RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1. Physicochemical properties of the activated carbons prepared from different agro-residues:

The production of activated carbon from agricultural by-products serves a double purpose. First, it helps in getting rid of the agricultural wastes. Second, activated carbons are increasingly used in water for removing organic chemical and heavy metals **(Wigmans, 1989).**

The characterization of the prepared activated carbons i.e. rice straw (RS_2 and RS_3), cotton stalk (CSSA71), date pits (DPS71-Fe) and olive stone (OS_3 and OS_5) are presented in Table (1).

Table (1):Physicochemical properties of the activated carbons prepared from different agro-residues

Source of the activated carbon		Specific surface area (S_{BET}) m^2/g	Total pore volume (VP) ml/g	Average pore radius r. 10^4 (A)	Density (g/cm^3)		pH	Ash %
					Apparent	Packed		
Rice straw	RS2	76.2	0.08	21	0.23	0.32	9.3	44
	RS3	63.0	0.09	28.57	0.21	0.28	9.07	40
Cotton stalk	CSSA71	338.0	0.29	17.16	0.34	0.51	9.02	7.86
Date pits	DPS 71Fe	154.0	0.47	61.04	0.65	0.88	2.45	5.56
Olive stone	OS_3	848	0.47	11.08	0.67	0.80	7.2	nd
	OS_5	457	0.24	10.50	0.77	0.93	9.6	nd

nd: not determined

The obtained results indicate that the higher ash contents (44% and 40%) characterized the activated carbon prepared from rice straw (RS_2 and RS_3) whereas the lowest ash contents i.e. 7.86 and 5.56% characterized the activated carbon prepared from the cotton stalk (CSSA71) and date pits (DPS71-Fe), respectively.

Locally produced activated carbon were dried at 120°C until were essentially moisture free. The specific surface area (S_{BET}) was determined by fitting the data to the BET (Bruanuer, Emmett and Teller) equation. Table (1) illustrates values of the specific surface area (S_{BET}) of the six prepared activated carbons. The data show that values of the specific surface area (S_{BET}) of the activated carbons prepared from rice straw RS_2 and RS_3 were lowest where they were 76.2 and 63.0 m^2/g respectively. On the other hand, the activated carbons prepared from the olive stone i.e. OS_3 and OS_5 showed the highest values of the specific surface area (S_{BET}), which are 848 and 457 m^2/g respectively. Whereas value of the specific surface area (S_{BET}) of the activated carbons prepared from the cotton stalk (CSSA71) and date pits (DPS 71 Fe), 338.0 and 154.0 m^2/g respectively. The total pore volume (VP) was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined, which was 0.98 for all samples. Table (1) shows that values of the total pore volume of the different prepared activated carbons RS_2, RS_3, CSSA71, DPS71Fe, OS_3 and OS_5 were 0.08, 0.09, 0.29, 0.47, 0.47 and 0.24ml/g, respectively. The average pore radius (r) was estimated by applying an empirical relation $R=2\ VP/S_{BET}$. The average pore radius (r) were found to be 21.00, 28.57, 17.16, 61.04, 11.08 and 10.50 for RS_2 and RS_3, CSSA71, DPS 71 Fe, OS_3 and OS_5, respectively. The apparent density was calculated by dividing the sample weights by the corresponding volumes of the graduated cylinder closely packed with the powdered samples .

The apparent density values were 0.23, 0.21, 0.34, 0.65, 0.67 and 0.77 g/cm^3 for the above six different prepared activated carbons, respectively. The corresponding values of packed density were 0.32, 0.28, 0.51, 0.88, 0.80 and 0.93 g/cm^3 for RS_2, RS_3, CSSA71, DPS71 Fe, OS_3 and OS_5, respectively.

Table (1) shows that the pH value of the activated carbon DPS71Fe is acidic in nature (2.45) while the other prepared activated carbons were of slightly alkaline or highly alkaline pH values ranging from 7.2 to 9.6. These results are in agreement with those reported by **Kim *et al.* (2001), Daifullah *et al.* (2003) and Ali (2007).**

4.2.Initial concentrations of some heavy metals (before treatment of wastewater):

The samples of the wastewater taken from Kaha Factory of the Chemical Industries and The Egyptian Company of Dying and Textile were analyzed for their initial concentrations of the studied heavy metals i.e. Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} before treatment and the obtained results are shown in Table (2).

Table (2):Initial concentrations of the studied heavy metals (before treatment) and their permissible levels.

Metal ions	Permissible Level[a] mg/l	Initial concentration (C_o) mg/l	
		Kaha Factory of the Chemical Industries	The Egyptian Company of Dying and Textile
Zn^{2+}	1.00	19.11	1.00
Cu^{2+}	1.00	4.41	0.80
Mn^{2+}	0.50	1.00	1.10
Pb^{2+}	0.05	0.85	0.16
Cd^{2+}	0.05	0.16	0.06

[a] **According to the Egyptian Environmental Affairs Agency Law # 4,1995.**

Table (2) shows that the initial concentrations of the studied heavy metals in the wastewaters were higher than the permissible levels reported by the Egyptian Environmental Affairs Agency (Low ≠ 4, 1995), where the permissible limits of Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} were 1.00, 1.00, 0.50, 0.05 and 0.05 mg/l, respectively while, the values of the initial concentrations of the above mentioned heavy metals in Kaha Factory of the Chemical Industries wastewater were 19.11, 4.41, 1.00, 0.85 and 0.16 mg/l, respectively whereas, the corresponding values were 1.00, 0.80, 1.10, 0.16 and 0.06 mg/l, respectively in the sample of the Egyptian Company of Dying and Textile wastewater.

4.3. Preliminary treatment of wastewater from different two sources:

The preliminary treatment conducted of the wastewater samples aimed at knowing the most efficient adsorbents in removing or reducing the studied heavy metals.

Data presented in Table (3) indicate that the activated carbon prepared from the date pits (DPS71 Fe) was the best adsorbent where it resulted in the highest total removal percentage of the heavy metals, Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} which were 62.3, 93.2, 69.0, 73.0 and 100%, respectively with percentage of whole removal efficiency (WRE) of about 79.5%. On the other hand, the activated carbons prepared from the rice straw (RS_2 and RS_3) were found to be of low efficiency for removal of Mn^{2+} and Cd^{2+} likewise, their (WRE) were lowest and did not exceed 58.68 and 48.8% respectively. The activated carbon produced from olive stone (OS_3) was found to be the second best adsorbent. The adsorbability and percentages of removal of Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} ions from the wastewater of Kaha Factory of the Chemical Industries were 27.0, 84.3, 88.0, 100.0 and 25.0%, respectively. The whole removal efficiency (WRE) was found to be 64.86%.

From these results, it can be concluded that the activated carbons prepared from date pits and olive stone seemed to be the most suitable and efficient adsorbents for removal or reduction of the heavy metals presented in Kaha Factory of the Chemical Industries wastewater.

Table (3): Removal percentages of the studied heavy metals from wastewater taken from Kaha Factory of the Chemical Industries

Metal ions	C_o mg/l	Source of the activated carbon											
		Date pits DPS 71-Fe			Rice straw RS_2			Rice straw RS_3			Olive stone OS_3		
		C_e mg/l	q_e mg/l	%R	C_e mg/l	q_e mg/l	%R	C_e mg/l	q_e mg/l	%R	C_e mg/l	q_e mg/l	%R
Zn^{2+}	19.11	7.20 ± 0.20	11.91	62.30	0.51 ± 0.01	18.60	97.50	1.40 ± 0.10	17.70	92.50	13.94 ± 0.32	5.17	27.00
Cu^{2+}	4.41	0.30 ± 0.10	4.11	93.20	0.44 ± 0.02	3.97	85.90	0.69 ± 0.02	3.72	84.50	0.69 ± 0.02	3.72	84.30
Mn^{2+}	1.00	0.31 ± 0.09	0.69	69.00	0.57 ± 0.04	0.43	43.00	1.10 ± 0.10	0.00	0.00	0.12 ± 0.01	0.88	88.00
Pb^{2+}	0.85	0.23 ± 0.02	0.62	73.00	0.28 ± 0.02	0.57	67.00	0.28 ± 0.03	0.57	67.00	0.00 ± 0.00	0.85	100.00
Cd^{2+}	0.16	0.00± 0.00	0.16	100.00	0.16 ± 0.01	0.00	0.00	0.16 ± 0.01	0.00	0.00	0.12 ± 0.01	0.04	25.00
WRE (%)				79.50			58.68			48.80			64.86
L.S.D. for treatment 0.05 (0.07)													
L.S.D. for metal ions 0.05 (0.08)													

C_O: Initial concentration of the solute
q_e : Adsorbed amount at equilibrium
WRE: % of the Whole removal efficiency

C_e : Equilibrium concentration of the solute
%R: Removal percentage

The removal percentages of the studied heavy metals due to the preliminary treatment of the wastewater taken from the Egyptian Company of Dying and Textile by usage of the activated carbons prepared from olive stone (OS_5) and cotton stalk (CSSA 71) are presented in Table (4).

The activated carbon prepared from the cotton stalk (CSSA 71) was found to be more efficient than the activated carbon prepared from the olive stone OS_5 in reducing or removing all the studied heavy metals i.e. Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} ions from the Egyptian Company of Dying and Textile wastewater.

