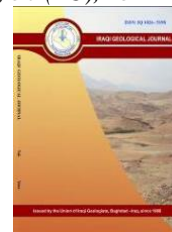




Iraqi Geological Journal

Journal homepage: <https://www.igi-iraq.org>



Glass Wastes Sorption Efficiency for Removing Cadmium from Aqueous Solutions

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Abstract

Received:
5 January 2023

Accepted:
5 March 2023

Published:
31 March 2023

This research aims to test the ability of glass waste powder to adsorb cadmium from aqueous solutions. The glass wastes were collected from the Glass Manufacturing Factory in Ramadi. The effect of concentration and reaction time on sorption was tested through a series of laboratory experiments. Four Cd concentrations (20, 40, 60, and 80) as each concentration was tested ten times for 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 min. Solid (glass wastes) to liquid was 2g to 30ml was fixed in each experiment where the total volume of the solution was 30ml. The pH, total dissolved salts and electrical conductivity were measured at 30°C. The equilibrium concentration was determined at 25 minutes, thereafter it was noted that the sorption (%) decreased whenever increasing Cd concentration. Langmuir and Freundlich's equations showed that the sorption intensity is 2.402 and the adsorption capacity is 3.126, and the sorption of Cd fits with the Freundlich equation. Consequently, it was clarified how glass waste material can be utilized for reducing the high levels of Cd concentrations from aqueous solutions as a step to combat environmental pollution.

Keywords: Glass waste; Cadmium; Sorption; Aqueous solutions

1. Introduction

Heavy metal pollution is one of the most important environmental issues as a result of the increase in industrial processes that increase the quantities of waste generated (Awadh and Ahmed, 2013; Awadh, 2015; Awadh and Al-Ghani, 2014; Awadh, 2018). Cadmium is one of the most toxic metals with a high effect on the environment as it influences human health (Awadh and Al-Kilabi, 2014; Awadh et al., 2023) as well as its selectivity towards silica (Mostafa et al., 2002). Cadmium enters natural systems through wastewater and may be sourced from some industries such as paints, battery production, dyes, etc (Awadh and Yousif, 2015; Awadh and Al-Jubury, 2015). Cadmium was found in high concentration in different water types (Awadh and Muslim, 2014; Awadh and Yousif, 2015). Cadmium and some heavy metals were tested to be removed from the aqueous solutions by many researchers for instance, Awadh and Abdulla (2017) studied the purification of aqueous solutions from Pb (II) by natural bentonite. The brackish water, surface water, groundwater, and oilfield water have a lot of cadmium as they contain high concentrations of heavy metals (Al-Azzawi, 2010; Awadh et al., 2019; Boschetti et al., 2018; Al-Mimar, and Awadh, 2019; Awadh et al., 2019; Awadh et al., 2021; Awadh and Al-Hamdani, 2019; Boschetti et al., 2020; Awadh et al., 2021; Alkhafaji et al., 2022; Awadh et al., 2022). Cadmium has health effects on human life that include diarrhoea, nausea, bone marrow damage, muscle spasms, and the formation of kidney stones (Penkova et al., 2009). Hence the importance of ridding the

DOI: [10.46717/igi.56.1C.2ms-2023-3-13](https://doi.org/10.46717/igi.56.1C.2ms-2023-3-13)

environment of cadmium, especially the aquatic environment. Heavy metal concentrations can be reduced in several ways, one of which is adsorption, which plays an important role in removing undesired components (Filho and Carmo, 2006; Al-Hamdani et al., 2016a; Al-Hamdani et al., 2016b). Many natural or synthetic substances can reduce heavy metal concentrations in solutions. In this research waste glass used as an adsorbent to remove cadmium from solutions. There are large quantities of glass waste in the glass manufacturing plant belongs to the State Company for Glass and Refractories (SCGR) in Ramadi in the form of scattered rubble that has not been used. Because of the abundant low-cost waste of this material, it has been tested as an adsorbent for the removal of cadmium from aqueous solutions. Mostly, researchers use clays such as montmorillonite and palygorskite in adsorption processes (Awadh and Tawfiq, 2013), and they also used glass to absorb polyesters. They showed that the rate of adsorption of polyesters on glass was very fast (Stromberg et al., 1959). The transistor screen glass wastes were used liquid crystal (TFT-LCD) for the manufacture of composite materials to make adsorbents, in which negatively charged functional groups act as an excellent adsorption capacity to remove metal ions, especially at pH range of 1.5-7.0 (Tsai et al., 2019). This research presents glass waste as a new material for cadmium absorption from aqueous solutions, and it is believed that the research will contribute to protecting the environment from these pollutants. This research aims to determine the adsorption efficiency of glass waste in removing cadmium from aqueous solutions.

