorb synthetic dyes and heavy metals adsorbents. It is well known that there are a number of available water purification techniques that can enable the recovery of metals from wastewaters. Techniques used for removal of heavy metal from polluted wastewater include precipitation (Grimshaw *et al.* 2011), adsorption (Sokker *et al.* 2004; Hashem *et al.* 2005a,b; Abdel-Halim *et al.* 2006; Hashem *et al.* 2007; Abdel-Halim and Al-Deyab 2011a, b, 2012; Hebeish *et al.* 2011; Lo *et al.* 2012; Abdel-Halim 2013; Abu-Saied *et al.* 2013), filtration (Ding *et al.* 2014), ion exchange (Pal and Banat 2014), and reverse osmosis (Ozaki *et al.* 2002). Precipitation is particularly efficient but requires huge volume tanks for settling, in addition to the need for subsequent treatments. Ion exchange using a synthetic resin has the advantage of possible recovery of some high-value metal ions, but it is still very expensive and involves very sophisticated operations. One example of an effective adsorbent for heavy metal removal is activated carbon, which was found to be effective in removing hexavalent chromium (Mohan and Pittman Jr 2006) and mercury (Anoop Krishnan and Anirudhan 2002). Removal of pollutants can be achieved through binding heavy metal ions to cellulosic agricultural wastes such as nut wastes (Kumar *et al.* 2011), sawdust (Wu *et al.* 2014), and tree bark (Balci *et al.* 2011). An adsorbent can be used as such or after chemical modification, mainly grafting synthetic polymer onto the cellulosic adsorbents. The initiation methods used conventionally for grafting involve use of different redox systems (Abdel-Halim *et al.* 2008a,b; Abdel-Halim 2012; Abdel-Halim and Al-Deyab 2014a,b,c;), irradiation initiation (Kornacka *et al.* 2014), microwave grafting (Alfaifi *et al.* 2014), initiation by use of electron beam (Abdel-Halim *et al.* 2010a; 2011), and many other different initiation techniques (Abdel-Halim *et al.* 2010b; 2014).

The aim of this paper is to utilize the poly(acrylic acid)/cellulose in removing methylene blue and lead from wastewater. This work is considered an extension of a previous study (Al-Hoqbani *et al.* 2014), in which simple chemical treatments were used to extract the cellulosic component of the agricultural waste, empty fruit bunch. In the same study, the so-extracted cellulose was used as a starting material to prepare poly(acrylic acid)/cellulose graft copolymer, which is used in the current study as an adsorbent to remove methylene blue and lead metal from industrial wastewater. The work described in the previous study (Al-Hoqbani *et al.* 2014) together with the current paper represents a model for an integrated study dealing with waste recycling and pollution control, through converting the low-value agricultural wastes, empty fruit bunch to high-value technical product, then utilizing this product to remove pollutants from industrial wastewater.

EXPERIMENTAL

Materials

Methylene blue and lead ion solutions

Stock solutions of methylene blue or lead ions were prepared by dissolving the dye or nickel nitrate (1 g) in double-distilled water (1 L). All solutions used in the batch adsorption studies were prepared by proper dilution from the previously prepared stock solutions by use of double-distilled water, and the pH of these solutions was adjusted by adding either 0.1 M NaOH solution or 0.1 M HCl solution.

Adsorbent

Cellulose was extracted from finely grinded empty fruit bunch by boiling the latter in 5% (w/v) aqueous sodium hydroxide solution for 60 min. Oxidative bleaching followed this alkaline treatment using 60 mL/L peracetic acid at 70 °C for 60 min. The extracted cellulose was then subjected to graft copolymerization reaction with 150% (based on weight of cellulose) acrylic acid for 120 min at 70 °C using potassium bromate / thiourea dioxide (30 mmole/100 g cellulose, each) as an initiator.

The resulting poly(acrylic acid)/cellulose graft copolymer was allowed to dry completely at 105 °C, finely ground, then sieved to obtain particle sizes of 0.25 to 0.40 mm. This palm tree waste cellulose, functionalized with poly(acrylic acid) graft, was stored in desiccators and used as adsorbent in the batch adsorption studies.

Methods

Batch adsorption study

The batch adsorption studies in both metal and dye removal experiments was performed in 250 mL quick fit conical flasks (Erlenmeyer flasks). This was done by mixing 100 mL of 250 mg/L aqueous lead ion solution with 0.2 g/L from the adsorbent or 100 mL of 25 mg/L aqueous methylene blue solution with 0.02 g/L from the adsorbent in the Erlenmeyer flasks. These flasks were agitated in a thermostatic shaking water bath for 120 min at a speed of 150 rpm. All system parameters that affect the adsorption efficiency, like adsorbent dose, agitation duration, and temperature were studied. At the end of the 2 h shaking duration, the adsorbent was removed from the adsorbate solution immediately, and the residual dye was determined in the adsorbate spectrophotometrically at wavelength 668 nm while the residual metal ions were determined using atomic absorption.

Determination of residual metal cations

The metal ions remaining after the adsorption experiments were estimated in the residual adsorbate solution by use of a Perkin Elmer Precisely Atomic Absorption Spectrometer AAnalyst 400 (USA). A calibration curve was initially constructed by measuring the atomic absorption of a series of lead ion standard solutions at different concentrations. The absorbance of these standard solutions was then plotted versus their corresponding concentrations to establish the calibration curve. To get the concentration of an unknown metal ion sample, its absorbance value was fitted to the calibration curve to get the corresponding concentration.

Determination of residual dye

Concentrations of remaining metal ions after adsorption experiments were estimated in the residual adsorbate solution by use of a Perkin Elmer Precisely Lambda 950 UV/VIS Spectrometer (USA). In order to determine the wavelength, which corresponds to maximum absorbance (λ_{max}), a standard methylene blue solution was scanned in the UV-Vis spectrophotometer, and this (λ_{max}) value was found to equal 668 nm. A standard calibration curve was constructed by determining the absorbance of properly prepared standard dye solutions having varying known concentrations. The concentration of the dye solution is related to its corresponding absorbance value in a linear manner at a particular wavelength. By measuring the absorbance of the exhausted dye solutions (after shaking with the adsorbent) and fitting them to the calibration curve, one gets the corresponding concentrations of the residual dye in these solutions.