The removal percentages of the above mentioned heavy metals were 87.0, 93.7, 95.5, 100.0 and 66.6% for the activated carbon prepared from the cotton stalk (CSSA 71) while, the activated carbon prepared from olive stone (OS_5) removed about to 75.0, 36.3, 0.0, 43.8 and 50.0%, respectively of these heavy metals. These results are partially in agreement with those reported by **Daifullah *et al.* (2003)** and **Sonume and Ghate (2004).**

The conducted preliminary experiments have proved that the activated carbon prepared from date pits DPS 71Fe was the most efficient adsorbent for removal the studied heavy metals when compared with the activated carbons prepared from rice straw (RS_2 and RS_3) and olive stone OS_3 from Kaha Factory of the Chemical Industries wastewater while the activated carbon prepared from the cotton stalk CSSA 71 was the most efficient adsorbent for removal of the studied metal ions when compared with the activated carbon prepared from olive stone (OS_5) from the Egyptian Company of Dying and Textile wastewater. Accordingly the main experimental work was designed to be conducted on these two activated carbons only.

4.4. The main experimental work:

4.4.1.Treatment of the wastewater taken from Kaha Factory of the Chemical Industries:

4.4.1.1. Factors affecting efficiency of the activated carbon prepared from the date pits (DPS 71Fe):

The major goal of this trial is to study the influence of various parameters such as adsorbent weight, pH and time of contact on the adsorption of some heavy metal ions, i.e Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} by DPS 71 Fe.

A. Adsorbent weight:

The removal of heavy metals ions from the wastewater taken from Kaha Factory of the Chemical Industries by adsorption seemed to be highly dependent on the adsorbent weights which were 0.02, 0.04, 0.06, 0.08 and 0.10 g from date pits (DPS 71-Fe).

The obtained results are presented in Table (5) and illustrated in Fig. (1a-e). From these results, it can be noticed that the removal percentages (R %) of the various metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) from wastewater was increased with increasing the adsorbent weight of the activated carbon.

Table (5): Relationship between the adsorbent weight (DPS 71-Fe) and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from Kaha Factory of the Chemical Industries.

Metal ions	Initial concentration C_o mg/l		Adsorbent weight (g)				
			0.02	0.04	0.06	0.08	0.1
Zn^{2+}	19.11	C_e	7.92 ±0.04	7.65 ±0.35	7.30 ±0.31	6.87 ± 0.25	6.62 ± 0.06
		q_e	11.19	11.46	11.81	12.24	12.49
		%R	58.55	59.96	61.80	64.00	65.35
Cu^{2+}	4.41	C_e	0.54 ±0.03	0.47 ±0.02	0.28 ±0.04	0.09 ± 0.03	0.080 ± 0.02
		q_e	387.00	3.94	4.13	4.32	4.33
		%R	87.75	89.34	93.65	97.95	98.18
Mn^{2+}	1.00	C_e	0.75 ±0.05	0.60 ±0.02	0.29 ±0.02	0.18 ± 0.03	0.10 ± 0.02
		q_e	0.25	0.40	0.71	0.82	0.90
		%R	25.00	40.00	71.00	82.00	90.00
Pb^{2+}	0.85	C_e	0.65 ± 0.2	0.55 ±0.04	0.28 ±0.03	0.15 ± 0.03	0.02 ± 0.01
		q_e	0.20	0.30	0.57	0.70	0.83
		%R	23.50	35.30	67.00	82.35	97.64
Cd^{2+}	0.16	C_e	0.03 ±0.01	0.02 ±0.02	0.01 ±0.00	0.01 ±0.01	0.002 ± 0.00
		q_e	0.13	0.14	0.15	0.15	0.158
		%R	81.25	87.50	93.75	93.75	98.75
L.S.D. for Adsorbent concentration 0.05 (0.08)							
L.S.D. for metal ions 0.05 (0.08)							
pH 7.6		Time of contact 3h.			Volume 400ml		

C_0: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

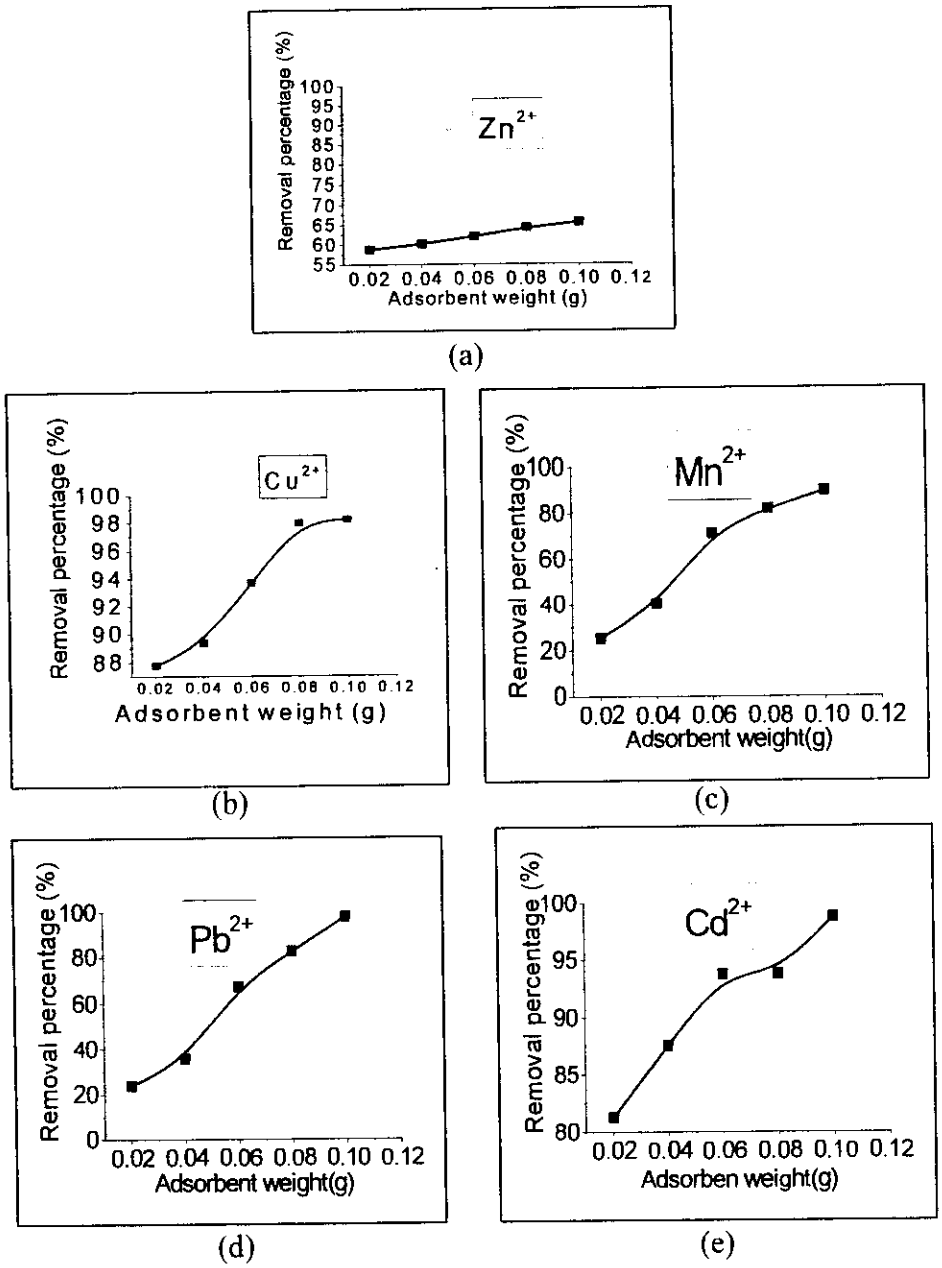

Fig. (1a-e): The percentages of removal of the studied heavy metals from wastewaters taken from Kaha Factory of the Chemical Industries

The maximum percentages of removal of the studied metal ions i.e. Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} were 65.35, 98.18, 90.00, 97.64 and 98.75%, respectively at 0.1 g of the adsorbent. These values were attained upon using Fig (1a-e) illustrates the relationship between the different weights of the adsorbent (DPS 71-Fe) and the corresponding removal percentages of the metal ions from Kaha Factory of the Chemical Industries wastewater.

These results are in agreement with those reported by **Bratek *et al.,* (2002), Hamdi *et al.,* (2004) and Ozdemir *et al.,* (2004).**

B. The pH:

The adsorption behavior was studied in aqueous solutions at different pH values ranging between (2-8.3) using 0.1 g of date pits (DPS 71-Fe) under fixed shaking time (3h). the results obtained are presented in Table (6) and Fig. (2a-e).

Figs (2a and b) show that adsorption of both the metal ions Zn^{2+} and Cu^{2+} was not affected withing the pH range 2 to 5 (acidic). This may be due to excess protons, which surround the surface of the adsorbent.

Thus adsorption of both (Zn^{2+}, $ZnOH^{+}$) and (Cu^{2+}, $CuOH^{+}$) species on the adsorbent surface (DPS 71-Fe) was not favoured. Yet, increasing the solution pH beyond 5 i.e. to pH values of 7.6 and 8.3 was associated with pronounced increase in adsorption percentages of both the ions. However, results in

Table (6): Relationship between the pH of solution and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from Kaha Factory of the Chemical Industries.

