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Removal Lead and Cadmium Ions in Industrial Wastewater Using Graphene Nano Sheets

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ABSTRACT

Industrial wastewater effluents especially that contain heavy metals considered a foremost problem of water pollution in the worldwide environment. Discharging this wastewater, that contains considerable heavy metals' concentrations into ground, water or streams and rivers causes deterioration of the ecological system. The present study aimed to synthesized the graphene nano sheets by electrochemical method and used for removal of lead Pb^{+2} and Cadmium Cd^{+2} ions that found in industrial wastewater. Graphene nano sheets synthetic in this study is characterized by X-ray diffraction XRD, scanning electron microscopy SEM, Raman spectroscopy and Fourier-Transformed Infrared Spectra (FT-IR). The abundant oxygen-containing functional groups on the surfaces of graphene nanosheets and strong surface complexion played an important role in (lead and cadmium ions) adsorption. Adsorption properties for (lead and cadmium ions) on graphene nanosheets were regularly investigated, including contact time, pH effect, adsorbent doses and initial concentrations for lead and cadmium solutions. The experimental data were evaluated by Langmuir, Freundlich models in order to describe the equilibrium isotherms. From the adsorption isotherms, the maximum adsorption capacities of lead ions on graphene calculated from Langmuir model were equivalent 476.19 (mg/g) at pH 6.2 and equilibrium contact time 35 min with adsorbent dose (40mg/L), and 188.679 (mg/g) at pH 5.2 and equilibrium contact time 40 min with adsorbent dose (20mg/L) for cadmium ions. The results of the present study demonstrated that graphene has respectable qualifications to removal (Pb^{+2}&Cd^{+2} ions) which found in industrial wastewater as compared to other adsorbents e.g. activated carbon.

Key words: Nano materials, Graphene, Heavy metals, Adsorption

INTRODUCTION

Industrial outputs was considered as most important causes that discharge large amounts of toxic chemicals for sewage system or water upstream [1].A lot of problems will being by discharge wastewater contaminated directly into sewage system or upstream. Traditionally techniques of soil remediation are costly and may cause the secondary pollution [2]. Moreover, over loads pollutants from industrial

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activities have been leading to increase the onus and cost of waste water treatment plant of city [3]. Typically There are expended the numerous nano technologies applications for removing heavy metals from wastewater. Among all the methods suggested for toxic metal impurities removal, adsorption is developed to be economical and efficient [4, 5]. Nano materials were being adequate for water purification, disinfection and wastewater treatment applications because of its high degree of functionalization, size dependent properties and affinity for specific target contaminates [6]. It had nanoscopic pores which help in sorbent. It can be reused and regeneration by several methods [7]. Treatment of water problems by nanotechnology is still distant and need for more investigations. Current investigation target to establish the effectiveness of different and marvelous characteristics of carbon form nano material (graphene) for different applications including adsorption heavy metals from aqueous solutions. Graphene is crystalline stuffs. It has lately been pinpointed and investigated [10]. Graphite is the generality prevalent modality of carbon. Which it be made up of flagged sheets of carbon with a hexagonal composition [11]. Lately, graphene applied as an adsorbent to remove contaminates in effluents and performance prominent adsorption capacity [12]. The use of graphene for removal metal has been two engineering advantages. First, aggregation of graphene sheets can induced by metal adsorption, which can precipitate metal- burdened graphene sheets out of water without the use of additional separation processes. The abstraction of separation is eligible because it lessens infrastructure investment, operational cost, and operational complication [13]. Second, metal-laden graphene oxide can be regenerated by acid wash to remove the adsorbed metal. In addition, this mastery reduced the volume for waste disposal, thereby raising the environmental friendliness of the removal process [14]. In Iraq, large quantity of heavy metals contaminated wastewater from industry zones is discharged into up streams or sewages. Therefore, we established it necessary to found an efficient, fast and safety technique that can be applied directly for dangerous metals removal from the wastewater before discharging into river or sewage nets. Graphene, as a new nano material, were prepared, purified, functionalized, and used as adsorption material to remove heavy metals ions (lead Pb^{+2} and cadmium Cd^{+2}) from aqueous solutions under different conditions.

Experiments

Materials& methods:

Graphene was prepared by electrochemical technique as shown in Fig.1. a. Graphite rod was considered anode and cathode electrodes immersed electrolyte baths (electrochemical cell) composed of ionic liquid and water for exfoliation process (Fig.1,a &b). Potentials of 10V had been applied, it was demanded that ionic-liquid-functionalized graphene sheets triggered. Prepared mixture ratio which used in experimental work was done firstly. Solution was arranged with great care. The solution mixed before application or applied in the synthetic cell with graphite rod. It had been applied by adding 1gm of HCl acid and 5gm of glacial acetic acid CH_3COOH, followed by the peroxide 1.5gm H_2O_2 diluted in 100 mL of distilled water.