RESULTS AND DISCUSSION

Methylene Blue and Lead Ion Removal

Effect of agitation time on percent removal

A 25 mg/L methylene blue aqueous solution and 250 mg/l Pb^{2+} aqueous solution were prepared by the proper dilution from the methylene blue and lead nitrate stock solutions, respectively. A volume of 100 mL from the methylene blue solution was shaken with 0.02 g of the adsorbent sample, having a graft yield of 60%, and 100 mL from lead ion solution was shaken with 0.2 g of the adsorbent sample, having graft yield of 60%. The shaking in each case continued for 120 min at 30 °C in a thermostatic water bath. Samples from both dye solution and metal ion solution were withdrawn throughout the adsorption process at different adsorption durations and the residual dye and metal ion concentrations in the withdrawn samples were estimated immediately by UV spectroscopy and atomic absorption, respectively.

Figure 1a represents the percent of methylene blue removal at different agitation durations. It is clear from Fig. 1a that there was a gradual increase in methylene blue adsorption with each increase in the agitation time, until complete methylene blue removal was attained after an agitation time of 60 min. However, it was noticed that up to 75% of methylene blue adsorption took place within the first 20 min of the adsorption duration. After 20 min, the adsorption started to slow down and then reached equilibrium. It was also noticed that an equilibrium state was established within an adsorption duration of 60 min for 25 mg/L dye concentration, where 100% of the dye was adsorbed. The curve representing the adsorption process was found to be single and continuous, and this indicates that the adsorption of methylene blue onto the adsorbent surface was monolayer adsorption. The remarkable decrease in the dye adsorption beyond a duration of 20 min can be attributed to the aggregates of dye molecules formed on the adsorbent surface, thus blocking its pores. Such aggregation would of course hinder the dye migration from the solution phase to the saturated adsorbent sites.

Figure 1b represents the percent lead ion removal at different agitation durations. The curve in Fig. 1b can be divided into three stages. The first stage started from 0 time and ended at 20 min; this stage was characterized by a sharp increase in the percent metal removal.

The second stage started at 20 min and ended at 35 min; this stage was characterized by a slow increase in the percent metal removal. The last stage started at 35 min, when 100% metal removal was attained, and continued until the end of the adsorption duration. The fast metal ion removal during the first stage was due to the high availability of adsorption active sites, which are free and ready for binding to metal ions. As time of adsorption increased, more and more active sites were occupied by metal ions, *i.e.*, the number of available adsorption active sites decreased, which is why the rate of metal ion removal decreased during the second stage.

The third stage was essentially at steady state, as 100% metal removal was attained after only 35 min. As is clear, the curve representing the adsorption process was found to be single and continuous, and this indicates that the adsorption of lead ion onto the adsorbent surface is monolayer adsorption. The high uptake of lead ions by the adsorbent, and the short time (35 min) required for 100% metal removal suggest the effectiveness of this material for wastewater treatment.

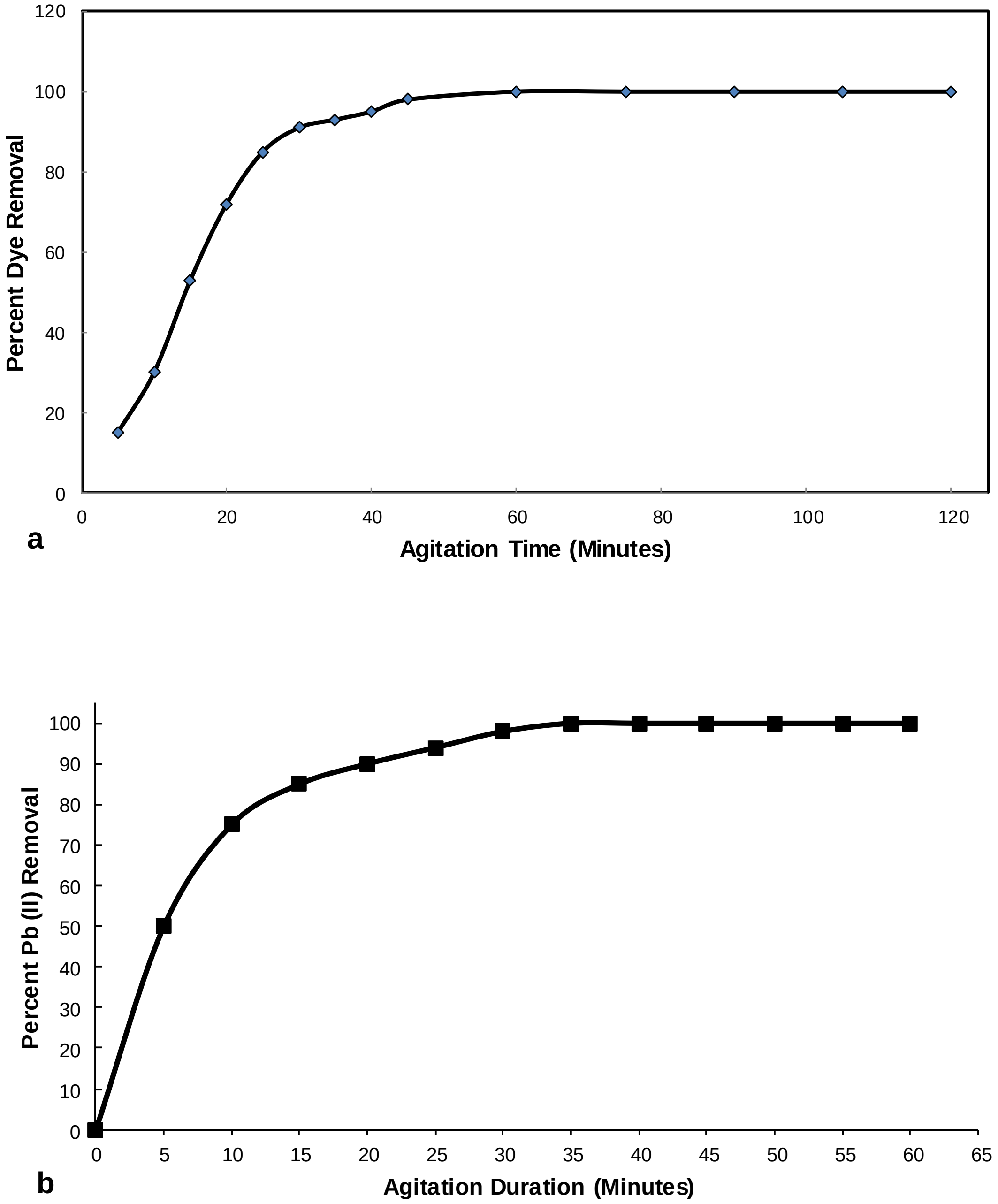


Fig. 1. Effect of agitation time on (a) methylene blue removal and (b) Pb^{2+} removal

Effect of adsorbate pH on percent removal

For methylene blue adsorption, 600 mL of its aqueous solution (25 mg/L) was prepared by diluting properly from its stock solution. Then, 100 mL from the dye solution was poured into a conical flask and the pH was adjusted. Adsorbent (0.02 g; GY 60%) was added, and the system was shaken for 120 min at 30 °C in a water bath under thermostatic conditions. At the end of this time interval, the residual dye concentration was estimated with a spectrometer.