Metal ions	Initial concentration C_o mg/l		pH				
			2	4	5	7.6	8.3
Zn^{2+}	19.11	C_e	19.11 ± 0.27	19.11 ± 0.30	19.10 ± 0.30	6.62 ± 0.46	0.24 ± 0.00
		q_e	0.00	0.00	0.00	12.49	18.87
		%R	0.00	0.00	0.00	65.35	98.74
Cu^{2+}	4.41	C_e	4.41 ± 0.04	4.41 ± 0.06	4.41 ± 0.06	0.08 ± 0.00	0.00 ± 0.00
		q_e	0.00	0.00	0.00	4.33	4.41
		%R	0.00	0.00	0.00	98.18	100.00
Mn^{2+}	1.00	C_e	0.90 ± 0.07	0.71 ± 0.09	0.50 ± 0.06	0.10 ± 0.03	0.00 ± 0.00
		q_e	0.10	0.29	0.50	0.90	1.00
		%R	10.00	29.00	50.00	90.00	100.00
Pb^{2+}	0.85	C_e	0.55 ± 0.07	0.43 ± 0.01	0.30 ± 0.01	0.02	0.00 ± 0.00
		q_e	0.30	0.42	0.55	0.00	0.85
		%R	35.00	49.00	65.00	97.64	100.00
Cd^{2+}	0.16	C_e	0.02 ± 0.00	0.018 ± 0.00	0.016 ± 0.00	0.002 ± 0.00	0.00 ± 0.00
		q_e	0.14	0.142	0.144	0.158	0.16
		%R	87.50	88.75	90.00	98.75	100.00
L.S.D. for pH		0.05	(0.11)				
L.S.D. for metal ions		0.05	(0.13)				
Adsorbent weight 0.1g		Time of contact	3h.		Volume		400ml

C_O: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

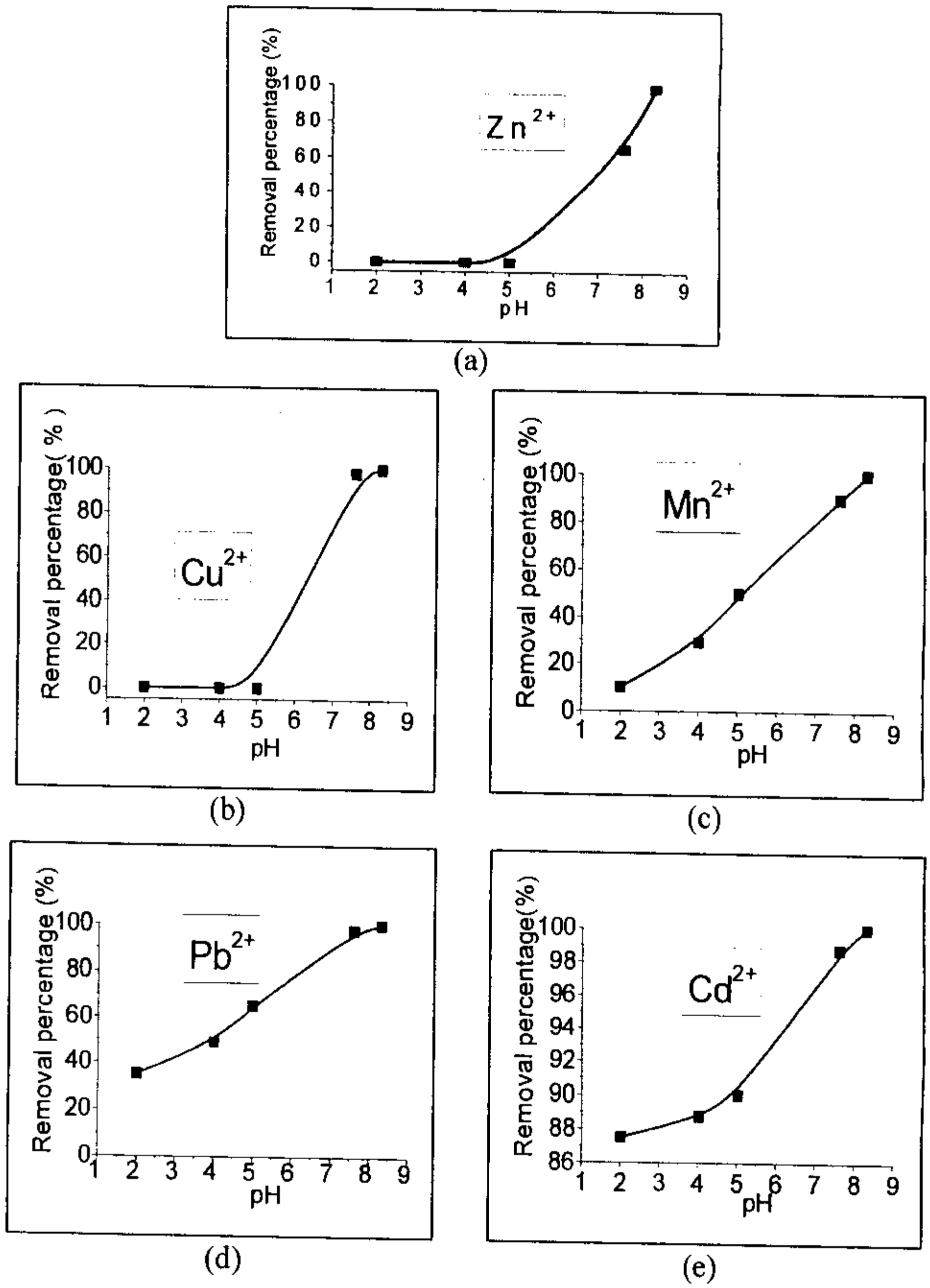

Fig. (2a-e): The percentages of removal of the studied heavy metals from wastewaters taken from Kaha Factory of the Chemical Industries

Table (6) and Fig. (2c, d and e) show that the percentages of removal increased with increasing pH values within the range of 2 to 7.6 for (Mn^{2+}, $MnOH^{+}$), (Pb^{2+}, $PbOH^{+}$) and (Cd^{2+}, $CdOH^{+}$) species. This occurred because the adsorbent surface became more negatively charged and consequently adsorption became more favoured and reached in maximum values around at pH value of 8.3.

PH values higher than 8.3 may cause precipitation of the studied metal ions in the form of metal hydroxides **(Belmouden *et al.*, 2000).**

These results seem to suggest that the adsorption of heavy metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) to activated carbon from date pits is mainly due to ionic attraction. The pH affects the ionization state of functional groups like carboxylate, phosphate and amino groups of the cell wall. The carboxylate and phosphate groups carry negative charges that allow the cell wall components to be potent scavengers of cations **(Ozdemir *et al.* 2004).**

According, it can be deduced that the removal percentages (R%) of the studied metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) from wastewater due to their adsorption by (DPS 71-Fe) seemed highly dependent on the pH of solution. This finding stands in well agreement with those of **Tran, *et al.* (1999) and Gündgan *et al.* (2004)**

C. The time of contact:

The effect of time of contact on the adsorption of metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) onto date pits (DPS 71-

Fe) at room temperature (25 ± 1°C) is shown in Table (7) and Fig. (3a-e). The removal percentages of the different studied metal ions increase with increasing shaking time. The maximum adsorption was attained completely after 3 h. of shaking for the metal ions Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+} and ½ h. for Pb^{2+} ion.

Therefore, three hours shaking time was considered to be sufficient for the adsorption of heavy metals and was used for all subsequent experiments. Basically, the adsorption mechanism is described by three consecutive steps. First, external (or film) mass transfer of solute molecules from the solution bulk to the sorbent particle surface. Secondly, the diffusion within the particle interval structure to the sorption sites where rapid uptake occurs. Third, is immeasurably fast and therefore contributes no resistance to the adsorption process so film mass transfer and intraparticle diffusion remain the rate determining steps. While, film transfer takes the first few minutes of process, intraparticle diffusion occurs over several hours constituting the main course of adsorption **(Hamdi *et al.*, 2004)**.

These results are in agreement with those reported by **Daifullah *et al.*, (2003), Feng and Aldrich (2004) and Ozdemir *et al.*, (2004).**

These results are interesting because equilibrium time is one of the important considerations for economical wastewater treatment applications **(Hawash *et al.*, 1992 and Lopez *et al.*, 1998).**

Table (7): Relationship between the time of contact and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from Kaha Factory of the Chemical Industries.