Then mechanical blending was fixed to achieve a uniform mixture. The small bias of 2.5 V was employed for 1 min, and then high voltages were utilized (alternating between 10 V). It could to demonstrate that the 10 V initiated the exfoliation and oxidized the graphene sheets. The formed functional groups were reduced when the bias is switched to (-10 V). It was used ultrasonic cleaner in (environmental research center /technology university) for deep cleaning purposes, such as removing contaminants, dirt, grease, waxes, and oils from metal, plastic parts, or glass-wear

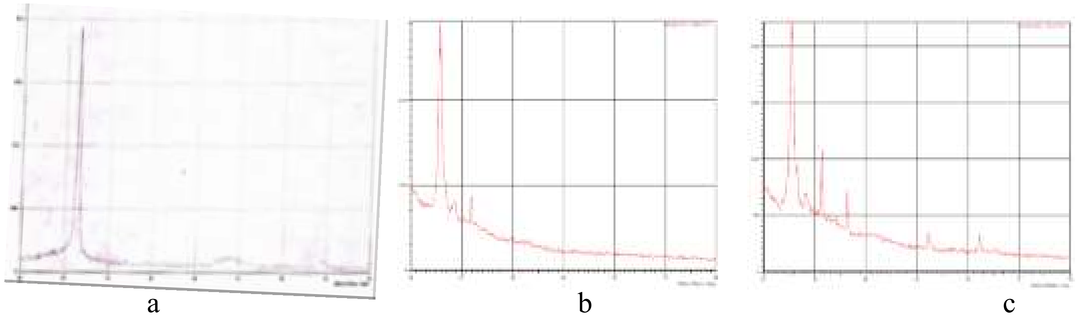
In order to make the graphene sheet suspension, the exfoliated graphene sheets were collected with Millipore membrane filter 0.45 µm (Chmlab group, Spain) and washed with distilled water. After drying, they were dispersed in acidic solution by gentle water-bath sonication (wise bath device) for 5 min. Additional, to remove unwanted large graphite particles produced in the exfoliation, the solution is left for 2or 3hours to take enough time to drop down to bottom, can then be used for further characterizations**.** All of these electrochemical exfoliation experiments were performed at room temperature (25 C^{o}).

Characterization Techniques:

Atypical techniques such as Scanning Electron Microscopy SEM, Raman spectra and X-Ray Diffraction XRD, were used to distinguish the structure and possessions of graphene fixed. (XRD) analysis had been reflected the crystal structures of graphene. It studied the changes in the crystal structure as result for preparing process. Figs.2 shows X-ray diffraction patterns analyses of raw graphite, graphene after chemical reduction and graphene after adsorbed Pb samples that established in this study. The XRD pattern of raw graphite sample delimited a very sharp and high intensity 002 peak near 2θ = 26.4^{O} and 004 peak near 2θ = 54.4^{O} (Fig. 2.a). Furthermore, it detected a similar diffraction and a shoulder for XRD pattern of graphene which obtained after chemical reduction by sonication. It contained a sharper at wide peak at 2θ =25.8 ^{O} and shifted shoulder at around 2θ = 30^{o} (Figure 2.b). (Figure 2.c) shows deferent peaks unless recognized for lead adsorbed on graphene.

a b c

Figure.(1): a/ schematics setup, b/ Graphite rod, c/ Experimental setup



a b c

Figure (2): XRD patterns of (a) raw graphite sample (b) GO after chemical reduction (c) GO after adsorbing pb

SEM images appeared the effect of acidic treatment on the graphene prepared. Fabric diaphanous and squashed graphite were fashioned with Sonication of graphene oxide samples that produced more separated layer structures as presented in (Fig.3). It is be indicated that the oxidation impacted through attach more oxygen atoms which caused loose structure compared to raw graphite. SEM analysis of all samples exposed successful of experimental procedure and acceded exfoliated graphene-based sheets. Irrevocably, SEM images had been demonstrating the graphene morphology since the regime of thicknesses sheets in nanometer.