For lead ion adsorption, 800 mL of its aqueous solution (250 mg/L) was prepared by diluting from its stock solution. Adsorption trials were run, each at a certain pH, ranging from pH 1 to pH 7. A volume of 100 mL from the metal ion solution was poured into a conical flask and the pH was adjusted using 0.1 M HCl. Adsorbent (0.02 g; GY 60%) was added and the system was shaken for 120 min at 30 °C in a water bath under thermostatic conditions. At the end of this time interval, the residual metal ion concentration was estimated by atomic absorption.

Figure 2a shows the relation between the pH of aqueous methylene blue solution and the percent dye removal. As is clear from the curve, the pH of the dye solution determines the extent of the adsorption. The percent dye removal was increased gradually with increasing of the adsorbate pH, and the adsorption reached its maximum value at pH 12. In the acid range (pH 2), there was small percent removal, and this percent increased continuously until it reached 100% removal at pH 12.

Figure 2b shows relation between the pH of aqueous Pb^{2+} solution and the percent metal removal. The percent metal removal was found to be 0 at pH 1, and it was increased gradually by increasing the adsorbate pH from 1 to 7 until the adsorption reached its maximum value 100% at pH 7.

The first step in ion exchange process assumed in this removal process is the deprotonation of the graft copolymer carboxylic groups and this is represented by Eq. 1, while the attachment of the adsorbate cation, either metal cation or dye cation (A^+) to the created carboxylate anion is represented by Eq. 2.

The low percent of dye removal at pH 2 or the zero percent metal ion removal at pH 1 can be better understood in terms of the fact that in this highly acidic medium, the presence of a high H^+ concentration in the adsorption medium will shift the equilibrium in Eq. 1 towards the left. This shift to the left makes the carboxyl groups of the graft copolymer stay protonated, and under such acidic conditions the adsorbate cations remain in the solution and do not exchange with the carboxyl groups. As the adsorbate pH increases, the equilibrium involved in Eq. 1 will shift to the right, giving rise to deprotonated carboxylate anions and as a result, the adsorption capacity will increase according to Eq. 2.

$$\text{POLY-COOH} \longleftrightarrow \text{POLY-COO}^- \qquad (1)$$

$$\text{POLY-COO}^- \xrightarrow{A^+} \text{POLY-COO-}A \qquad (2)$$

Effect of adsorbent dose on percent removal

To investigate the effect of varying the adsorbent concentration in the adsorption medium on the percent adsorbate removal, the concentration of adsorbent for methylene blue removal was varied in the range of 0.05 g/L to 0.5 g/L, while for lead ion removal, the concentration of adsorbent was varied in the range of 0.5 g/L to 5 g/L. The adsorption process was carried out using the batch technique by immersing the adsorbent separately, in the adsorbate solution of fixed concentration (25 mg/L for the dye and 250 mg/L for lead) and pH (12 for the dye and 7 for lead) at 30 °C for 120 min.

The relation between the adsorbent doses incorporated into the dye solution and the percent dye removal is presented in Fig. 3a. As is clear from the curve in Fig. 3a, the percent dye removal reached 42% upon using adsorbent concentration of 0.05 g/L. There was a proportional increase in the percent dye removal with each increase in the adsorbent concentration incorporated to the adsorbate solution, and the percent removal reached 100% upon using adsorbent concentration starting from 0.2 g/L and up. This indicates that the adsorbent dose 0.2 g/L was optimum for the complete removal of the dye.