2. Materials and Methods

Various shapes and volumes of glass waste were collected from the SCGR in Ramadi which are accumulated rubbles into huge quantities near the company (Fig. 1).



Fig. 1. Glass waste accumulation from the State Company for Glass and Refractories in Ramadi

The samples were prepared in the Instrumental Analytical Laboratory in the Department of Chemistry at the University of Anbar. The samples were ground using an electric grinder after washing and drying. This was followed by grain size analyses, and the silt size (0.002 to 0.05 mm in diameter) was chosen to test these particle sizes in the sorption process (Fig. 2). The samples were subjected to mineralogical analysis using XRD and chemical analysis using XRF. Cadmium nitrate with a weight of 2.7443 g was used, dissolved in 1L distilled water (Fig. 3) to prepare a cadmium solution with a concentration of 1000 ppm. From this solution, several solutions with 20, 40, 60, and 80 ppm were prepared. Experiments were carried out using 2 g of glass powder with 30 ml of cadmium solution. Before starting each experiment, pH, EC and TDS were measured. Forty experiments were conducted during which, the solutions were placed in the vibrator at a fixed temperature of 30 °C to test the efficiency of glass sorption.



Fig. 2. a) Glass waste sample;b) Powder of glass waste to a silt size

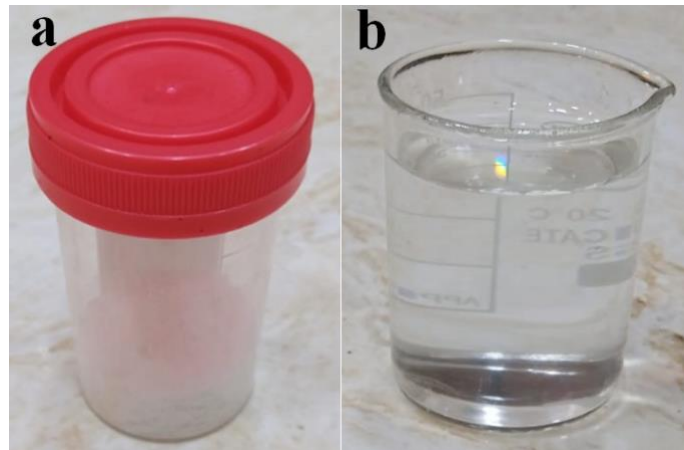


Fig. 3. a) Cadmium nitrate; b) soluble cadmium nitrate 1000 ppm

The equilibrium state was determined by measuring the time to completion of the reaction between cadmium and glass powder. It was tested by measuring the sorption efficiency using 10 solutions with a concentration of 20 ppm every 5 min. As conclusion, after every 5 minutes, one of the solutions is removed from the shaker and filtered using filter paper (Fig. 4). The process was repeated for the ten samples. The cadmium concentration and the pH, EC, and TDS were measured at the equilibrium state using the atomic absorption spectrophotometer (Fig. 5); the Hanna Device was used in measuring pH, EC and TDS. The procedure was repeated for the rest concentrations in the same manner.



Fig. 4. The filtration of the cadmium solution from the crushed glass waste after completing the adsorption process



Fig. 5. a) Atomic absorption spectrophotometer; b) EC meter; and c) pH meter.

3. Results and Discussion

3.1 Mineralogy and Composition of Glass Wastes

The XRD diffractogram of the glass waste shows a non-crystalline material (Fig. 6).