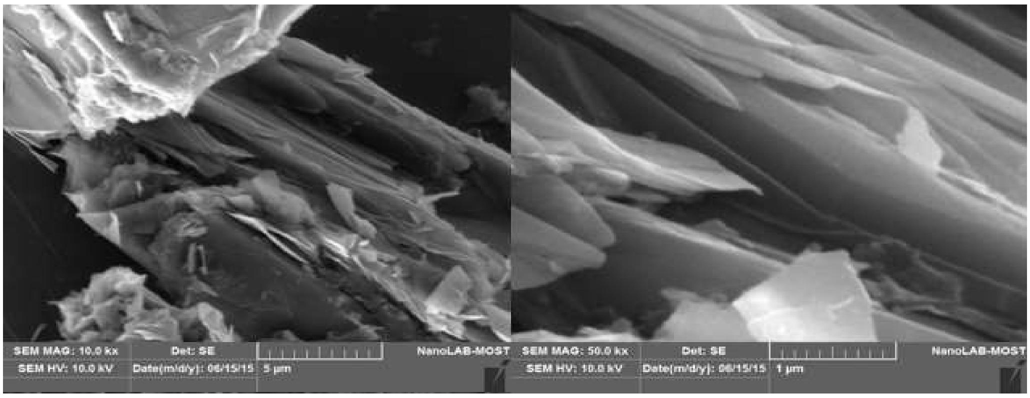


Figure (3): SEM images of graphene nanosheets

Raman spectroscopy is a swift and specific technique to determine the number of graphene layers. The graphene had changes of crystal structure in preparing after chemical treatments; it could be specified with Raman spectroscopy. Raman spectrum of graphene oxide prepared in this study was shown in Fig. 4. It can be noticed that the G line was broadened and shifted to 1584.5 cm^{-1}and intensity of D line around 1357cm^{-1} as illustrated in table 1.

Table (1): shows the parameters of carve in Fig. 4

Peaks	D	G	D'	D+G	—	—	I(G)/I(D')
Raman shift (cm^{-1})	1357	1584.5	2724	2941.5	0.9567	4.599 nm	1.031
Intensity (absunits)	1317.904	1377.538	1334.94				

It was indicated that the substantial reduction due to oxidation and sonication processes, and the development of graphene nano sheets having highly adapted crystal structure. The ratio between the intensity of D and G line, I (D) and I (G), changes inversely with the size of the crystalline grains [15]. For the comparison I (D)/I (G) values for raw graphite 0.2[16] and 0.95 for graphene oxide prepared in this study. It was argument the increase in obvious (D)/I (G) values for the structure of graphene oxide prepared with highest order. It was requested the ratio between I (G)/I (D') when it had demonstrated the layer number less than five or not. The increase in the ratio between the intensity of G and D' peak denoted an increase in the number of graphene layers [17]. I(G)/I(D') values for present work was 1.031as shown in table (1) and this outcome good compliance with the results obtained by(Saner, et al. 2010) that it had I(G)/I(D') equal 1.5 for raw graphite. The highest ratio of I (G)/I (D') demonstrated the largest number of graphene layers.

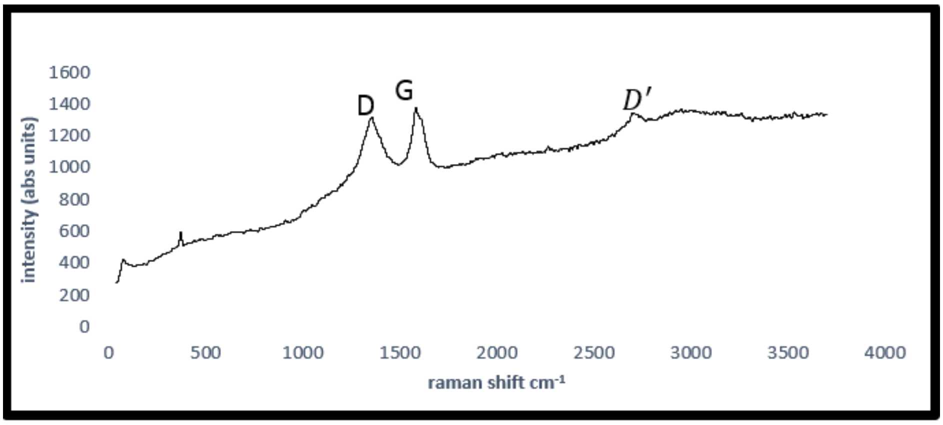


Figure (4): Raman spectrum of graphene from experiment (electrochemical exfoliation- graphite- graphite electrode)

The attendance of ionic liquid groups also inveterate by FTIR analysis (Fig. 5), in which the presence of the C–H vibration of 1465.9 cm^{-1} was evidenced. Different functional groups are found in the FTIR spectrum, i.e., C-O group at 1103.2 cm^{-1} and, C=O group at 1745.5 cm^{-1} , C=C at 1654.9 cm^{-1} and $^{-}$COOH at 908.4 cm^{-1} [18]. It indicates that large amounts of oxygen-containing functional groups exist on graphene oxide nanosheets.