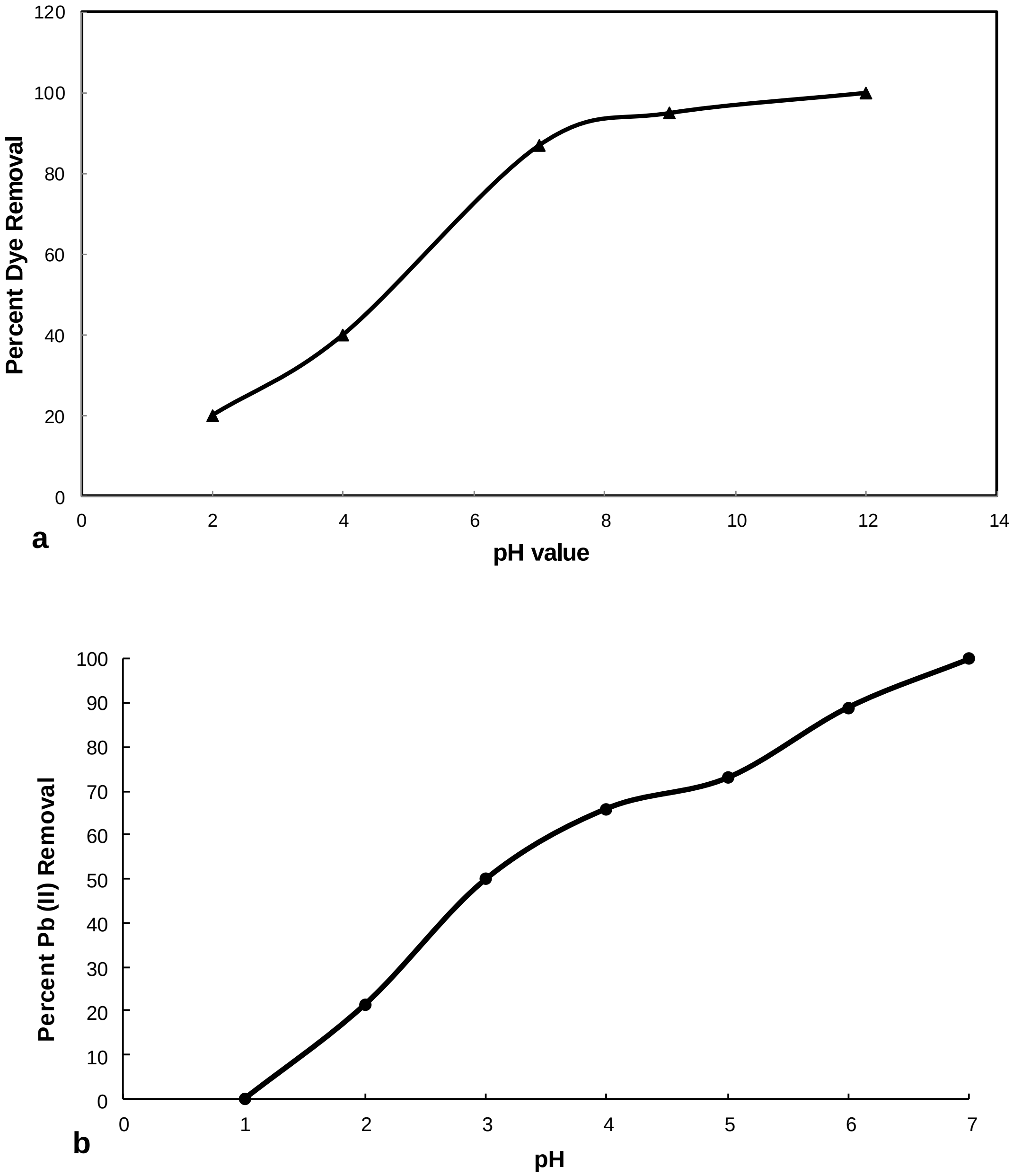


Fig. 2. Effect of adsorbate pH on (a) methylene blue removal and (b) Pb^{2+} removal

The relation between the adsorbent doses added to the lead ion solution and the percent metal removal is presented in Fig. 3b. As is clear from the curve in Fig. 3b, the percent metal removal reached 20% upon using adsorbent concentration of 0.5 g/L. There was a proportional increase in the percent metal removal with each increase in the adsorbent concentration incorporated to the adsorbate solution, and the percent removal reached 60% upon using adsorbent concentration starting from 1 g/L and then the percent metal removal jumped to 100% on using adsorbent doses of 2 g/L and up. This indicates that an adsorbent dose of 2 g/L was optimum for the complete removal of the metal ion.

The gradual increase in the percent dye and/or metal removal with each increase in adsorbent concentration incorporated to the adsorbate solution during the first stage of the adsorption process can be understood in terms of the greater availability of the exchangeable carboxyl groups of the adsorbent. The leveling in the adsorption capacity at high adsorbent dose could be due to the full exhaustion of the adsorbate molecules at these high adsorbent doses.

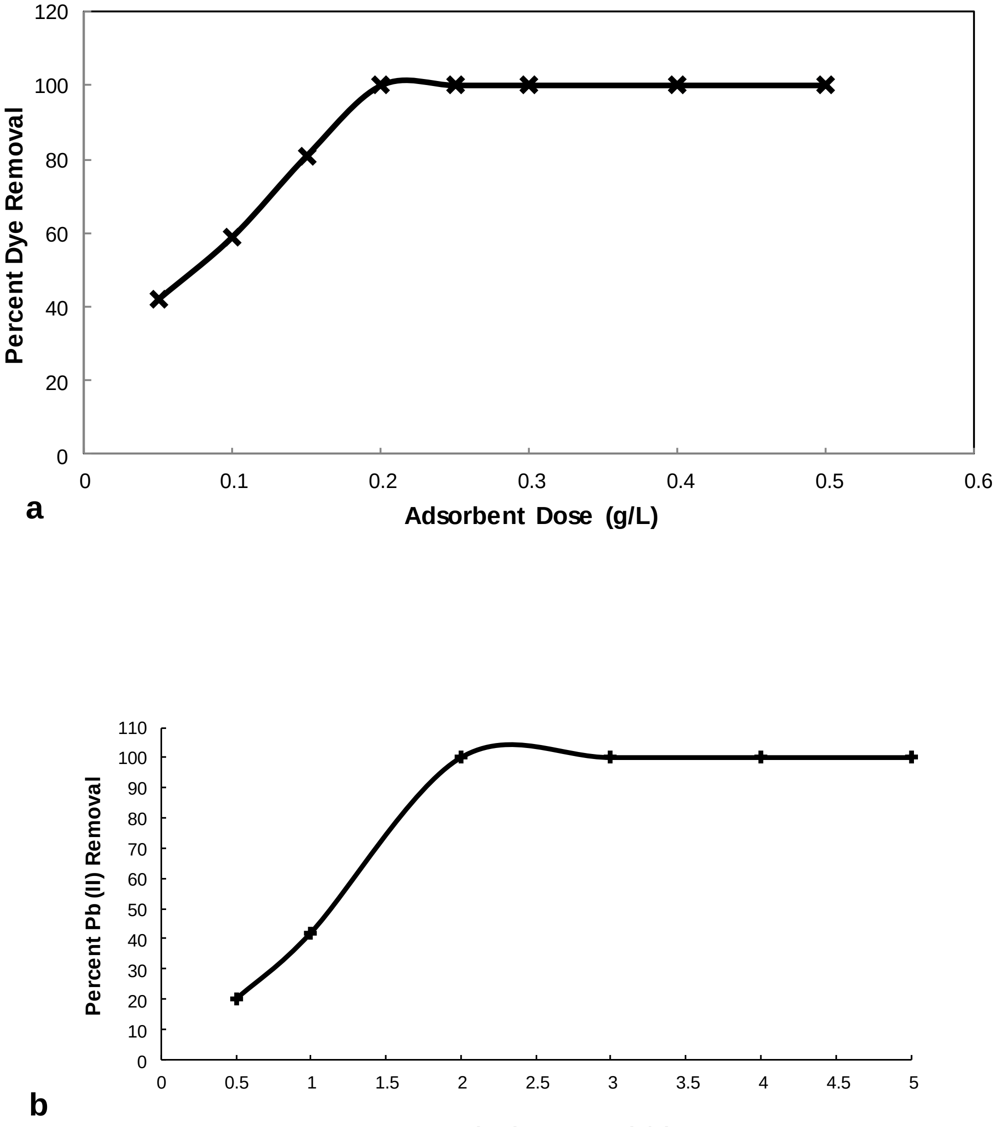


Fig. 3. Effect of adsorbent dose on (a) methylene blue removal and (b) Pb^{2+} removal

Effect of adsorbent graft yield on percent removal

Figures 4a and 4b show relations between the adsorbents percent graft yield, represented in terms of available carboxyl groups and their adsorption capacities towards methylene blue and lead ion, respectively. According to the data presented in Fig. 4a and Fig. 4b, the adsorbents having 0% graft yield showed 15% and 35% dye removal and metal removal, respectively. These capacities of the adsorbents having 0% graft yield for removal demonstrate the potential of the carboxyl groups, whatever comes from the oxidation of empty fruit bunch cellulose or from the grafted acrylic acid chains, to bind to the dye cations or metal cations and removes them from their aqueous solutions. The amounts of removed methylene blue and lead ion were increased by each increase in the adsorbent percent graft yield until they reached 100% removal at graft yields of 60% and 39%, respectively. Beyond these values for the graft yield, there was a decrease in the amount of adsorbed dye or metal ion by each increase in the percent graft yield. The increased adsorption capacities of the adsorbents by the increase in the graft yield in the first stage of each curve is understood to indicate that the increased graft yield means an increased number of carboxyl groups due to the grafted polyacrylic acid chains, which will be available by their residual carboxyl groups for adsorption or ion exchange as active sites.