Metal ions	Initial concentration C_o mg/l		Time (h)				
			½	1 ½	2	3	4
Zn^{2+}	19.11	C_e	14.26 ± 0.29	10.50 ± 0.20	9.55 ±0.28	0.24 ± 0.00	0.25 ± 0.01
		q_e	4.85	8.61	9.56	18.87	18.86
		%R	25.00	45.00	50.00	98.74	98.70
Cu^{2+}	4.41	C_e	0.22 ± 0.02	0.13 ± 0.01	0.11 ±0.01	0.00 ± 0.00	0.08 ± 0.00
		q_e	4.19	4.28	4.30	4.41	4.33
		%R	95.00	97.00	97.50	100.00	98.10
Mn^{2+}	1.00	C_e	0.62 ± 0.00	0.40 ± 0.04	0.29 ±0.01	0.00 ± 0.00	0.01 ± 0.03
		q_e	0.38	0.60	0.71	1.00	0.99
		%R	38.00	60.00	71.00	100	99.00
Pb^{2+}	0.85	C_e	0.00 ± 0.00	0.00 ± 0.00	0.00 ±0.00	0.00 ± 0.00	0.00 ± 0.00
		q_e	0.85	0.85	0.85	0.85	0.85
		%R	100.00	100.00	100.00	100.00	100.00
Cd^{2+}	0.16	C_e	0.08 ± 0.01	0.04 ± 0.00	0.03 ±0.00	0.00 ± 0.00	0.00 ± 0.00
		q_e	0.08	0.12	0.13	0.16	0.16
		%R	50.00	75.00	81.20	100.00	100.00
L.S.D. for pH			0.05	(0.09)			
L.S.D. for metal ions			0.05	(0.08)			
Adsorbent weight 0.1g	pH			8.3	Volume		400ml

C_O: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

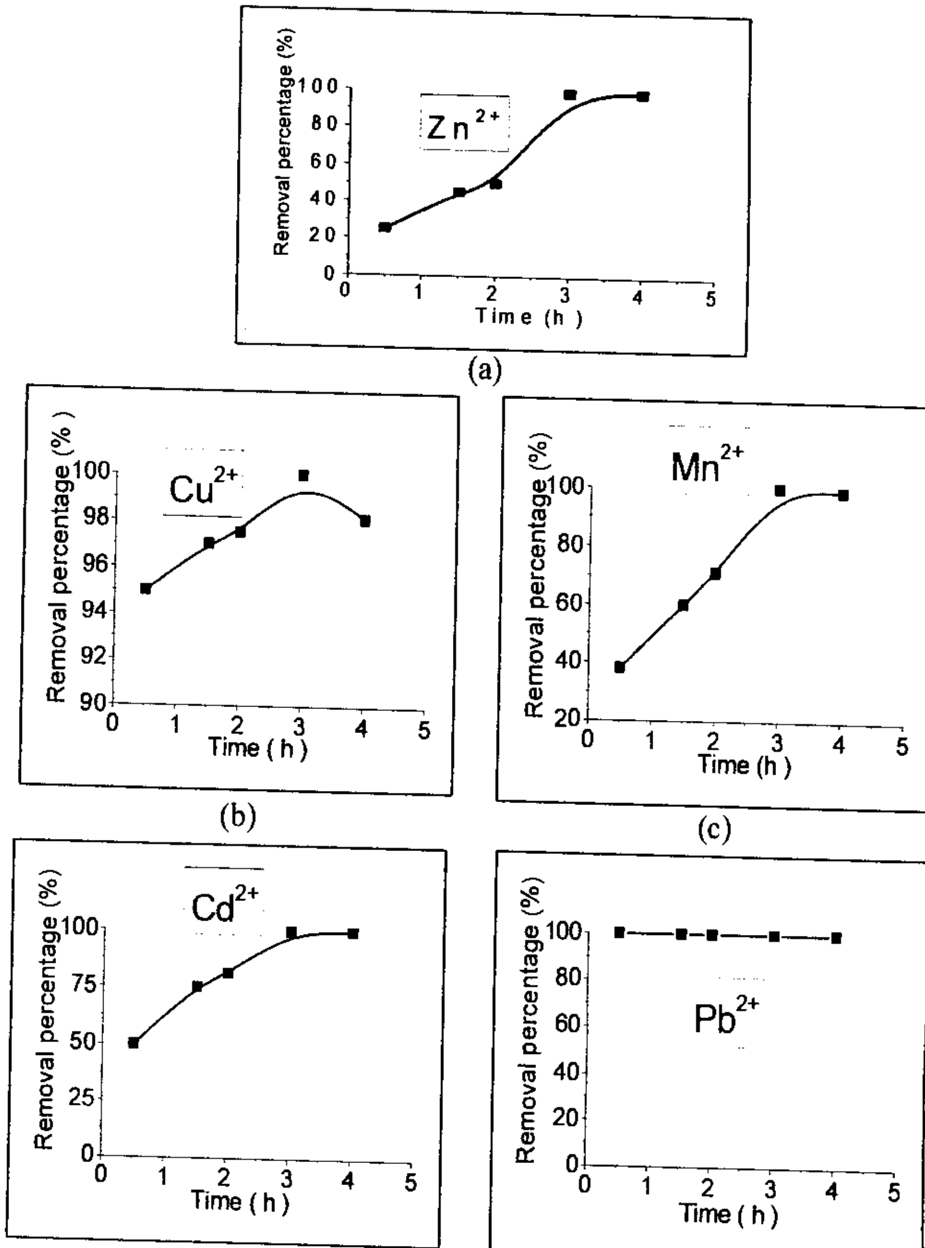

Fig. (3a-e): The percentages of removal of the studied heavy metals from wastewaters taken from Kaha Factory of the Chemical Industries

4.5. Adsorption isotherms:

Adosprtion data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherm such as the Langmuir and Freundlich isotherms, which relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration of the solute C_e.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of asdorbate in the plane of the surface.

The Langmuir isotherm is represented by two convenient linear:

$$\frac{C_e}{q_e} = \frac{1}{bq^o} + \frac{C_e}{q_e} \quad \text{.. (4.1)}$$

$$\frac{1}{q_e} = \frac{1}{q^o} + \left[\frac{1}{b^o q}\right]\left[\frac{1}{C_e}\right] \quad \text{................................ (4.2)}$$

Where: C_e is the equilibrium concentration of the solute (mg/l), qe is the amount of solute adsorbed per unit weight of adsorbent (mg/l) and q^o and b are Langmiur constants related to adsorption capacity and energy of adsorption, respectively **(Jusch *et al.*, 2005)**, which can be calculated from the 1/qe vs. 1/ce plot.

The obtained results are tabulated in Table (8) and graphically Fig. (4a-e).

The q^o values calculated from the linear from of Langmir equation were found to be 34.6, 32.35, 0.53, 26.47 and 33.3 mg/l for the metal ions Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}, respectively. The adsorption capacity of DPS 71-Fe carbon for the studied heavy metals seemed to follow the descending order: Zn> Cd> Cu> Pb> Mn. The Freundlich adsorption isotherm was also applied for the adsorption of Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} ions onto (DPS 71-Fe) activated carbon as shown in Fig. (5a-e).

The Freundlich equation is presented as:

$$q_e = K_f . C_e^{1/n_f} \quad \text{.......} \quad \textbf{(4.3)}$$

Lee *et al.* (1995)

Rearranging Equilibrium in a logarithmic from gives

$$\text{Log } q_e = \text{Log } k_f + 1/n \text{ Log} C_e \quad \text{.......} \quad \textbf{(4.3)}$$

Where K_f is a constant related to adsorption capacity, and nf is a constant related to the adsorption intensity which can be calculated from the a plot of log qe vs. Log C_e. The constants are listed in Table (8).

The Langmuir isotherm, showed consistently higher correlation coefficients than Freundlich isotherm between C_e and q_e (0.988, 0.967, 0.995, 0.999 and 0.978 for Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}, respectively) as compared with the corresponding ones of Freundlich isotherm (0.978, 0.955, 0.961, 0.948 and 0.986 in the same respective order).

Table (8): Langmuir and Freundlich constants for metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) sorption using activated carbon (DPS 71-Fe)

Adsorption isotherm	Langmuir		Freundlich	
Calculated parameters	qo	b	kf	n
Zn^{2+}	34.60	0.006	4.08	0.127
Cu^{2+}	32.35	0.15	1.69	2.49
Mn^{2+}	0.53	2.09	2.73	6.32
Pb^{2+}	26.74	0.015	3.10	18.76
Cd^{2+}	33.30	0.005	1.33	2.90