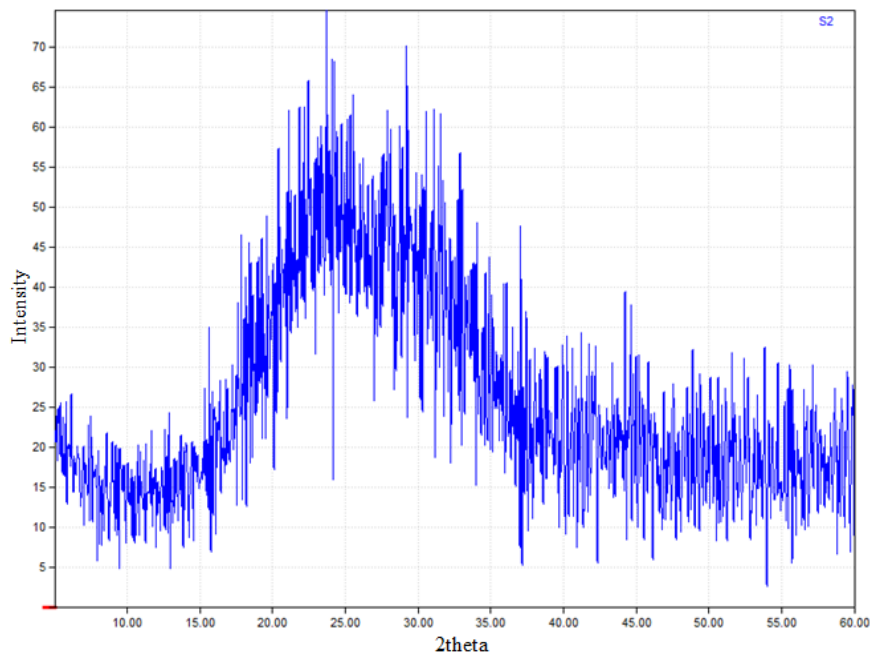


Fig. 6. Diffractogram of glass waste shows no crystallinity

The raw material (glass wastes) is made from a mixture composed of glass sand (62%), sodium carbonate (17%), limestone and dolomite (14%), Flint (3%) sodium sulfate (3%) and very little amount (10-20 gm) coloring materials (State Company for Glass and Refractories (SCGR, 2021)) (Table 1). This mixture is used for industrializing glass products by the SCGR. The components of glass raw materials are presented in Table 2.

Table 1. The raw material of the glass (SCGR, 2021)

Materials	%
glass sand	62%
Soda ash (sodium carbonate)	17%
limestone and dolomite	14%
Flint	3%
Sodium sulfate	3%

Table 2. Chemical composition of glass waste using XRF technique.

Oxides	%
SiO ₂	75.0
CaO	9.1
Na ₂ O	5.6
MgO	0.84
Fe ₂ O ₃	0.79
Al ₂ O ₃	0.71
SO ₃	0.31
TiO ₂	0.17
Cr ₂ O ₃	0.11
ZrO ₂	0.06
P ₂ O ₅	0.04
Cl	0.02
CuO	0.01
SrO	0.07
K ₂ O	< 0.0012
LOI	8.0
Total	99.83

3.2. Sorption efficiency

3.2.1. Effect of Initial Concentration

To test the effect of the initial concentration on the reaction time, all factors (cadmium concentration, temperature and amount of solid to liquid) were fixed, and the experiments were carried out at different concentrations:

- At a concentration of 20 ppm

To know the end time of the reaction (chemical equilibrium), ten laboratory experiments were conducted on Cd-solutions at different times (5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 min), while fixing all the other factors, which are the Cd concentration of 20 ppm, the temperature of 30 °C, and the volume of solid: liquid (2gm: 30 ml). Through these experiments, the completion time of the reaction was determined at 25 minutes, as the best sorption was recorded as 96.4% (Table 3), and sorption was 19.28 ppm (Fig. 7).