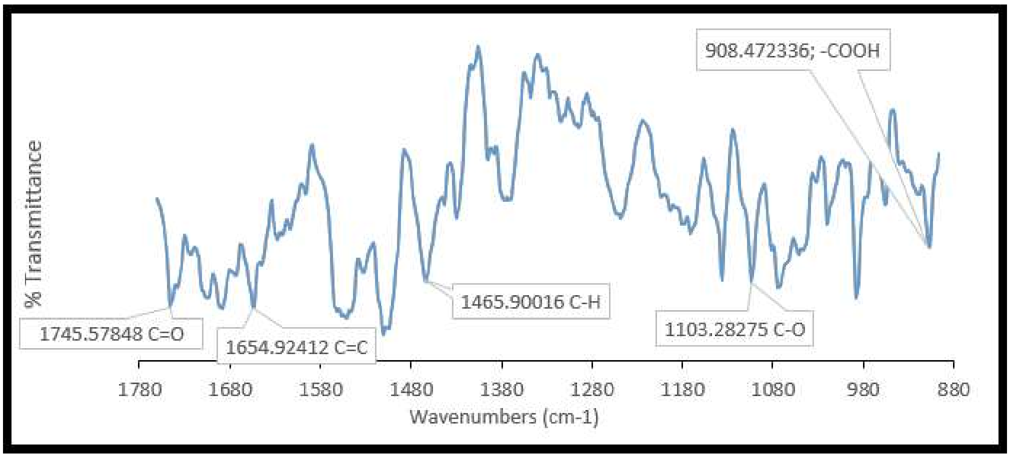


Figure (5): FTIR of functionalized grapheme

Batch Adsorption Experiments*:* The stock solution of heavy metals was prepared according to the equation: N1 V_1= N_2 V_2 to preparing the desired concentration for experiments. The stock solution of heavy metals was prepared by diluting the desired initial concentrations of (5, 10, 15, and 20) mg/L for Pb and (2, 4, 6and8) mg/L for Cd. Primary amount 2mg for Pb and 1 mg for Cd of adsorbent (graphene) were added into 100 mL conical flasks filled with 50 mL of heavy metals solutions of known initial concentrations. The conical flasks were located internal the shaker that set the speed into 250 rpm at room temperature (25 ± 2 °C) and samples were taken at determined time intervals. Heavy metals concentrations after sorption were analyzed using an Atomic device available in building and construction department/ University of Technology. Then, repeat the same procedure by determined equilibrium time from previous step with change the pH values as shown in table (2) to evaluate effect and optimum pH. Subsequently, it fixed the finest period and pH into next step that shifting dosage of graphene as listed in table 2 to investigate the effect of dosages. The effects of various variables affecting the adsorption of it over graphene were determined during batch experiments. The pH of each solution was adjusted using 0.1 M HCl or 0.1 M NaOH. The amount of heavy metals adsorbed onto Graphene, q (mg/g), was calculated by the mass balance relationship:

—— …… (1)

Where: q= Adsorption capacity (mg/g)
m= the mass of adsorbent graphene (g)
V= the volume of metal solution (L)
C_o= the initial concentration of metal solution (mg/L)
C_f= the final concentration of metal solution (mg/L)

The adsorption percentage (removal efficiency), Re %, of each metals was calculated as follows:

—— …. (2)

Table(2): Variable values of batch adsorption process

Variables	Ranges								
Time (min) for Pb	5	10	15	20	25		30	35	40
Time (min) for Cd	5	10	15	20	25	30	35	40	45
Mass of Graphene (mg) for Pb	2		4				6		
Mass of Graphene (mg) for Cd	1		3				5		
pH	4		5.2		6.2		8.2		9.2

Results and Discussion

Variables effect on adsorption heavy metals by graphene:

Effect of Contact Time: The Figs. (6 a, b) explained relationships of effect contact time versus the removal efficiency and adsorption capacity (q mg/g) of Pb ions respectively. It can be noticed that the behavior of adsorption in obvious graphs, the curves clearly increases at first then gradually reaches the adsorption equilibrium. It was upshot availability a considerable number of free surface sites for adsorption through the initial period then it might be occupied [19]. It had been implying that the adsorption system of graphene is uncommon from that other kinds of adsorbent like activated carbon. It correspond with standpoint that adsorbates diffused through pores of activated carbon which takes time, while the specific planar construction of graphene arranged adequate sites for the adsorption heavy metals through insert into the interlayer spaces[14,20].

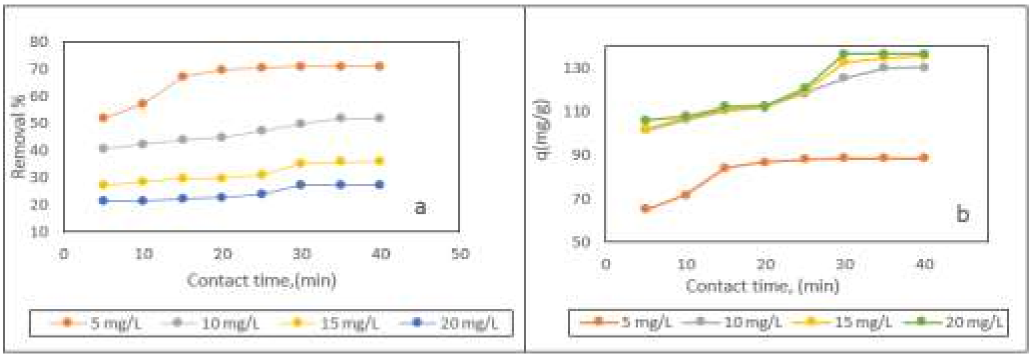


Figure. (6): (a) Removal efficiency of Pb^{+2} ions on graphene as a function of contact time (pH=4, dose =40 mg/L) (b) Adsorbed capacity (q mg/g) of Pb^{+2} ions on graphene as a function of contact time (pH=4, dose =40 mg/L)

Effect of pH:

Fig. (7a, b) shows the relationships between the solution pH and (lead, cadmium) ions removal efficiency and adsorption capacity by graphene. It obvious that the maximum adsorption for both is almost the same which is just over pH=6.2. Graphically, the adsorption of Pb^{+2},Cd^{+2} ions on graphene increases with the pH increasing from 1 to 7, and then decreases with increasing pH values at pH > 7. This may due to plentiful oxygen-containing functional groups on graphene. It is attributed to the oxygen containing functional groups the enhancing adsorption of heavy metals ions on graphene, which create strong surface complexes with metals ions on graphene.