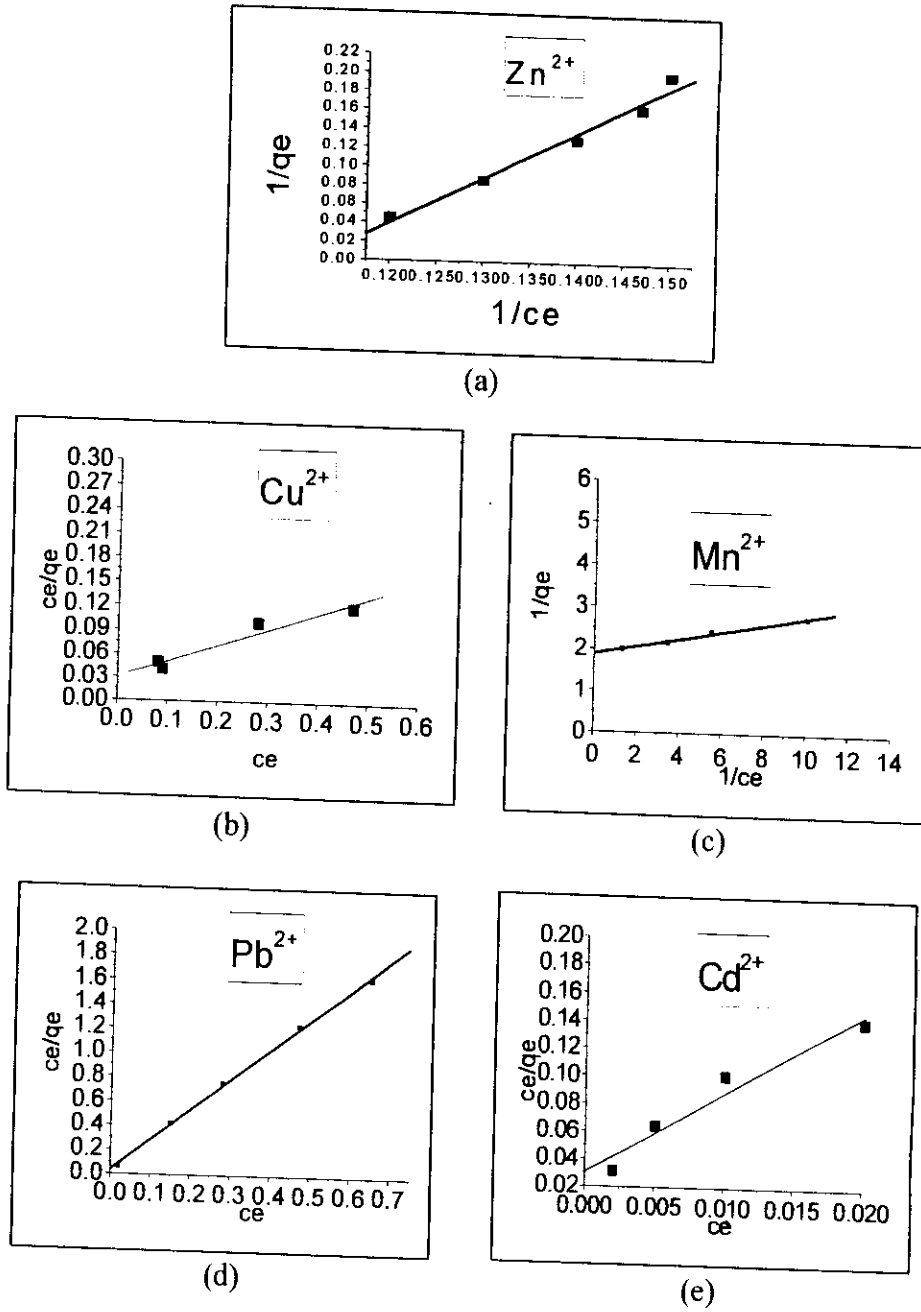

Fig. (4a-e): The linearized Langmuir adsorption isotherms of the studied heavy metals from wastewaters taken from Kaha Factory of the Chemical Industries

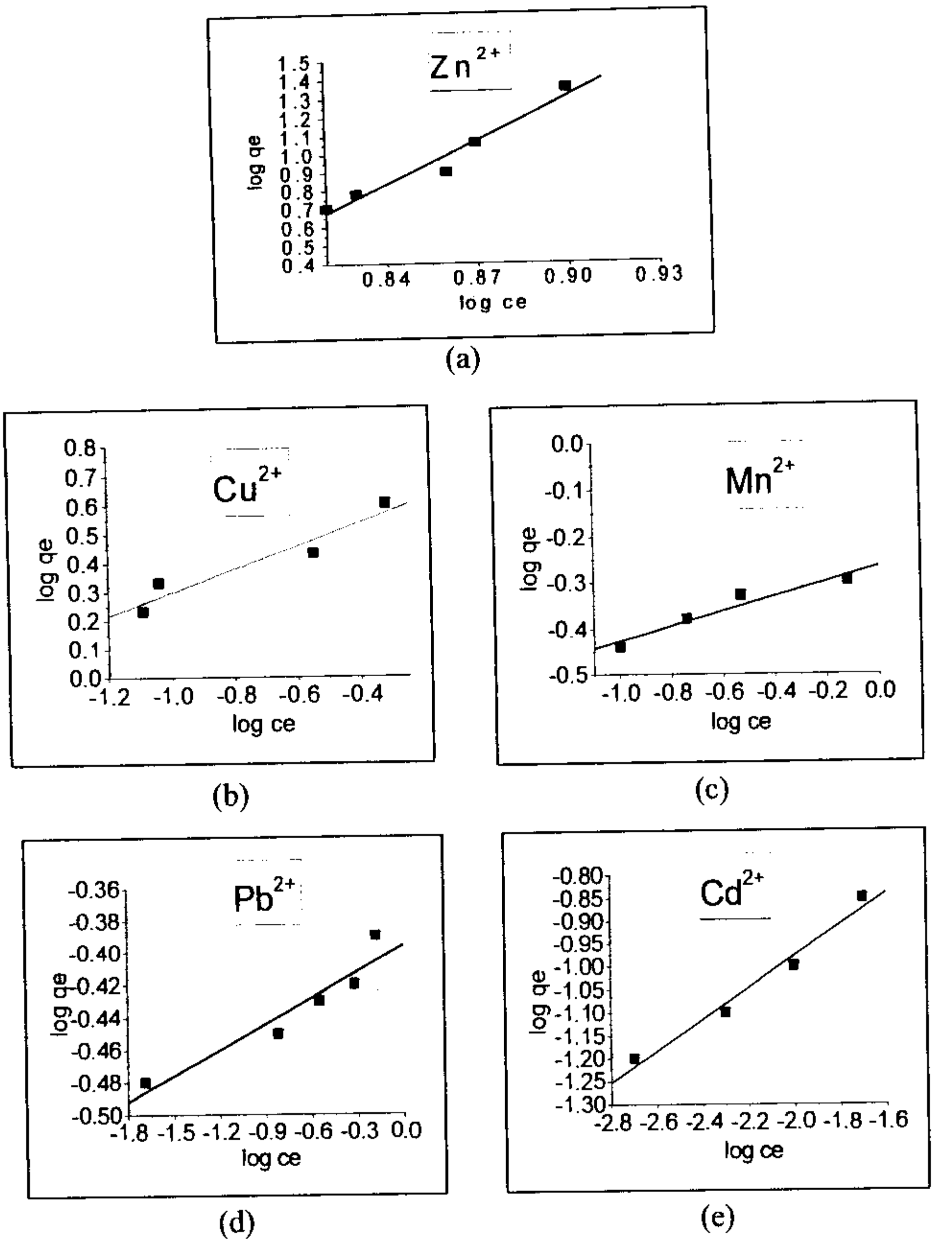

Fig. (5a-e): The linearized Freundlich adsorption isotherms of the studied heavy metals from wastewaters taken from the Kaha Factory of the Chemical Industries.

4.6. Treatment of the wastewater taken from the Egyptian Company of Dying and Textile:

4.6.1. Factors affecting efficiency of the activated carbon prepared from the cotton stalk (CSSA-71):

A. Adsorbent weight:

Table (9) and Fig. (6a-e) show the relationship between the percentages of removal (R%) of the studied metal ions i.e. Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} from wastewater taken from the Egyptian Company of Dying and Textile against different weights of the activated carbon prepared from the cotton stalk (CSSA-71).

In this concern, the weights used from this adsorbent type are in the range of 0.005 to 0.02 g. the obtained results showed that the percentages of removal (R%) of the various studied metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) in the wastewater was increased with increasing the weight of the activated carbon. The adsorbent weight 0.02 g resulted in the highest percentages of removal (R%) for all the studied metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}). Where the maximum percentages of removal (R%) of these metal ions were 95.45, 90, 100, 100 and 85, respectively. These results are in agreement with those reported by **Hamdi *et al.* (2004) and Ali (2007).**

Table (9): Relationship between the adsorbent weight (CSSA-71) and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from the Egyptian Company of Dying and Textile

Metal ions	Initial concentration C_o mg/l		Adsorbent weight (g)				
			0.005	0.01	0.015	0.018	0.02
Zn^{2+}	1.00	C_e	0.89 ± 0.00	0.80 ±0.10	0.46 ±0.00	0.23 ±0.00	0.10 ±0.02
		q_e	0.11	0.20	0.54	0.77	0.90
		%R	11.00	20.00	54.00	77.00	90.00
Cu^{2+}	0.80	C_e	0.30 ± 0.00	0.28 ±0.00	0.25 ±0.00	0.21 ±0.03	0.00 ±0.00
		q_e	0.50	0.52	0.55	0.59	0.80
		%R	62.50	65.00	68.75	73.75	100.00
Mn^{2+}	1.10	C_e	0.77 ± 0.00	0.71 ±0.00	0.16 ±0.02	0.115 ±0.06	0.05 ±0.01
		q_e	0.33	0.39	0.94	0.985	1.05
		%R	30.00	35.50	85.45	89.50	95.45
Pb^{2+}	0.16	C_e	0.01 ± 0.00	0.006 ±0.04	0.002 ±0.00	0.00 ±0.00	0.00 ±0.00
		q_e	0.15	0.154	0.158	0.16	0.16
		%R	93.75	96.25	98.75	100.00	100.00
Cd^{2+}	0.06	C_e	0.06 ± 0.01	0.06 ±0.02	0.04 ±0.00	0.01 ±0.00	0.009 ±0.011
		q_e	0.00	0.00	0.02	0.05	0.051
		%R	0.00	0.00	33.30	83.30	85.00
L.S.D. for Adsorbent concentration			0.05 (0.02)				
L.S.D. for metal ions			0.05 (0.02)				
pH 8.3		Time of contact 4h.			Volume 500ml		