Table 3. Results of laboratory experiments of cadmium sorption on glass in ten solutions (20 ppm) at the temperature of 30 °C

Sample	Before experiment					After experiment				
	Time	pH	EC (µs/cm)	TDS(mg/l)	pH	EC (µs/cm)	TDS(mg/l)	Final conc. (ppm)	Sorption (ppm)	Sorption (%)
1Cd	5	4.61	69.8	34.8	9.75	379	188	6.11	13.89	69.45
2Cd	10	4.61	69.8	34.8	9.84	388	192	4.92	15.08	75.4
3 Cd	15	4.61	69.8	34.8	9.97	395	195	2.65	17.35	86.75
4 Cd	20	4.61	69.8	34.8	10.04	399	198	1.23	18.77	93.85
5 Cd	25	4.61	69.8	34.8	10.13	406	202	0.720	19.28	96.40
6 Cd	30	4.61	69.8	34.8	10.2	410	404.5	0.613	19.38	96.93
7 Cd	35	4.61	69.8	34.8	10.24	412	205	0.491	19.50	97.54
8 Cd	40	4.61	69.8	34.8	10.25	413	206	0.315	19.68	98.42
9 Cd	45	4.61	69.8	34.8	10.25	415	207	0.315	19.68	98.42
10 Cd	50	4.61	69.8	34.8	10.26	415	207	0.307	19.69	98.46

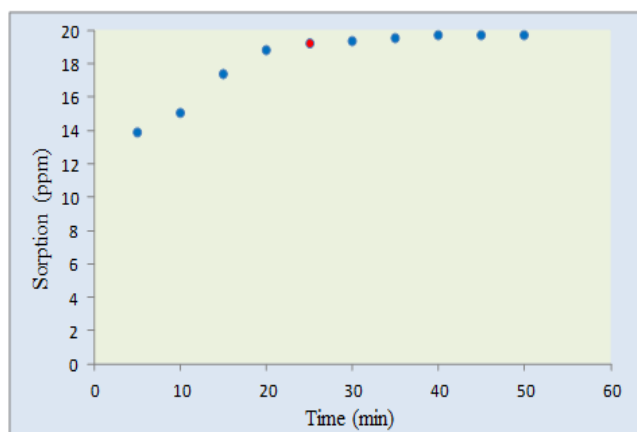


Fig. 7. Sorption efficiency of the glass waste in removing Cd from solutions (20 ppm) of 20 ppm at 25 min

The same procedure was applied to test the sorption efficiency at an initial Cd concentration of 40 ppm, The best sorption was 88.87% (Table 4), and the sorption was 35.55 ppm (Fig. 8). The best sorption (%) of the solution that has Cd concentration of 60 ppm was 88.87% (Table 5), and the sorption was 51.35 ppm (Fig. 9). However, at a concentration of 80 ppm for cadmium solution, the best absorption was 83.5% (Table 6), and the sorption was 66.8 ppm (Fig. 10).

Table 4. Results of laboratory experiments of cadmium sorption on glass in ten solutions (40 ppm) at the temperature of 30 °C

Samples	Before experiment					After experiment				
	Time	pH	EC (µs/cm)	TDS (mg/l)	pH	EC (µs/cm)	TDS (mg/l)	Final conc. (ppm)	Sorption (ppm)	Sorption (%)
1Cd	5	4.9	107.6	53.5	9.79	410	204	13.25	26.75	66.87
2 Cd	10	4.9	107.6	53.5	9.85	419	208.5	11.43	28.57	71.42
3 Cd	15	4.9	107.6	53.5	9.89	425	212	6.71	33.29	83.22
4 Cd	20	4.9	107.6	53.5	9.94	430	214	5.48	34.52	86.30
5 Cd	25	4.9	107.6	53.5	9.98	435	216	4.25	35.55	88.87
6 Cd	30	4.9	107.6	53.5	10.01	438	218	4.27	35.73	89.32
7 Cd	35	4.9	107.6	53.5	10.07	440	219	4.1	35.9	89.75
8 Cd	40	4.9	107.6	53.5	10.1	442	221	4.2	35.8	89.50
9 Cd	45	4.9	107.6	53.5	10.11	443	221	3.96	36.04	90.10
10 Cd	50	4.9	107.6	53.5	10.13	441	220.5	3.96	36.04	90.10