Effect of graphene dosage*:*

Three doses of adsorbent were investigated (40, 80 and 120 mg/L) for Pb^{+2} ions and (20, 60 and 100 mg/L) for Cd^{+2} ions to find the optimum dosage of graphene. It considered other test conditions as pH and contact time (6.2 and 35 min) and (5.2 and 40 min) for lead and cadmium respectivly. Fig.(8) shows the correlation between dosage of graphene and adsorption capacity for lead and cadmium respectively. Obviously, it was reverse proportionality between graphene dosages via adsorbed capacity. It can be explained this correlation to the growth of assemblies at higher (Graphene/aqueous solution) ratios or to sediment of grains [21].

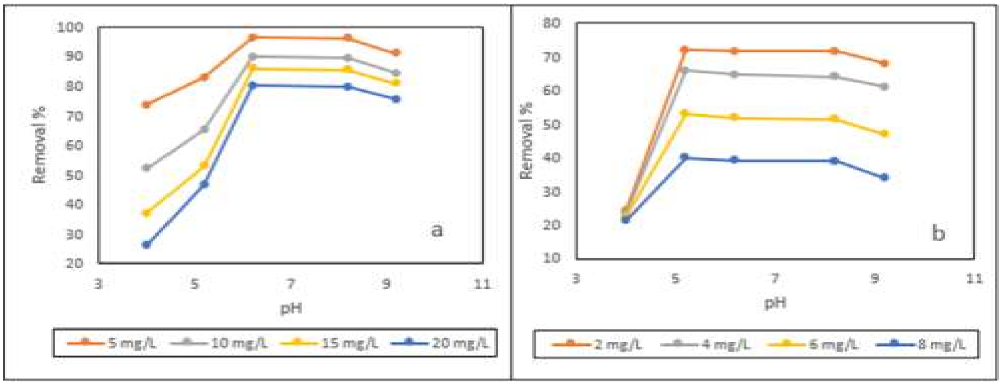


Figure (7): (a) Removal efficiency of Pb^{+2} ions on graphene as a function of pH (dose =40 mg/L, contact time =35 min), (b) Removal efficiency of Cd^{+2} ions on graphene as a function of pH (dose =20 mg/L, contact time =40 min)

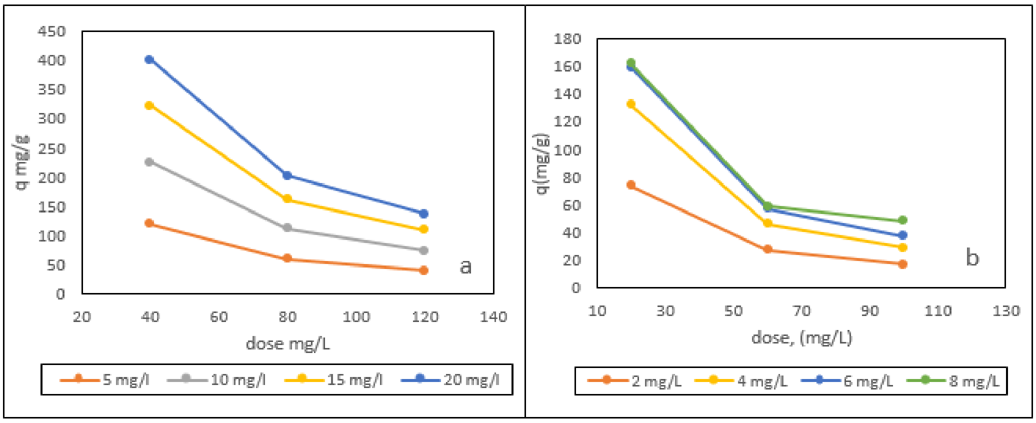


Figure (8): (a) Adsorbed capacity (q mg/g) of Pb^{+2} ions on graphene as a function of dose (PH=6.2, contact time =35 min), (b) Adsorbed capacity (q mg/g) of Cd^{+2} ions on graphene as a function of dose (PH=5.2, contact time =40 min)

Adsorption Isotherms:

Adsorption isotherms provide qualitative information on the capacity of the adsorbent as well as the nature of the solute-surface interaction. Equilibrium characteristics of adsorption were described in this study through two isotherm models (Langmuir and Freundlich). The Langmuir and Freundlich isotherm models are expressed as:

———— …. (3)

– … (4)

Where

*C*e is the equilibrium concentration of heavy metals ions(Pb and Cd) in aqueous solution ($mg.L^{-1}$), q_e is the amount of metals (II) ions adsorbed on graphene ($mg.g^{-1}$), q_{max} is the maximum amount of metals (II) ions adsorbed per unit weight of graphene to form complete monolayer coverage on the surface at high equilibrium metals(II) concentration, *K*L represents the enthalpy of adsorption and should vary with temperature, *K*F and *n* are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The Langmuir and Freundlich isotherm parameters for lead and cadmium are listed in table (3and 4) respectively.