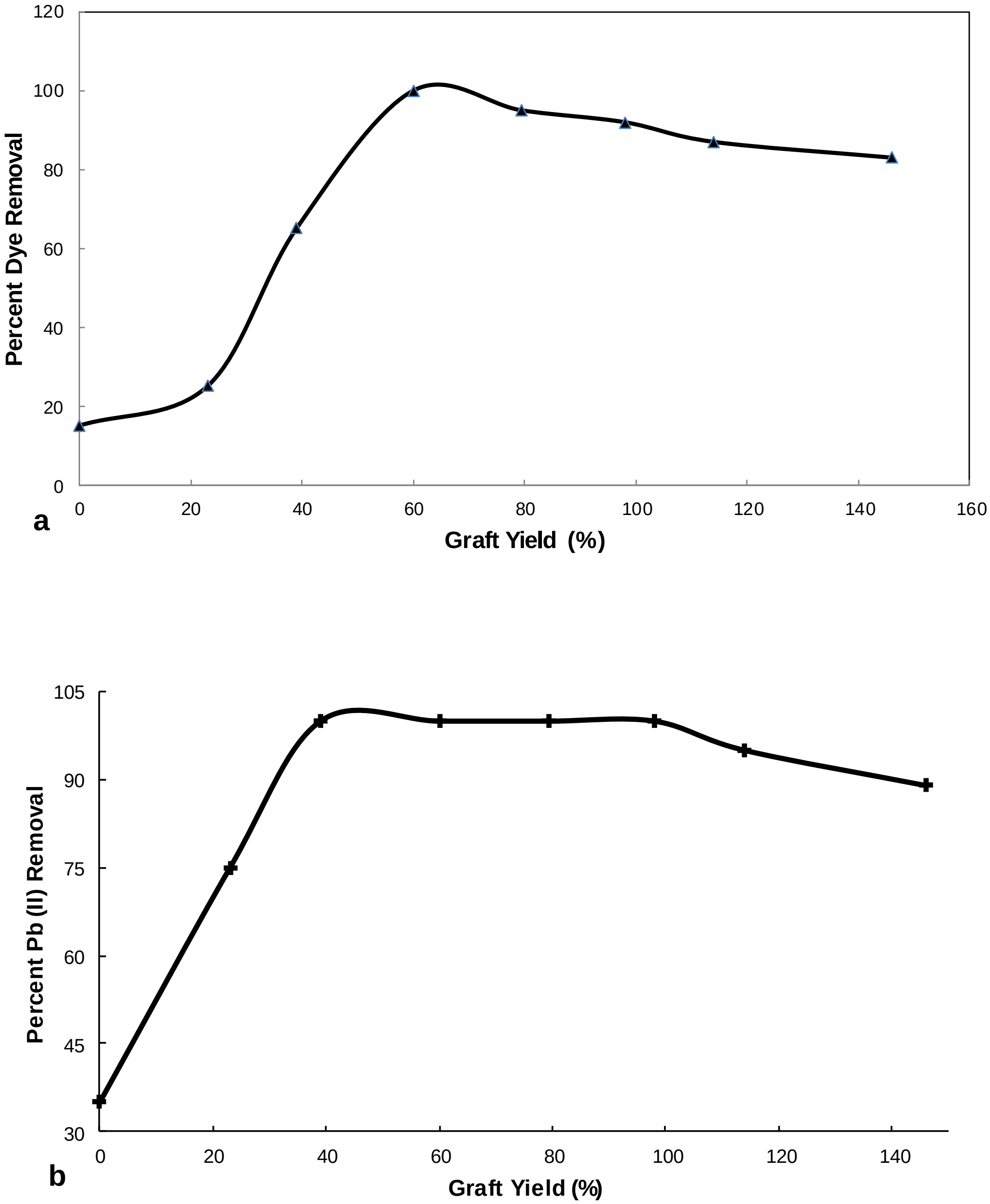


Fig. 4. Effect of adsorbent graft yield on (a) methylene blue removal and (b) Pb^{2+} removal

The decrease in dye and metal ion removal upon the increase in the graft yield through the second stage of each curve was not expected. This unexpected behavior can be interpreted in terms of the increased compactness of the graft copolymer structure upon increasing the graft yield above certain limit. This compactness will make the copolymer less swollen to a great extent, and accordingly this will lead to decreased surface area and decreased pore size. This reduction in the pore size will lead to reduced diffusion of the adsorbate molecules, either dye or metal ion from the solution phase to the adsorbent phase.

Effect of initial adsorbate concentration on percent removal

The adsorption isotherm is a mathematical relationship between the adsorbate molecules still existing in the adsorbate solution and the adsorbate molecules adsorbed onto the adsorbent surface. This relationship can show how the adsorbate molecules can be distributed between the adsorbent phase and the adsorbate phase, when the whole adsorption process is in a thermodynamic equilibrium state.

To show the role of the initial concentration of methylene blue in affecting the whole adsorption process, different batch adsorption processes were run by varying the initial methylene blue concentrations from 100 mg/L to 1500 mg/L, keeping other factors, such as adsorbate pH and adsorbate temperature, fixed at 12 and 30 °C, respectively. For lead ion solution, the initial concentration was varied between 400 mg/L and 1500 mg/L, keeping other factors, such as adsorbate pH and adsorbate temperature, fixed at 7 and 30 °C, respectively. The adsorption process was allowed in each case to proceed for a duration of 120 min.

Collecting adsorption data for the adsorption process involving a wide range of adsorbate concentrations is considered to be the best known technique described by famous adsorption isotherms, such as the Freundlich isotherm (Freundlich 1907) or Langmuir isotherm (Langmuir 1918). These two adsorption models establish a relationship between the adsorption densities, q_e (the uptake of adsorbate molecules per the weight unit of an adsorbent) and the equilibrium concentration of the adsorbate in the liquid phase, C_e.