C_O: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

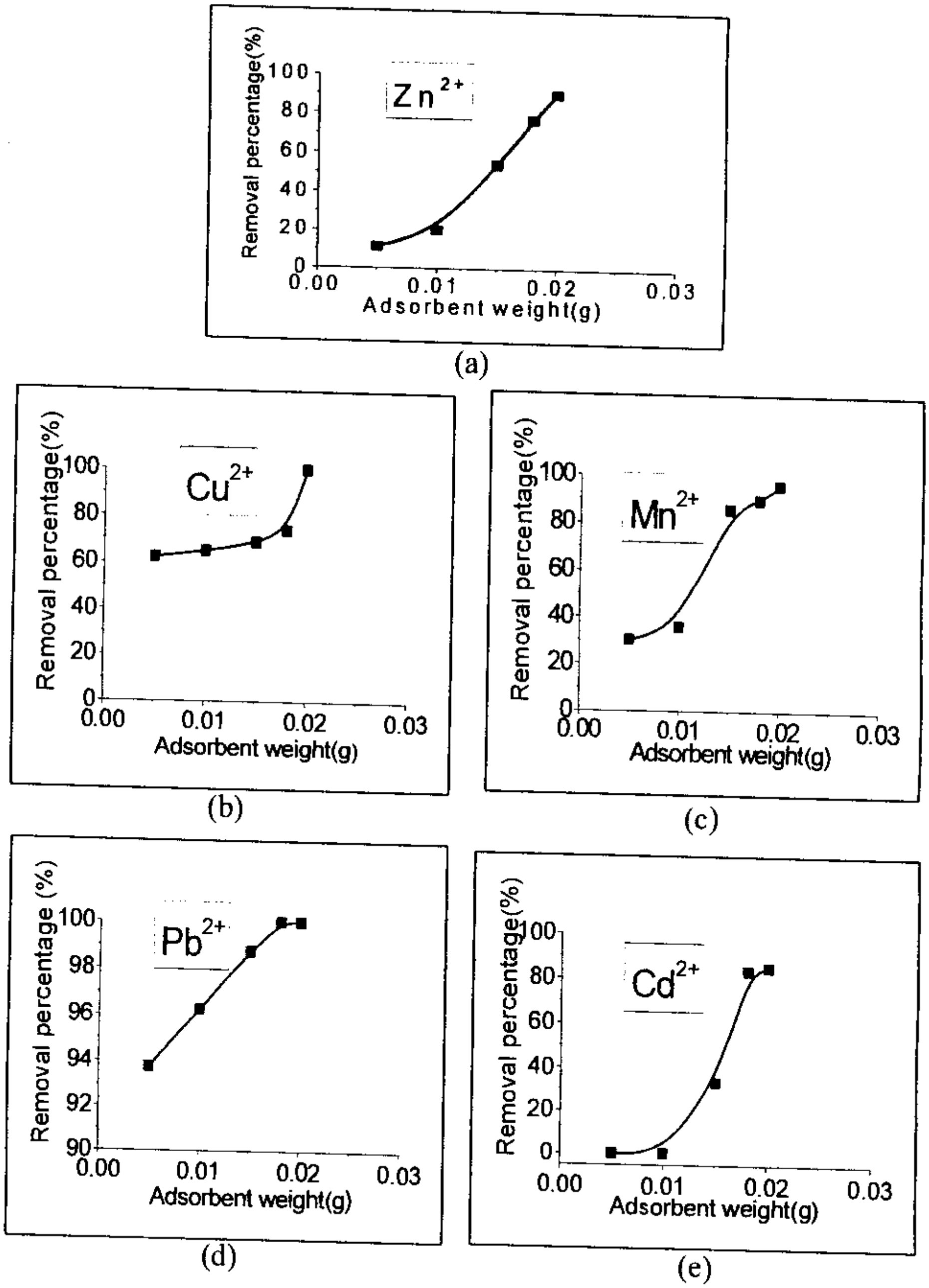

Fig. (6a-e): The percentages of removal of the studied heavy metals from wastewaters taken from the Egyptian Company of Dying and Textile

B. The pH:

The results presented in Table (10) and illustrated in Fig. (7a-e) confirm to a great extent this statement. These results reveal that at the pH value ranging from 2.0-5.0 the (CSSA-71) could not remove or reduce any detectable amount of Zn^{2+}, Cd^{2+} and Mn^{2+} concentration was not affected also but at the lowest studied pH value i.e. 2. However, increasing values of pH beyond the above mentioned ones was associated with pronounced increases in percentages of removal of these metal ions and achieved their highest values at pH value of 7.3. increasing pH of the wastewater, resulted in proportional corresponding increases in percentage of removal of Cu^{2+} ion.

Unlike the other studied metal ions, Pb^{2+} seemed to be completely adsorbed on the used activated carbon (CSSA-71) as soon as the wastewater was shaken with the adsorbent. Such a finding may force us to say that there are probably, sites on this adsorbent very specific for adsorption of Pb^{2+} regardless to the pH value. On the other hand, the low adsorption of Zn^{2+}, Mn^{2+} and Cd^{2+} metal ions at the low pH values up to 5 (acidic) may be due to the adsorbent gained a positive charge as a result of the excess protons which surround the surface of the adsorbent.

Thus, repulsion occurred between the adsorbent and the positively charged metal ions (Zn^{2+}, $ZnOH^{+}$), (Mn^{2+}, $MnOH^{+}$) and (Cd^{2+}, $CdOH^{+}$) species.

Table (10): Relationship between the pH on the solution and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from the Egyptian Company of Dying and Textile

Metal ions	Initial concentration C_o mg/l		pH				
			2	4	5	7.6	8.3
Zn^{2+}	1.00	C_e	1.07 ±0.06	1.00 ±0.26	1.00 ±0.17	0.59 ±0.02	0.25 ±0.22
		q_e	0.00	0.00	0.00	0.41	0.90
		%R	0.00	0.00	0.00	41.00	90.00
Cu^{2+}	0.80	C_e	0.20 ±0.10	0.12 ±0.01	0.10 ±0.02	0.04 ±0.01	0.00 ±0.00
		q_e	0.60	0.68	0.70	0.76	0.80
		%R	75.00	85.00	87.50	95.00	100.00
Mn^{2+}	1.10	C_e	0.10 ±0.13	1.06 ±0.03	1.01 ±0.12	0.30 ±0.10	0.05 ±0.01
		q_e	0.00	0.04	0.09	0.80	1.05
		%R	0.00	3.60	8.20	72.70	95.45
Pb^{2+}	0.16	C_e	0.00 ±0.00	0.00 ±0.00	0.00 ±0.00	0.00 ±0.00	0.00 ±0.00
		q_e	0.16	0.16	0.16	0.16	0.16
		%R	100.00	100.00	100.00	100.00	100.00
Cd^{2+}	0.06	C_e	0.06 ±0.03	0.06 ±0.02	0.06 ±0.03	0.02 ±0.00	0.009 ±0.00
		q_e	0.00	0.00	0.00	0.04	0.05
		%R	0.00	0.00	0.00	67.00	85.00
L.S.D. for pH		0.05	(0.08)				
L.S.D. for metal ions		0.05	(0.07)				
Absorbent weight0.02g		Time of contact 4h.			Volume 500ml		

C_O: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

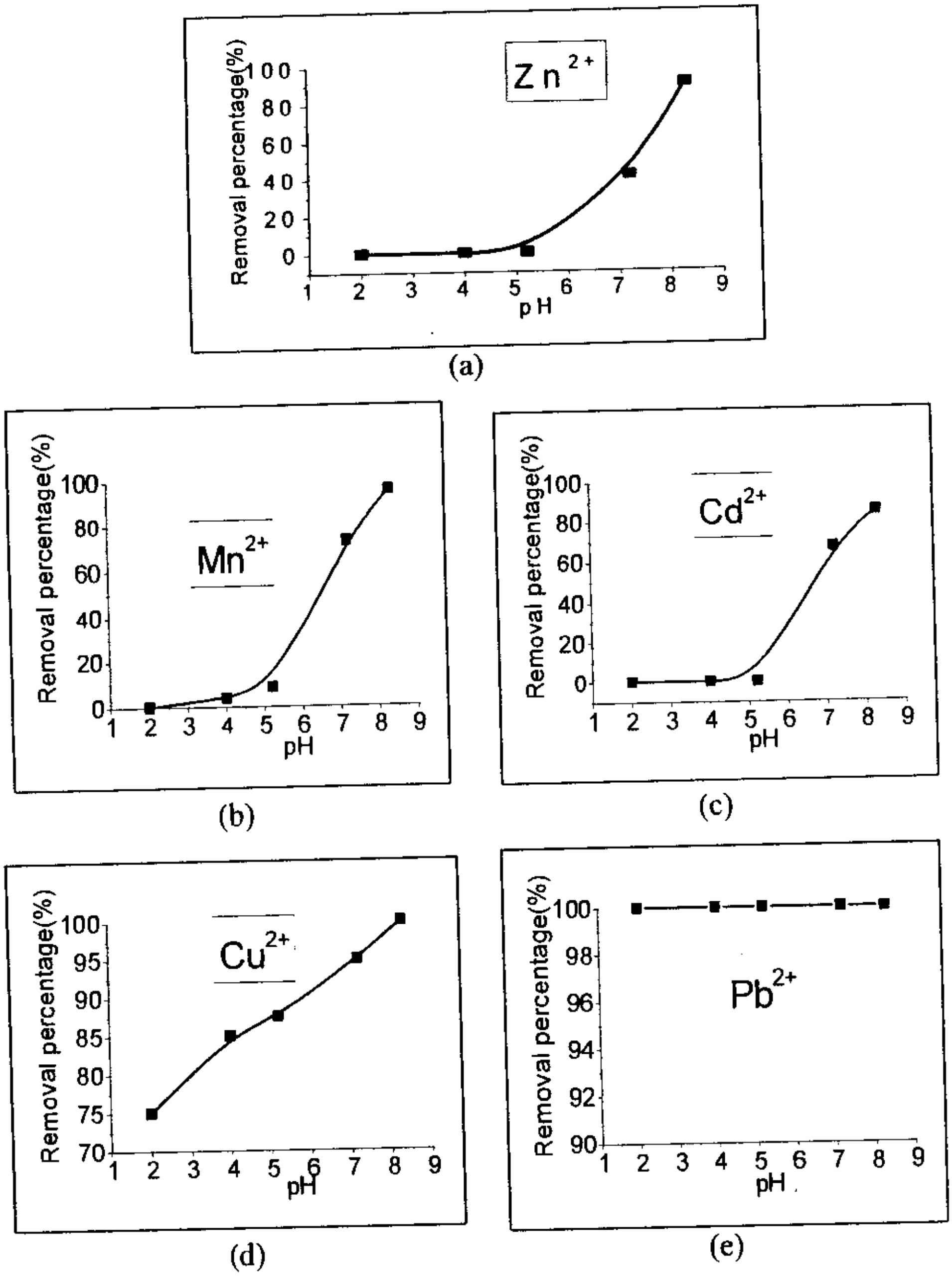

Fig. (7a-e): The percentages of removal of the studied heavy metals from wastewaters taken from the Egyptian Company of Dying and Textile