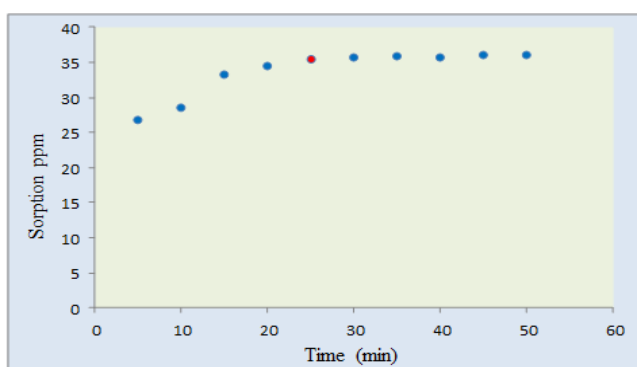
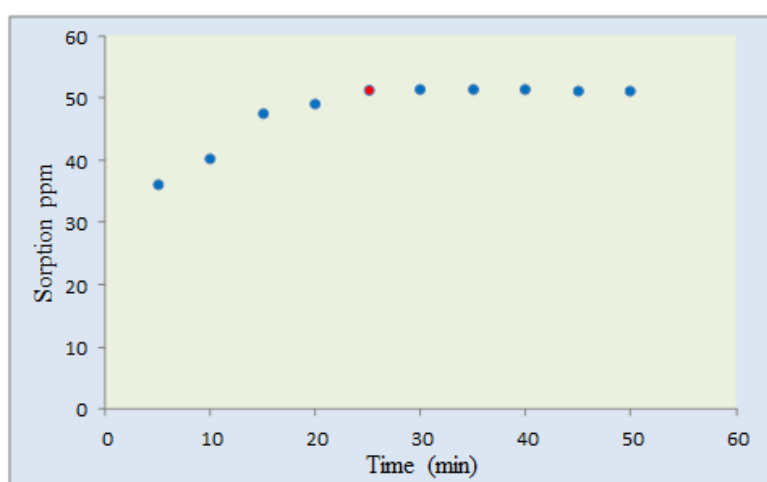


Fig. 8. Sorption efficiency of the glass waste in removing Cd from solutions of 40 ppm at 25 min

Table 5. Results of laboratory experiments of cadmium sorption on glass in ten solutions (60 ppm) at the temperature of 30 °C

Samples	Before experiment				After experiment					
	Time	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/l)	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/l)	Final conc. (ppm)	Sorption (ppm)	Sorption (%)
1Cd	5	5.18	152.5	76	9.83	444	221	23.9	36.1	60.16
2 Cd	10	5.18	152.5	76	9.87	451	225	19.64	40.36	67.26
3 Cd	15	5.18	152.5	76	9.9	457	228	12.25	47.6	79.33
4 Cd	20	5.18	152.5	76	9.92	461	230	10.92	49.08	81.8
5 Cd	25	5.18	152.5	76	9.96	464	231	8.65	51.35	85.58
6 Cd	30	5.18	152.5	76	9.99	466	233	8.57	51.43	85.71
7 Cd	35	5.18	152.5	76	10.02	467	233.5	8.51	51.49	85.81
8 Cd	40	5.18	152.5	76	10.05	469	234	8.63	51.37	85.61
9 Cd	45	5.18	152.5	76	10.06	470	234	8.9	51.1	85.16
10 Cd	50	5.18	152.5	76	10.08	471	235	8.91	51.09	85.15

**Fig. 9.** Sorption efficiency of the glass waste in removing Cd from solutions of 60 ppm at 25 min**Table 6.** Results of laboratory experiments of cadmium sorption on glass in ten solutions (80 ppm) at the temperature of 30 °C.