Figure 5a shows the mathematical relationship between the equilibrium concentration of methylene blue in the bulk of the adsorbate phase (C_e) and the uptake of the dye per the weight unit of the adsorbent (q_e). It is clear from the curve that the value of q_e rose from 8.54 mg/g to 41.6 mg/g upon the increase in the initial concentration of methylene blue from 100 mg/L to 1000 mg/L.

Figure 5b shows the mathematical relationship between the equilibrium concentration of lead ion in the bulk of the adsorbate phase (C_e) and the uptake of the metal per the weight unit of the adsorbent (q_e). Again the value of q_e rose from 52 mg/g to 226 mg/g upon the increase in the initial concentration of lead nitrate from 400 mg/L to 1500 mg/L. These findings in each case are in good accordance with the results reported previously by other researchers (Gupta *et al.* 2011; 2012).

The noticed increase in the capacity of adsorption in the first stage of each curve is attributed to more interaction between the adsorbate molecules and adsorbent surface active sites upon increasing the adsorbate concentration. The high amount of adsorbed dye and metal ions at high adsorbate concentrations may be also due to more diffusion into the adsorbent pores and less resistance to the uptake of the adsorbate molecules by the adsorbent surface. Moreover, any increase in the adsorbate concentration in the second stage of the curve was found not to be accompanied by an equivalent increase in the adsorbate uptake, and this indicates that the adsorption sites were saturated at these limits.

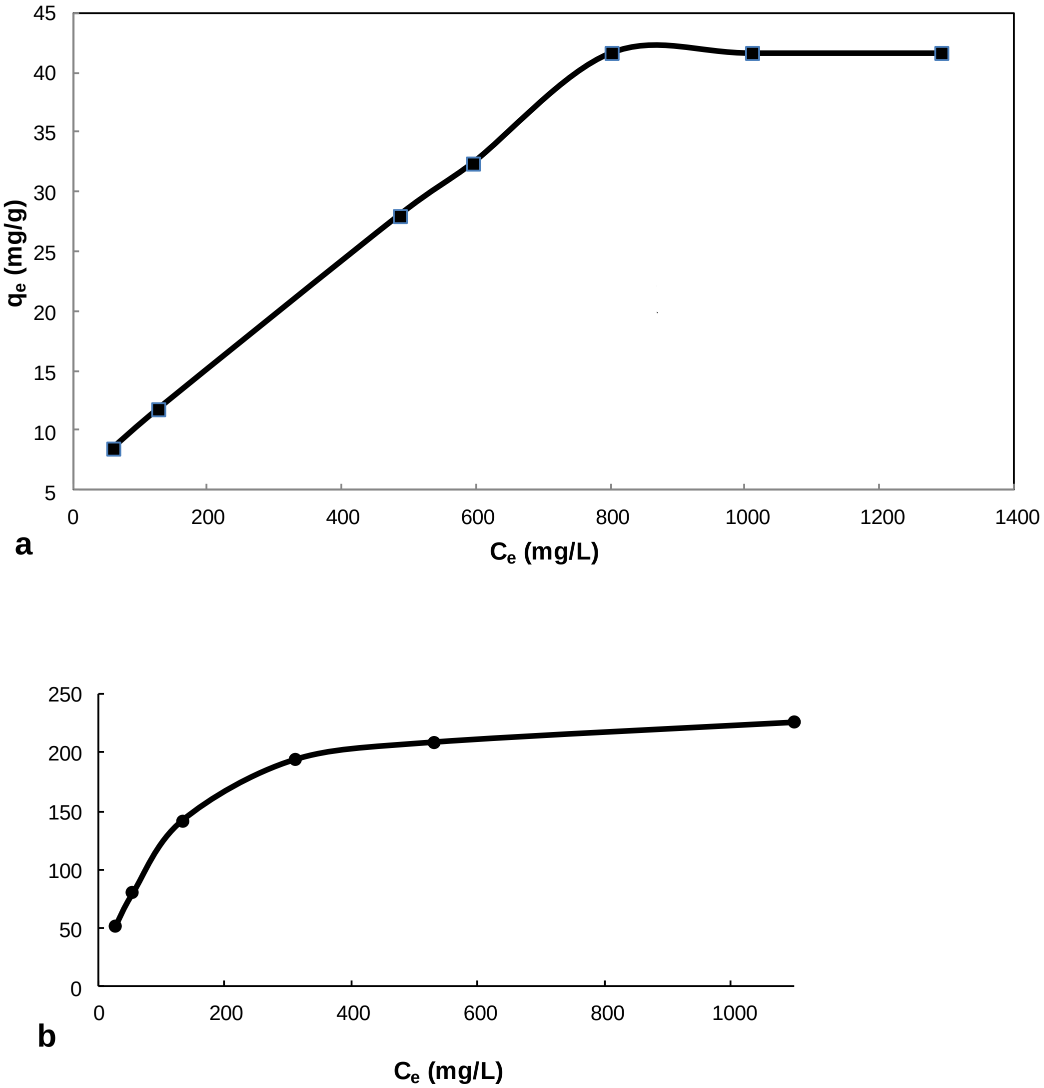


Fig. 5. Effect of initial adsorbate concentration on (a) methylene blue removal and (b) Pb^{2+} removals

Langmuir Isotherm for Adsorption

Langmuir treatment (Langmuir 1918) was applied to the adsorption equilibrium of both methylene blue and lead ion onto the graft copolymer as an adsorbent. According to the Langmuir treatment, maximum adsorption takes place when the adsorbent surface is saturated with a monolayer of the adsorbate molecules, such as when the adsorption energy is constant at this moment and no further transmigration of the adsorbate molecules in the plane surface can take place. The Langmuir isotherm can be represented in the form of the straight-line equation (Eq. 3),

$$C_e / q_e = (C_e / Q_o) + (1/Q_o * b) \tag{3}$$

where C_e is the adsorbate equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed by unit weight of the adsorbent (mg/g), Q_o is the Langmuir constant related to maximum adsorption capacity (mg/g), and *b* is the Langmuir constant related to energy of adsorption (L/mg).

The Langmuir equilibrium constant, K_L, is used to determine the enthalpy of adsorption, ΔH, and can be obtained from Eq. 4:

$$K_L = Q_o * b \tag{4}$$

For a given adsorption process, when the values of (C_e/q_e) are plotted against the corresponding values of C_e, one obtains a straight line. The slope of this straight line represents the reciprocal of Q_o, ($1/Q_o$) and its intercept represents the value $1/(Q_o*b)$.