Figs. 9.a and 10.a for lead and cadmium heavy metals respectively, illustrate Langmuir isotherm plot for experimental data (Ce versus C_e/q). Figs. 9.b and 10.b illustrate Freundlich isotherm plot for experimental data (log c versus log q). It be concluded that the adsorption of lead and cadmium by graphene, best fitted to the Langmuir isotherm equation. The high correlation coefficients (0.9784, 0.9717 and 0.9518) for Pb^{+2} ions and (0.994, 0.999 and 0.944) for Cd^{+2} ions was indicates that high affinity between surfaces of graphene and metals which lead to occurrence of adsorption. The convenience of the adsorption data with the Langmuir isotherm related to Freundlich is attributed to assorted surface of adsorbent. It was denote that the adsorption of heavy metals is being on graphene oxide nanosheets have being monolayer coverage [23, 24]. For Frenundlich model the values of n, gave a hint of the preference of adsorption when it was bigger than one [25, 26]. The maximum adsorption capacity (mg/g) values of Pb, Cd ions on graphene in this investigation were 476.19, 188.679 as outlined in tables 3 and 4. Matching to other kind of adsorbents, the obvious (q_{max}) values are highest as shown in table 5. From the elucidation stated overhead, the strong interaction between lead and cadmium ions via graphene is intelligible.

Table (3): Adsorption Isotherm constants for Langmuir and Freundlich model of Pb^{+2} ions (pH=6.2 and contact time= 35 min)

	Langmuir			**Freundlich**		
Graphene dosage(mg/L)	**q_{max}**	**K_L**	**R^2**	**n**	**K_F**	**R^2**
40	476.19	1.31	0.978	2.608	234.747	0.998
80	232.558	1.38	0.971	2.689	122.151	0.995
120	156.25	1.6	0.951	2.956	86.81	0.979

Table (4): Adsorption Isotherm constants for Langmuir and Freundlich model of Cd^{+2} ions (pH=5.2 and contact time= 40 min)

	Langmuir			**Freundlich**		
Graphene dosage(mg/L)	**q_{max}**	**K_L**	**R^2**	**n**	**K_F**	**R^2**
20	188.679	1.514	0.994	2.77	102.96	0.8885
60	65.36	2.217	0.999	3.28	40.63	0.9438
100	57.8	1.161	0.944	2.437	28.84	0.9849

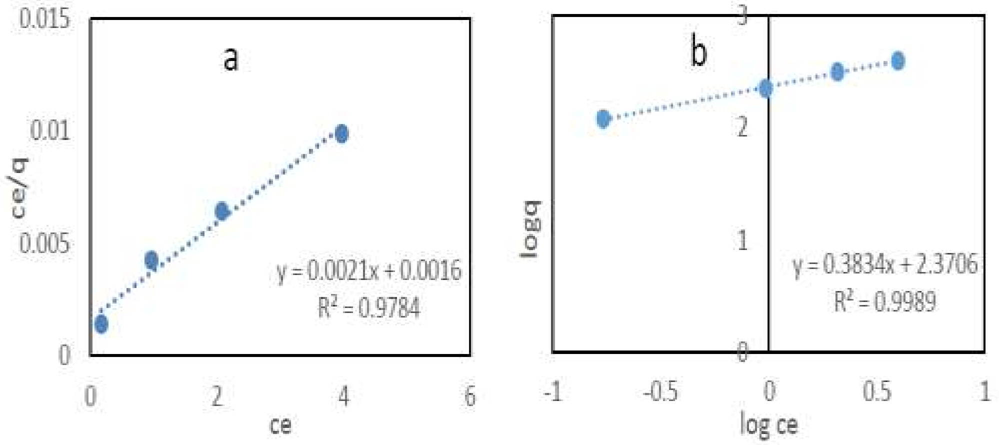


Figure (9): Isotherm model of Pb^{+2} ions adsorption onto graphene :(a) Langmuir (b) Freundlich (pH=6.2, dose =40 mg/L, contact time=35 min)