Samples	Before experiment				After experiment					
	Time	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/l)	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/l)	Final conc. (ppm)	Sorption (ppm)	Sorption (%)
1Cd	5	5.49	187.1	93.5	9.86	488	244	36.14	43.86	54.82
2 Cd	10	5.49	187.1	93.5	9.89	494	247	28.32	51.68	64.6
3 Cd	15	5.49	187.1	93.5	9.92	499	249	17.05	62.95	78.68
4 Cd	20	5.49	187.1	93.5	9.94	502	251	15.64	64.36	80.45
5 Cd	25	5.49	187.1	93.5	9.95	505	252	13.2	66.8	83.5
6 Cd	30	5.49	187.1	93.5	9.96	506	253	13.05	66.95	83.68
7 Cd	35	5.49	187.1	93.5	9.97	507	253.5	12.87	67.13	83.91
8 Cd	40	5.49	187.1	93.5	9.97	508	254	12.9	67.1	83.87
9 Cd	45	5.49	187.1	93.5	9.98	510	255	12.71	67.29	84.11
10 Cd	50	5.49	187.1	93.5	9.98	510	255	12.93	67.07	83.837

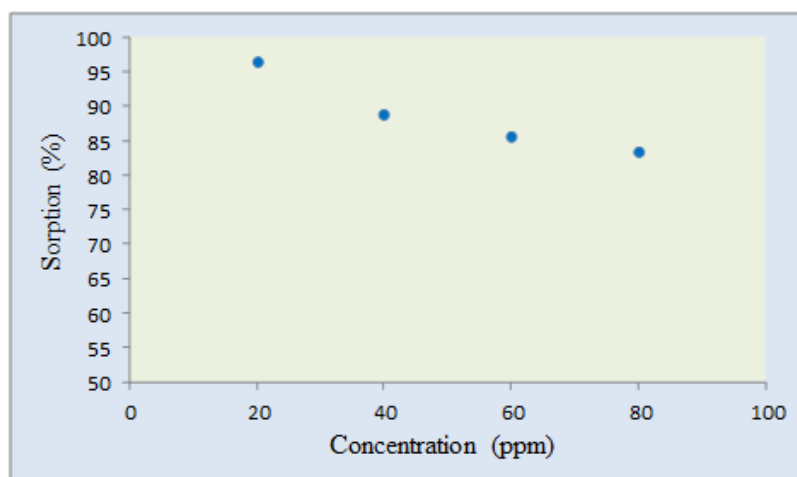


Fig. 10. Sorption efficiency of the glass waste in removing Cd from solutions of 80 ppm at 25 min.

The sorption states (%) were studied for four Cd concentrations (20, 40, 60 and 80 ppm), as Fig. 11 shows a negative correlation between the sorption and concentration. Consequently, the best adsorption (96.4) occurred in the Cd-solution with an initial concentration of 20 ppm.

4. Adsorption Equations

They are the equations that represent the relationship between the amount of adsorbent material (Cd) on the adsorbent surface (Glass waste) and the equilibrium concentration, at a constant temperature (Alyaa et al., 2016).

4.1. Langmuir Equation

Langmuir developed an adsorption theory in which he assumed that the adsorbent surface contains several effective sites that are proportional to the surface area of the adsorbent material, and only one molecule is adsorbed on each of those effective sites, as each site has an adsorption energy equivalent to the energy of any other site. The bond between the surface and adsorbed molecules is either physical or chemical. Adsorbed molecules do not move across the surface and are not affected by neighboring molecules.

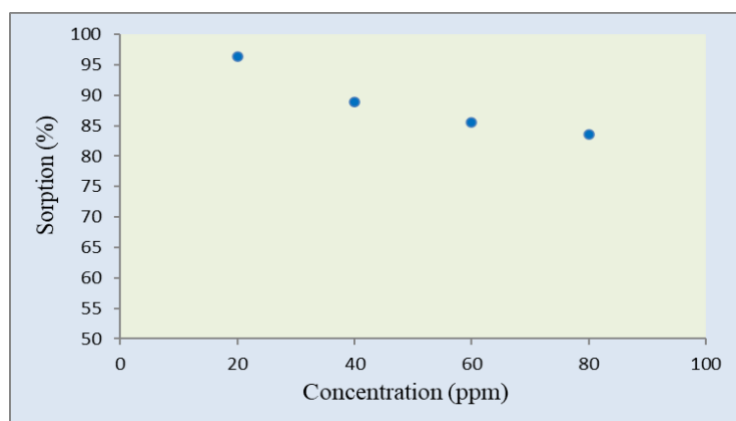


Fig. 11. Sorption efficiency (%) of different Cd concentrations of equilibrium state

Langmuir also assumed that single-molecule adsorption occurs and that the amount of adsorption increases rapidly at the beginning of adsorption and then begins to stabilize gradually, due to the

separation of some molecules from the surface due to thermal excitation, causing the occurrence of what is known as desorption (Dong et al., 2016).