Figures 6a and 6b show the Langmuir adsorption isotherms for the adsorption of methylene blue and lead ion, respectively, onto the adsorbent.

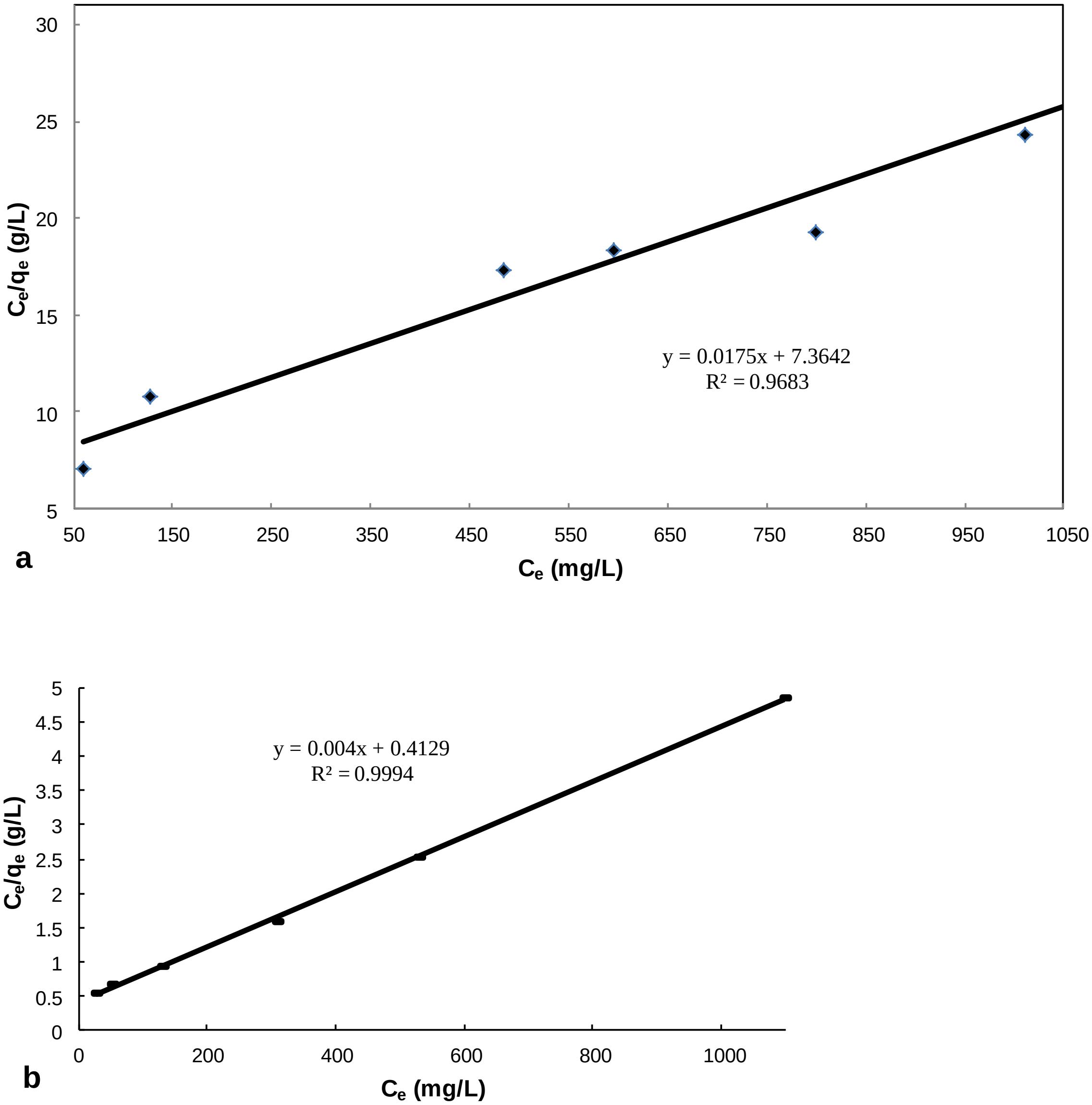


Fig. 6. Langmuir isotherm of (a) methylene blue adsorption and (b) Pb^{2+} adsorption

The Langmuir constants, Q_o and b, in each case can be obtained from the straight-line equation corresponding to each adsorption process, and the corresponding K_L constant can be calculated by substituting in Eq. 4. The values of Langmuir constants for adsorption of methylene blue onto the adsorbent, Q_o, b, K_L, and R^2 were found to be 57 mg/g, $2.4\text{x}10^{-3}$ L/mg, 0.136 L/g, and 0.9683, respectively. The corresponding Langmuir constants for adsorption of lead ion onto the adsorbent, Q_o, b, K_L, and R^2 were found to be 250 mg/g, $1\text{x}10^{-3}$ L/mg, 2042 L/g, and 0.9994, respectively.

The dimensionless equilibrium parameter, R_L, can describe the type of isotherm according to its numerical value, which can be obtained from Eq. 5,

$$R_L = 1/(1+bC_o) \tag{5}$$

where C_o (mg/L) is the initial adsorbate concentration in the solution.

According to the value of the parameter, R_L, the type of isotherm may be unfavorable (if $R_L > 1$), linear (if $R_L = 1$), favorable (if $0 < R_L < 1$), or irreversible (if $R_L = 0$).

The R_L values for adsorption using different initial concentrations from either methylene blue or lead ions are given in Table 1. As is clear from Table 1, all R_L values lay in the region $0 < R_L < 1$, which indicates that the adsorption of both methylene blue and lead ions onto the graft copolymer is favorable. Moreover, the correlation coefficient, R^2 value for methylene blue adsorption and lead ion adsorption onto the graft copolymer were found to be 0.9683 and 0.9994, respectively, indicating that both adsorption processes were well fitted on Langmuir adsorption isotherm.