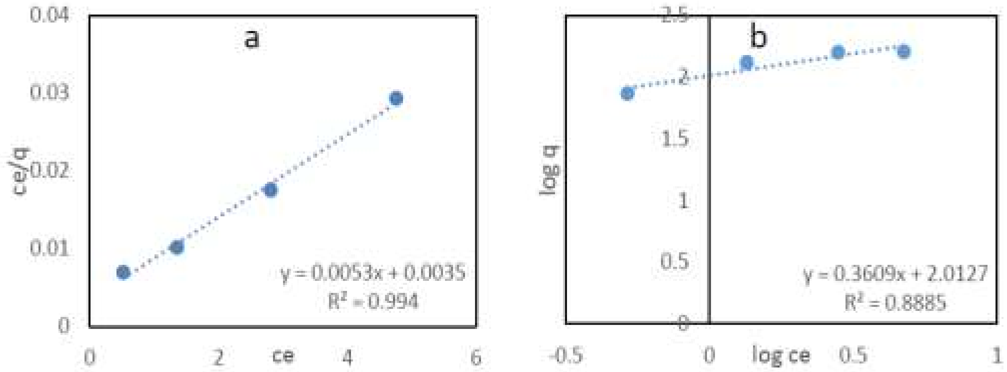


Figure (10): Isotherm model of Cd^{+2} ions adsorption onto grapheme :(a) langmuir (b) Freundlich (pH=5.2, dose =20 mg/L, contact time=40 min)

Table: (5) Maximum adsorption capacity of Pb, Cd ions on various adsorbents

Heavy metals ion	**Adsorbent**	**q_{max} (mg/g)**	**Conditions**	**Reference**
Lead Pb	Activated carbon	21.8	PH=6,T303K	(Rao, *et al.*, 2009)
Lead Pb	Iron oxide	36	pH= 5.5,T298K	(Nassar,2010)
Lead Pb	Graphene	406.6	pH= 5.1,T298K	(Deng, *et al.*, 2010)
Lead Pb	Oxidized $MWCNT_s$	2.06	pH= 6,T298K	(Xu, *et al.*, 2008)
Lead Pb	Graphene	476.19	pH= 6.2,T298K	This work
Cadmium Cd	activated carbon fiber oxide	50	pH =5,T 298 K	(Moreno-Castilla, *et al.*, 2004)
Cadmium Cd	activated carbon cloth	23.5	pH =5,T 298 K	(Moreno-Castilla, *et al.*, 2004)
Cadmium Cd	granular activated carbon	10.1	pH =5 ,T 298 K	(*Moreno-Castilla, et al.*, 2004)
Cadmium Cd	filtrasorb 400	9.5	pH =6 and T 298 K	(Sanchez-Polo and Rivera-Utrilla, 2002)
Cadmium Cd	Graphene	188.679	pH= 5.2,T298K	This work

CONCLUSIONS

The graphene prepared in this study are successfully used in complete removals of specific (Pb, Cd) heavy metals ions from aqueous solutions. Such process may be considered as a promising method for removal of toxic from wastewater before discharge into river or sewage system. The graphene which was prepared in this study have been efficient for the adsorption of lead and cadmium ions as shown in batch adsorption section. The removal percentage of metals increases with increase in the contact time and graphene dosage to reach equilibrium time 35min and 40min via dosage 120 mg/L and 100 for lead and cadmium respectively, and decreases with increase in concentrations of metals. The adsorption of heavy metals onto graphene in this work was effective with pH range from pH=4 to pH=6.2 and reaches maximum in the pH of 6.2 for lead and pH range from pH=4 to pH=5.2 and reaches maximum in the pH of 5.2 for cadmium. The adsorption isotherms of both metals have been well fitted by Langmuir model compared with Freundlich model. Results of existing investigation exhibited that graphene has respectable qualifications to adsorption contaminates like heavy metals by efficiency beastly from other adsorbents e.g. activated carbon related to qmax, equilibrium time and adsorption percentage.

REFERENCES

[1]. Mishra, A.K. and S. Ramaprabhu, Functionalized graphene sheets for arsenic removal and desalination of sea water. Desalination, 2011. 282: p. 39-45.

[2]. Nazir, A., et al., Hyperaccumulators of heavy metals of industrial areas of Islamabad and Rawalpindi. Pak J Bot, 2011. 43(4): p. 1925-1933.

[3]. Madoni, P., et al., Toxic effect of heavy metals on the activated sludge protozoan community. Water Research, 1996. 30(1): p. 135-141.

[4]. Slokar, Y.M. and A.M Le Marechal, Methods of decoloration of textile wastewater. Dyes and pigments, 1998. 37(4): p. 335-356.

[5]. Qiu, H., et al., Critical review in adsorption Kinetic models. Journal of Zhejiang University Sciences A, 2009. 10(5): p. 716-724.

[6]. Dhakras, P. Nanotechnology applications in water purification and wastewater treatment: a review in Nano science, Engineering and Technology (ICONSET), 2011 International Conference on. 2011. IEEE.

[7]. Zhong, L.S., et al., Self-Assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. Advanced Materials, 2006. 18(18): p. 2426-2431.