The Langmuir equation for adsorption in solutions can be mathematically expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{Q_o} \quad (1)$$

Where: C_e = the equilibrium concentration of adsorbate (mg/L); Q_e = the amount of material adsorbed per gram of the adsorbent at equilibrium (mg/g); Q_o = maximum monolayer coverage capacity (mg/g); $K_L Q_o$: Langmuir empirical constants.

By plotting C_e/Q_e against C_e . It was found a straight line with a slope of $1/Q_o$ and an intersection of the amount of $1/K_L Q_o$, where Q_o and K_L were computed from the slope and intercept of the Langmuir plot (Adamson and Gast, 2001) as shown in Fig. 12.

(The Q_o represents the maximum adsorption capacity, and the K_L is an equilibrium constant expressing the bond energy between the adsorbent and adsorbate (Adamson and Gast, 2001). The amount of adsorbent was calculated according to the equation:

$$Q_e = \frac{V_{sol}(C_o - C_e)}{M} \quad (2)$$

V_{sol} = volume of the adsorbent solution (L); C_o = initial concentration of the adsorbent solution (mg/l); M = mass of adsorbent (grams); The removal efficiency was determined by computing the percentage sorption using the following formula:

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

Were: $R\%$ = percentage of adsorption (adsorption efficiency). $R\%$ = Sorption%; C_o = the concentration before adsorption; C_e = the concentration after adsorption.

Table 7. Adsorption of cadmium (%) by glass waste with different concentrations and their corresponding C_e and Q_e values

Sample	Cd (mg/L)	R %	C_e (mg/L)	Q_e (mg/g)	C_e / Q_e (g/L)
1	20	96.40	0.72	0.2892	2.4896
2	40	88.87	4.25	0.5362	7.9261
3	60	85.58	8.65	0.77025	11.2301
4	80	83.50	13.20	1.002	13.1736

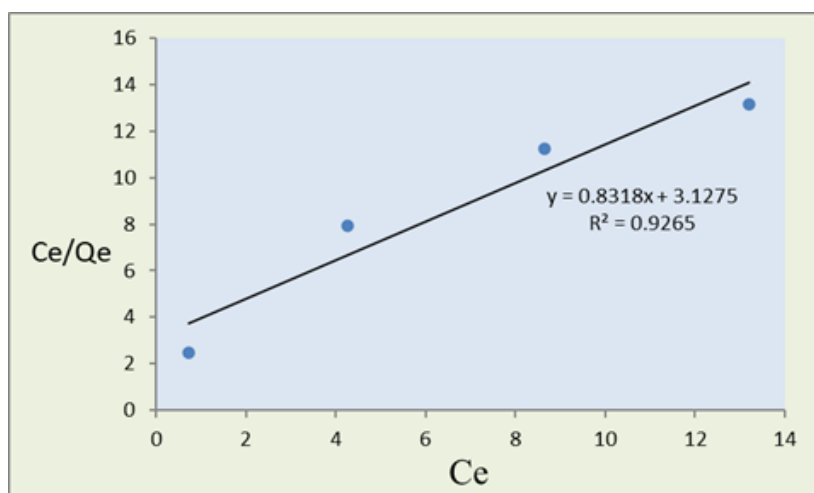


Fig. 12. Langmuir diagram shows the adsorbing Cd to the adsorbent (glass waste)

The maximum monolayer coverage capacity (Q_o) from the Langmuir Isotherm model was determined to be 1.202 mg/g. The constant related to the energy of adsorption (KL)(Langmuir Constant) is 0.266. The sorption is well correlated to the Langmuir equation where R^2 is 0.926 (Fig. 12), proving that the sorption data fitted well with the Langmuir Isotherm model.