The increase in adsorption of the studied metal ions by increasing soil pH is due to the increase in the adsorbents negative charge since in the alkaline pH there is an excess of OH^- ions and hence a pH dependent charge increased. This finding stands in well agreement with those of **Tran, *et al.* (1999) and Gündogan *et al.* (2004).**

C. The time of contact:

Kinetic adsorption experiments were carried out in order to determine the effect time of contact on the adsorption. Table (11) and Fig. (8a-e) show the effect of shaking time on the removal percentages of the studied metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) by adsorbents prepared from the cotton stalk (CSSA-71).

The adsorption of the studied metal ions, except for Cu^{2+} and Pb^{2+}, seemed to indirect proportion to time of contact between the adsorbent on one hand and the amount of the adsorbed metal ions on the other hand.

However, 4h period of contact was quite enough for these metal ions to be completely adsorbed on the (CSSA-71). In other words, percentages of adsorption increased with time of contact and achieved their highest values just after 4h.

Mean while half an hour was quite enough time for both Cu^{2+} and Pb^{2+} to be adsorbed completely on surface of CSSA-71 i.e., the highest value of adsorption percentage (100%) was probably attained within a period of half an hour or less than that period.

Table (11): Relationship between the time of contact and the corresponding removal percentages of the studied heavy metal ions from wastewater taken from the Egyptian Company of Dying and Textile.

Metal ions	Initial concentration C_o mg/l		Time (h)				
			½	1 ½	2	3	4
Zn^{2+}	1.00	C_e	1.00 ±0.25	0.80 ±0.10	0.60 ±0.10	0.25 ±0.03	0.10 ±0.04
		q_e	0.00	0.20	0.40	0.75	0.90
		%R	0.00	20.00	40.00	75.00	90.00
Cu^{2+}	0.80	C_e	0.00	0.00	0.00	0.00	0.00
		q_e	0.80	0.80	0.80	0.80	0.80
		%R	100.00	100.00	100.00	100.00	100.00
Mn^{2+}	1.10	C_e	1.00 ±0.06	0.375 ±0.01	0.306 ±0.00	0.175 ±0.00	0.05 ±0.01
		q_e	0.10	0.725	0.794	0.925	1.05
		%R	9.00	65.90	72.20	84.00	95.45
Pb^{2+}	0.16	C_e	0.00	0.00	0.00	0.00	0.00
		q_e	0.16	0.16	0.16	0.16	0.16
		%R	100.00	100.00	100.00	100.00	100.00
Cd^{2+}	0.06	C_e	0.06 ±0.02	0.05 ±0.00	0.04 ±0.00	0.02 ±0.00	0.009 ±0.00
		q_e	0.00	0.01	0.02	0.04	0.051
		%R	0.00	16.60	33.00	66.60	85.00
L.S.D. for time			0.05	(0.07)			
L.S.D. for metal ions			0.05	(0.06)			
Adsorbent weight 0.02g		pH		8.3	Volume		500ml

C_O: Initial concentration of the solute
C_e : Equilibrium concentration of the solute
q_e : Adsorbed amount at equilibrium
%R: Removal percentage

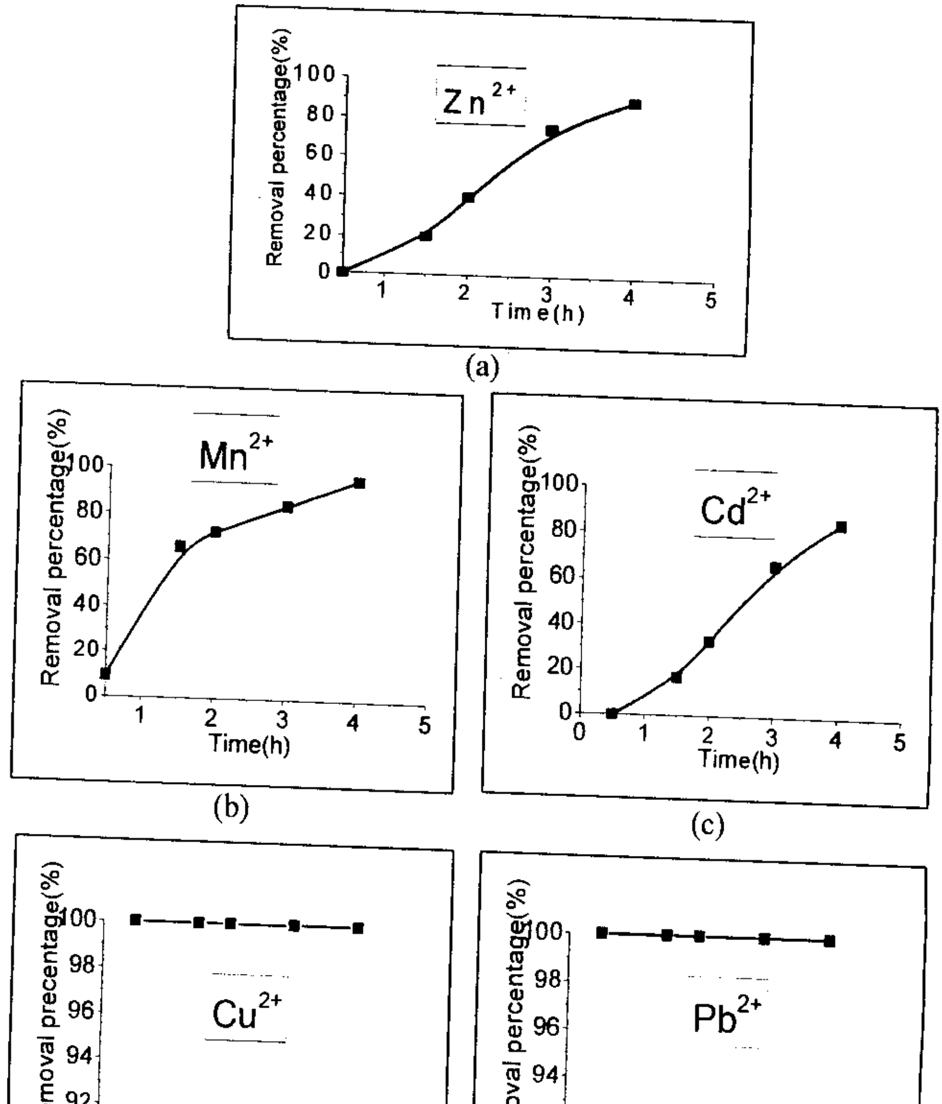

Fig. (8a-e): The percentages of removal of the studied heavy metals from wastewaters taken from the Egyptian Company of Dying and Textile

These results proved that adsorption is a process dependent on time of contact between the adsorbate and the adsorbent.

This result is important because equilibrium time is one of the important considerations for economical wastewater treatment applications **(Hawash *et al.*, 1992 and Lopez *et al.*,1998).**

4.7. Adsorption isotherms:

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherm such as Freundlich and Langmiur isothorms, which relate adsorption density q_e (is the amount of solute adsorbed per unit weight of adsorbent) to equilibrium adsorbate concentration of the solute C_e.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following two equations :

$$\frac{C_e}{q_e} = \frac{1}{bq^0} + \frac{C_e}{q^0} \quad \text{.. (4.5)}$$

$$\frac{1}{q_e} = \frac{1}{q^0} + \left(\frac{1}{bq^0}\right)\left(\frac{1}{C_e}\right) \quad \text{.. (4.6)}$$

Where q_e is the amount adsorbed at equilibrium time (mg/l), C_e is the equilibrium concentration of the solute (mg/l) and b and q^0 are constants related to adsorption capacity and energy of adsorption, respectively **(Jusch *et al.,* 2005)**, which can be calculated from the linear forms of Langmuir equations. Shown in Fig. (9a-e) the Langmuir parameters were found to be 30.3, 9.61, 208.33, 1000 and 0.27 mg/l for q^o for the metal ions zinc, copper, manganese, lead and cadmium respectively shown Table (12).

This finding means that using activated carbon prepared from the cotton stalk (CSSA-71) could be considered an excellent adsorbent for reducing or removing metal ions from the wastewater polluted with these metals.