[8]. Hillie, T. and M. Hlophe, Nanotechnology and the challenge of clean water. Nature Nanotechnology, 2007. 2(11): p. 663-664.

[9]. Theron, J., J. Walker, and T. Cloete, Nanotechnology and water treatment: applications and emerging opportunities. Critical reviews in microbiology, 2008. 34(1): p. 43-69.

[10]. Novoselov, K.S., et al., Electric field effect in atomically thin carbon films. Science, 2004. 306(5696): p. 666-669.

[11]. Novoselov, S., The Nobel prize in physics 2010 honours two scientists, who have made the decisive contributions to this development. They are Andre K. Geim and Konstantin S. Novoselov, both at the University of Manchester, UK. They have succeeded in producing, isolating, identifying and characterizing graphene. 2010.

[12]. Luo, L.L., et al. Advances in graphene for adsorption of heavy metals in wastewater. In Advances Materials Research. 2012. Trans Tech Publ.

[13]. Park, S., et al., Graphene oxide papers modified by divalent ions-enhancing mechanical properties via chemical cross-linking. ACS Nano, 2008. 2(3): p. 572-578.

[14]. Zhao, G., et al., Removal of Pb (II) ions from aqueous solutions on few-layered graphene oxide nanosheets. Dalton Transactions, 2011. 40(41): p. 10945-10952.

[15]. Ferrari, A.C. and J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon. Physical review B, 2000. 61(20): P. 14095.

[16]. Saner, B., F. Okyay, and Y. Yürüm, Utilization of multiple graphene layers in fuel cells. 1. An improved technique for the exfoliation of graphene-based nanosheets from graphite. Fuel, 2010. 89(8): p. 1903-1910.

[17]. Gupta, A., et al., Raman scattering from high-frequency phonons in supported n-graphene layer films. Nano letters, 2006. 6(12): p. 2667-2673.

[18]. Nyquist, R. and W. Potts, Characteristic infrared absorption frequencies of thiol esters and related compounds. Spectrochimica Acta, 1959. 15: p. 514-538.

[19]. Varma, S., et al., Removal of nickel from waste water using graphene nanocomposite. International Journal of Chemical and Physical Sciences IJCPS, 2013. 2.

[20]. Hulicova-Jurcakova, D., et al., Combined Effect of Nitrogen-and Oxygen-Containing Functional Groups of Microporous Activated Carbon on its Electrochemical Performance in Supercapacitors. Advanced functional materials, 2009. 19(3): p. 438-447.

[21]. Anandkumar, J. and B. Mandal, Removal of Cr (VI) from aqueous solution using Bael fruit (Aegle marmelos correa) shell as an adsorbent. Journal of hazardous materials, 2009. 168(2): p. 633-640.

[22]. Safari, G.H. and S. Bashiri, Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions: kinetic, equilibrium and thermodynamic studies. 2012, DOI: 10.1186/1735-2746-9-9.

[23]. Zhao, G., et al., Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environmental science & technology, 2011. 45(24): p. 10454-10462.

[24]. Fakhri, A., Adsorption characteristics of graphene oxide as a solid adsorbent for aniline removal from aqueous solutions: Kinetics, thermodynamics and mechanism studies. Journal of Saudi Chemical Society, 2013. http://dx.doi.org/10.1016/j.jscs.2013.10.002.

[25]. Sekar, M., V. Sakthi, and S. Rengaraj, Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. Journal of colloid and interface science, 2004. 279(2): p. 307-313.

[26]. Srivastava, S.K., et al., Differential Catalytic Efficiency of Allelic Variants of Human GlutathioneS-Transferase Pi in Catalyzing the Glutathione Conjugation of Thiotepa. Archives of biochemistry and biophysics, 1999. 366(1): p. 89-94.

[27]. Rao, M.M., et al., Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls. Journal of hazardous materials, 2009. 166(2): p. 1006-1013.

[28]. Nassar, N.N., Rapid removal and recovery of Pb (II) from wastewater by magnetic nanoadsorbents. Journal of hazardous materials, 2010. 184(1): p. 538-546.

[29]. Deng, X., et al., The adsorption properties of Pb (II) and Cd (II) on functionalized graphene prepared by electrolysis method. Journal of hazardous materials, 2010. 183(1): p. 923-930.

[30]. Xu, D., et al., Removal of Pb (II) from aqueous solution by oxidized multiwalled carbon nanotubes. Journal of Hazardous Materials, 2008. 154(1): p. 407-416.

[31]. Moreno-Castilla, C., et al., Cadmium ion adsorption on different carbon adsorbents from aqueous solutions. Effect of surface chemistry, pore texture, ionic strength, and dissolved natural organic matter. Langmuir, 2004. 20(19): p. 8142-8148.

[32]. Sanchez-Polo, Rivera-Utrilla M. and J., Adsorbent-adsorbate interactions in the adsorption of Cd (II) and Hg (II) on ozonized activated carbons. Environmental science & technology, 2002. 36(17): p. 3850-3854.