4.2. Freundlich Equation

The Langmuir equation did not apply to many systems of adsorption from solution, because adsorption is likely to occur in multiple molecular layers (multilayer), and most solid surfaces are heterogeneous due to the irregularity of the potential energy changes on them as a result of the adsorption sites having different levels of energy (Gregg and Sing, 1982). Therefore, Freundlich, a German scientist developed an equation that represents the change in the amount of the adsorbed substance per unit area or mass of the adsorbed substance with the equilibrium concentration as follows (Dada et al., 2012).

$$Q_e = KfC_e^{1/n} \quad (4)$$

Where: Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g); C_e = the equilibrium concentration of adsorbate (mg/L); Kf = Freundlich constant (mg/g); n = adsorption intensity.

The equation 5 is derived from the previous linearizing equation:

$$\text{Log } Q_e = \text{Log } Kf + \frac{1}{n} \text{Log } C_e \quad (5)$$

The constant Kf is an approximate indicator of adsorption capacity, the constant n represents adsorption intensity, and $1/n$ is a function of the strength of adsorption in the adsorption process (Voudrias et al., 2002). The values of $1/n$ and $\text{Log } Kf$ were computed from the slope and intercept of the Freundlich plot (Fig. 13).

From the data in Table 8, Fig. 13 the value of $1/n = 0.416$ that's mean $n = 2.402$, $Kf = 3.126$, R^2 value is 0.98, indicating that the sorption of cadmium is consistent with the Freundlich equation.

Table 8. Adsorption of Cd by glass waste at different concentrations and their corresponding $\text{Log } Q_e$, $\text{Log } C_e$ values.

Sample	C_o (mg/l)	(R %)	C_e (mg/L)	Q_e (mg/g)	$\text{Log } C_e$	$\text{Log } Q_e$
1	20	96.4	0.72	0.2892	-0.1426	-0.5388
2	40	88.875	4.25	0.5362	0.6283	-0.2706
3	60	85.58	8.65	0.77025	0.9370	-0.1133
4	80	83.5	13.2	1.002	1.1205	0.000867

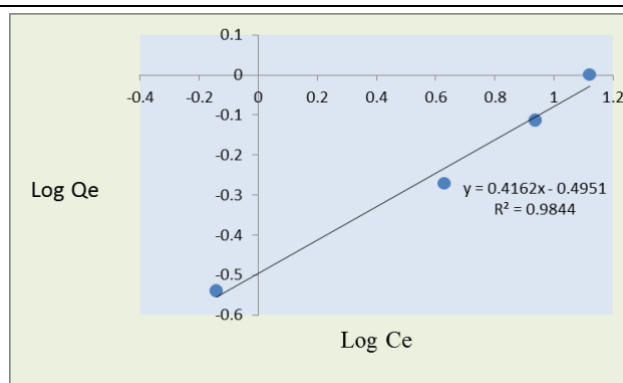


Fig. 13. Freundlich model for Cd adsorption with glass waste

5. Conclusions

The equilibrium state was determined at 25 minutes for concentrations of 20, 40, 60, and 80 ppm.

A positive correlation was found between sorption (%) and mass of waste glass due to the glass waste saturation. There is a significant difference in the removal rate (96.4 - 83.5%) with an increase in the cadmium concentrations from 20 to 80 ppm.

It is clear from the results obtained that the particle size of the glass (the size of the silt) is the most effective size for the adsorption of cadmium from aqueous solutions, and the evidence is that the adsorption reached 98.46% in 50 minutes at a concentration of 20 ppm. Accordingly, glass wastes of silt size are good adsorbents for Cd from aqueous solutions.

Acknowledgements

The authors are very grateful to the staff of the Glass Manufacturing Factory in Ramadi, and the State Company for Glass and Refractories (SCGR) in Ramadi as they are providing us with some necessary information in addition to the glass waste samples. Our thanks go to the reviewers who did the best and our comments enhanced the scientific value of the research.

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