The Freundlich adsorption isotherm was also applied for the adsorption of metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, and Cd^{2+}) onto activated carbon prepared from the cotton stalk (CSS A-71). Shown in Fig. (10a- e). The Freundlich equation is presented as

$$q_e = K_f\, C_e^{1/n}$$

Lee, *et al.* (1995).

Rearranging equilibrium in a logarithmic from gives.

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e$$

Where : K_f is a constant related to adsorption capacity, and nf is a constant related to the adsorption intensity. Hence, a plot of Log q_e vs. Log C_e enables the constants K_f and exponent n to be calculated.

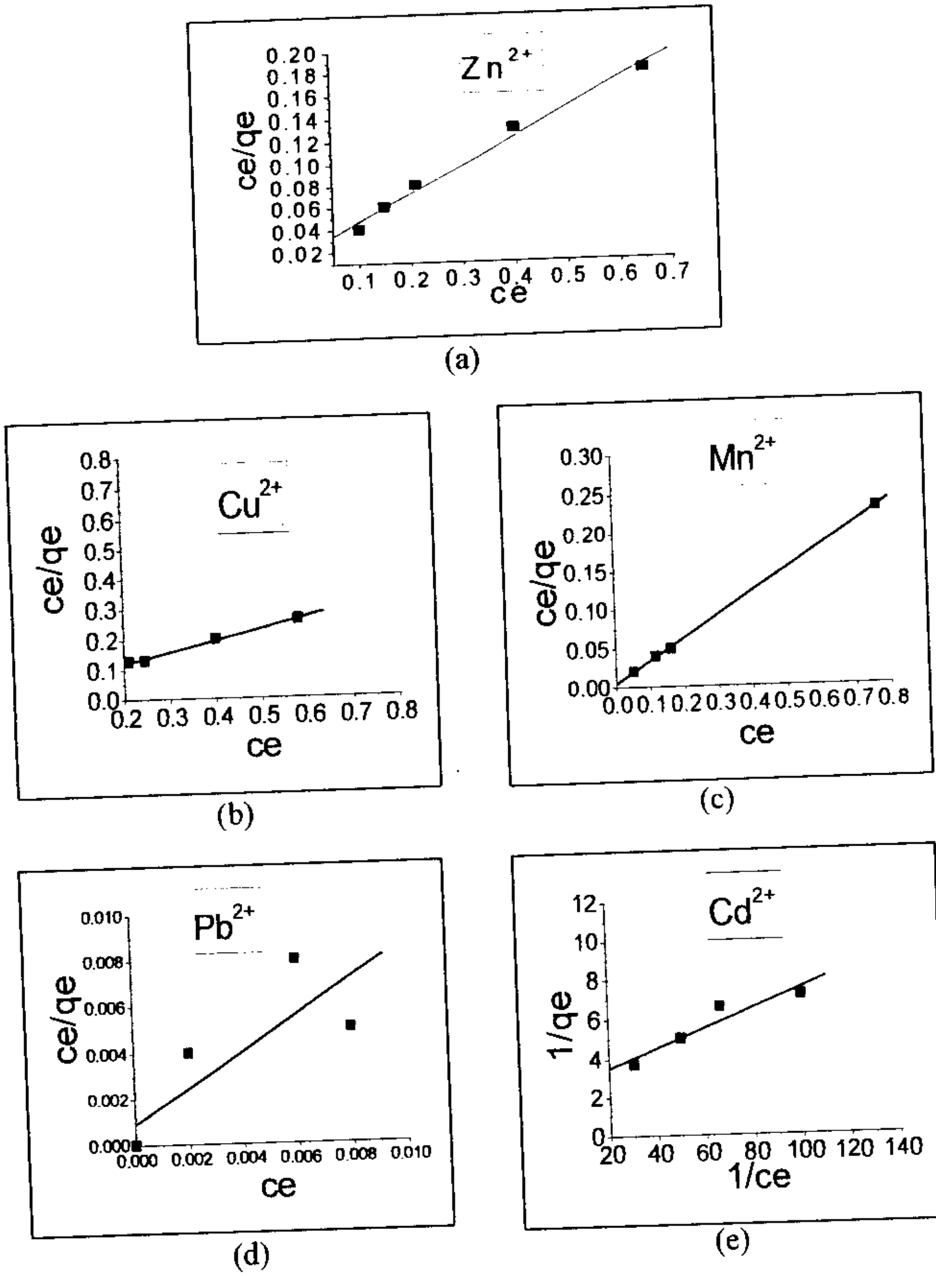

Fig. (9a-e): The linearized Langmuir adsorption of the studied heavy metals from wastewaters taken from the Egyptian Company of Dying and Textile

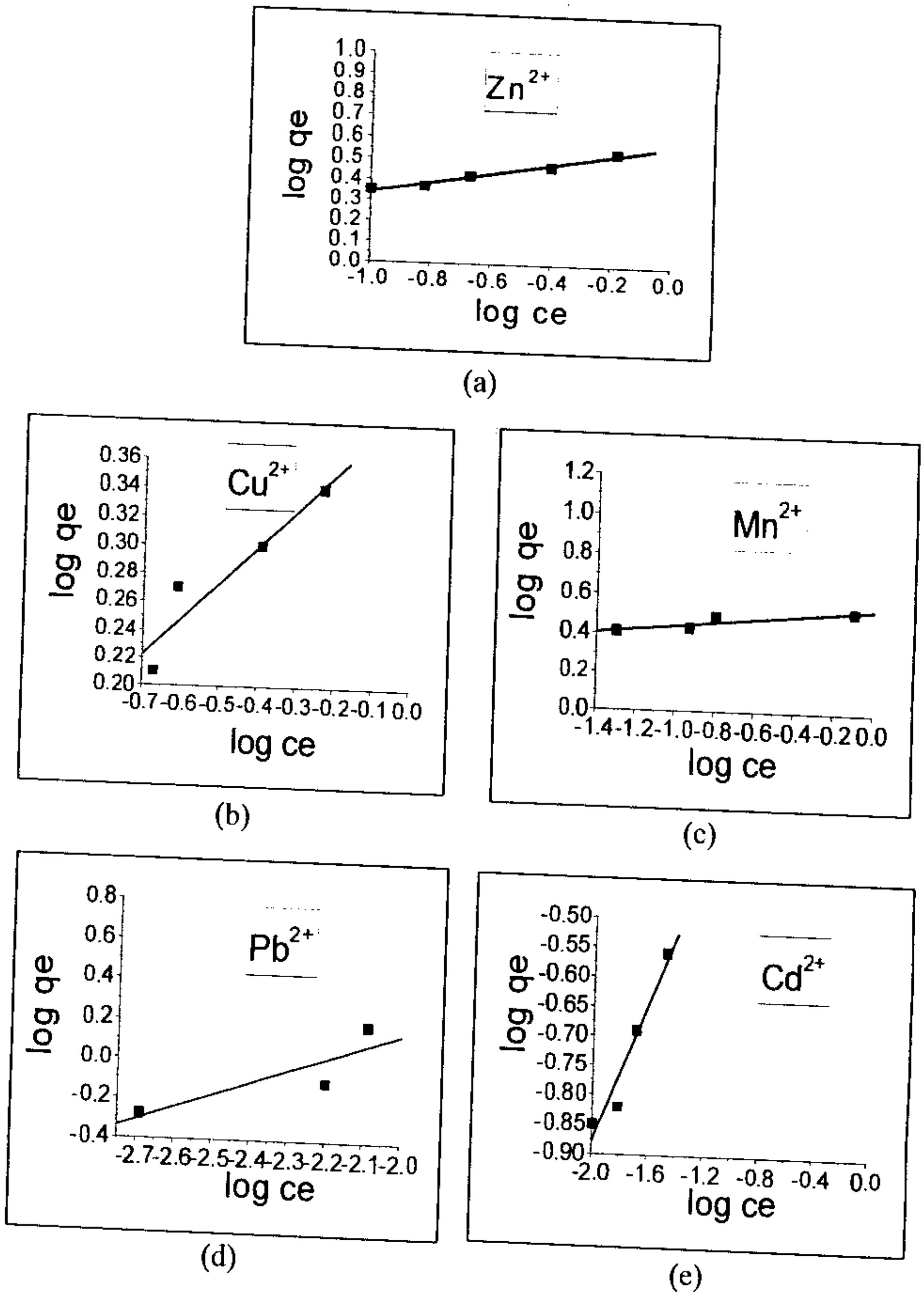

Fig. (10a-e): The linearized Freundlich adsorption of the studied heavy metals from wastewaters taken from the Egyptian Company of Dying and Textile

Values of these constants are listed in Table (12). The Langmuir isotherm showed consistently higher correlation coefficients than Freundlich isother between C_e and q_e (0.993, 0.993, 0.999, 0.858 and 0.942 for Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} respectively) as compared with the corresponding ones of Freundlich isotherm (0.990, 0.944, 0.916, 0.878 and 0.968 in the same respective order).

Table (12): Langmuir and freundlich constants for metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) sorption using activated carbon (CSSA-71).

Adsorption isotherm	Langmuir		Freundlich	
Calculated parameters	q^o	b	k_f	n
Zn^{2+}	30.30	0.01	2.17	3.22
Cu^{2+}	9.61	0.36	1.66	4.00
Mn^{2+}	208.30	0.016	2.51	10.68
Pb^{2+}	1000	0.00125	2.13	1.56
Cd^{2+}	0.27	76.9	7.62	1.70