Table 1. R_L Values for Adsorption of Methylene Blue and Lead Ion Based on Langmuir Equation

Methylene Blue		Lead ion	
Initial concentration (mg/L)	R_L values	Initial concentration (mg/L)	R_L values
104	0.8	400	0.71
195	0.68	600	0.625
612	0.4	800	0.55
751	0.35	1000	0.0.5
1012	0.29	1200	0.45
1210	0.25	1500	0.4
1490	0.2		

Freundlich Isotherm for Adsorption

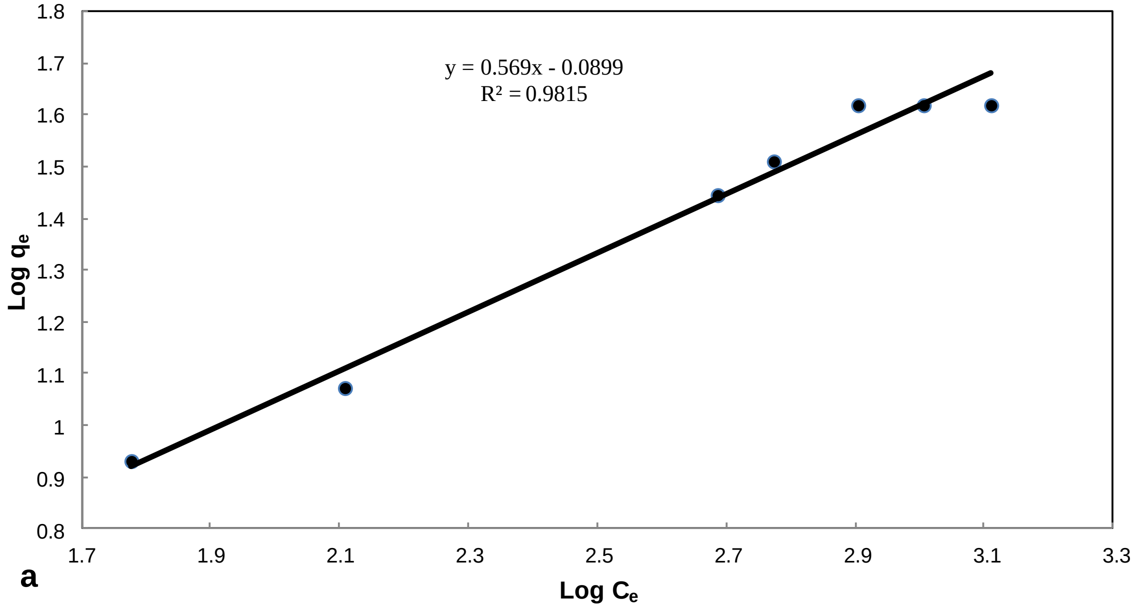
To examine the applicability of Freundlich adsorption model (Freundlich 1907) on methylene blue and lead ion adsorption, the Freundlich equation was applied for the said adsorption processes. The empirical model for Freundlich equation is appropriate and characteristic for the heterogeneous surfaces characterized by active centers having exponential distribution. According to Freundlich treatment, the adsorbed amount of solute, q_e, was strongly related to the equilibrium concentration of the solute in the solution, C_e. This is best represented by the linear Freundlich isotherm equation (Eq. 6) (Freundlich 1907),

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

where C_e is the adsorbate equilibrium concentration (mg/L), q_e is the adsorbed amount of adsorbate (mg/g), K_F (mg/g) is the Freundlich constant that is related to the adsorbed amount, and n is the Freundlich constant, which gives an idea about the adsorption favorability.

When plotting the values of log q_e for a given adsorption process against the corresponding log C_e values, one gets a straight line. The slope of this straight line is the reciprocal of the constant n, $(1/n)$, and its intercept will correspond to log K_F.

Figures 7a and 7b show the Freundlich adsorption isotherms for the adsorption of methylene blue and lead ion, respectively, onto the adsorbent.



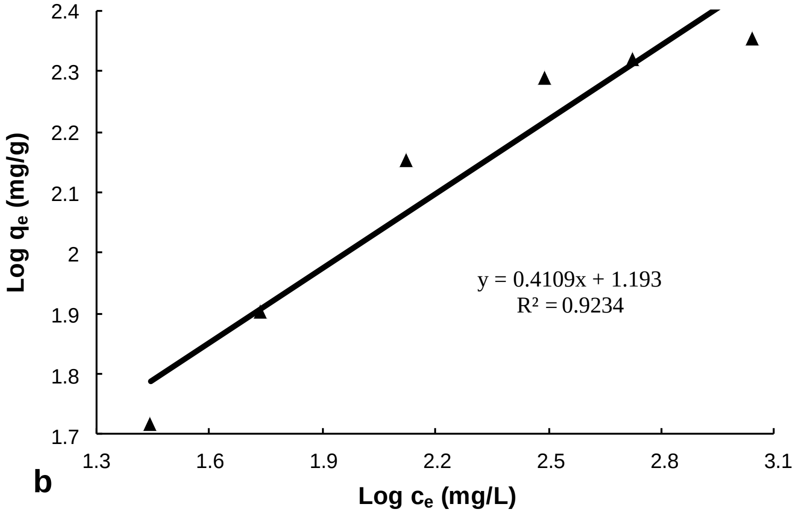


Fig. 7. Freundlich isotherm of (a) methylene blue adsorption and (b) Pb^{2+} adsorption

The Freundlich constants, *n* and K_F, in each case can be obtained from the straight-line equation corresponding to each adsorption process. The values of Freundlich constants for adsorption of methylene blue onto the adsorbent, *n*, K_F, and R^2 were found to be 1.757, 1.23 mg/g, and 0.9815, respectively.

The corresponding Freundlich constants for adsorption of lead ion onto the adsorbent, *n*, K_F, and R^2 were found to be 2.43, 15.6 mg/g, and 0.9234, respectively. The value of n in each adsorption process was found to lay in the region ($0 < n < 10$), indicating that both the adsorption of methylene blue and the adsorption of lead ion onto the graft copolymer is favorable. Moreover, the correlation coefficient, R^2 value for methylene blue adsorption, and lead ion adsorption onto the graft copolymer were found to be 0.9815 and 0.9234, respectively, indicating that both adsorption processes are well fitted on Freundlich adsorption isotherm.

CONCLUSIONS

1. Poly(acrylic acid)/cellulose graft copolymer was used in this study as an adsorbent to remove the heavy metal lead and the cationic dye methylene blue from the industrial wastewater.
2. The adsorption process was found to be pH dependent, and the percent removal was found to increase gradually by increasing the adsorbate pH, to reach its maximum value for methylene blue at pH 12 and for lead ion at pH 7.
3. The extent of dye and metal removal were found to increase upon increasing the graft yield of the adsorbent poly(acrylic acid)/cellulose graft copolymer to 60% for methylene blue and 40% for lead ion, then decrease again upon further increase in the graft yield due to increased graft copolymer compactness.
4. The adsorption of both lead ions and methylene blue onto the adsorbent poly(acrylic acid)/cellulose graft copolymer was found to obey both the Langmuir model (R^2 for methylene blue and lead ion adsorption were 0.9683 and 0.9994, respectively) and the Freundlich model (R^2 for methylene blue and lead ion adsorption are 0.9815 and 0.9234, respectively).

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