



Purification of drinking water and wastewater from heavy metal ions using rice husk and rice husk ash.

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Abstract:

In this study, we focused on rice husks and rice husk ash to purify drinking water as well as the wastewater that is dumped into river streams without treatment in our areas from heavy metal ions. These ions are needed by the body in very small quantities, but their excess causes diseases and serious harm to humans. Here the process was done using more rice hull ash than the rice hulls themselves, and the reason is due to the high percentage of silica in the rice hull ash. Rice husks were obtained from the waste of rice mills that spread in our areas and throw rice husks in deserts or burn them because they are useless waste.

Keywords: adsorption, heavy metal ions, rice husk, rice husk ash, purification.

تنقية مياه الشرب ومياه الصرف الصحي من أيونات المعادن الثقيلة باستخدام قشر الأرز ورماد قشر الأرز

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الملخص:

ركزنا في هذه الدراسة على الامتزاز على قشور الأرز ورماد قشور الأرز لتنقية مياه الشرب وكذلك مياه الصرف الصحي التي تصب في مجاري الأنهار دون معالجة في مناطقنا من أيونات المعادن الثقيلة. وهذه الأيونات يحتاجها الجسم بكميات قليلة جداً، إلا أن فائضها يسبب أمراضاً وأضراراً جسيمة للإنسان. هنا تمت العملية باستخدام المزيد من قشور الأرز ورماد قشور الأرز نفسه، والسبب يرجع إلى ارتفاع نسبة السليكا في رماد قشر الأرز. يتم الحصول على قشور الأرز من مخلفات مطاحن الأرز المنتشرة في مناطقنا وتقوم برمي قشور الأرز في الصحاري أو حرقها لأنها نفايات عديمة الفائدة.

الكلمات المفتاحية: الامتزاز، التنقية، أيونات المعادن الثقيلة، قشر الأرز، رماد قشر الأرز.

1. Introduction:



Rice hulls are one of the industrial wastes of rice production in the world and are composed of three polymers: cellulose, hemicellulose, and lignin [1]. Rice hulls have different uses based on their physical and chemical properties, such as silicon compounds. We also use them as fuel. The lignin present in rice hulls is important in obtaining Activated carbon is an effective absorbent material because it has a surface area[2]

Average dry foundation composition as organic matter: 80% and 20% ash. The organic fraction consists of approximately 42.8% cellulose, 22.5% lignin, 32.7% hemicellulose and other organic matter about 2%. Hemicellulose (xilan) is a mixture of D-xylose -17.52%, L-arabinose - 6.53%, methylglucuronic acid - 3.27%, galactose- 2.37%[3].

Chemical analysis of the inorganic fraction in rice hulls showed that the main component is amorphous silica and a small amount of some alkali oxides, alkaline earths, metals, aluminum and iron. Rice hulls have now become a major source as raw biomass materials for manufacturing valuable silicon compound products, including silicon carbide, silicon nitride, silicon tetrachloride, magnesium silicon, pure silicon, Zeolites, rubber and plastic composite fillers, adsorbents and heterogeneous catalyst supports. Controlled

Pyrolysis of rice hulls in air or inert (nitrogen) atmosphere produces white rice hull ash (WRHA) and black rice hull ash (BRHA), respectively, which have an amorphous and porous structure with high specific surface area. The purpose of this study was to examine the adsorption ability of activated carbon from rice husk to adsorb phenol. The activated carbon used in these studies was burned at 300 and 400 °C and then activated with 10% ZnCl₂. The activated carbon was characterized using infrared spectroscopy, X-ray diffraction, scanning electron microscope and gas absorption analyzer. The best activated carbon is activated to absorb heavy ion Carbon resulting from the combustion of rice husk at a temperature of 400°C and activated with 10% ZnCl₂ for 24 hours. The best adsorption capacity of activated carbon was 3.9370 mg/g sorbent with a Gibbs free energy of -25.493 kJ/mol[3]. Industrial development as well as science and technology give beneficial effects not only to humans but also to the surrounding environment. This can be found in increases in the number and types of pollutants in the industrial sector and then the environment, especially the marine environment The majority of metal ions are toxic, including copper, cadmium, lead, mercury, nickel, zinc, and selenium, and they are released in quantities that pose a threat to humans and their health [4]. These materials are released largely from various industries such as metal plating, battery manufacturing, agricultural pesticides, dyes, and fertilizers, and these ions are not biodegradable [4]. Heavy metal ions affect water resources and soil fertility, threaten the aquatic ecosystem, aquatic organisms, and soil, and cause human diseases, including cancer [5]. These heavy ions can accumulate in the human



body through the food chain, and this can be reduced partially or completely by methods including adsorption, membrane filtration, chemical precipitation, and advanced oxidation [6].

Chromium is produced from the processes of metal plating, rubber manufacturing, and photography. Chromium (III) is one of the components of the diet and plays a role in metabolism, while carob (VI) is a carcinogen and causes heart and liver diseases. [2] Manganese also plays a role in the metabolism of carbohydrates and cholesterol. And amino acids, but high concentrations cause diseases such as infertility in men, neurological disorders, birth defects, and bone deformity [2]. Copper, which is produced from the rayon industry and electrical industries, plays a role in the physiological functions of the human body, but excessive amounts cause damage to the intestines, liver, stomach damage, skin cancer, neuropathy, and vascular diseases [2]. As for cadmium, if it is in excess quantities, it is produced phosphate fertilizers, electronics, and dyes, it can harm the lungs, liver, kidneys, and bones and cause lung cancer and immune system disorders [2]. Arsenic is a product of phosphate manufacturing, fertilizers, mining, dyes, and textile operations. With the advancement of technology and the abundance of water dumped in rivers and fresh lakes without treatment, the percentage of heavy ions has increased beyond the recommended limit[2].

It is permitted globally [2]. A series of damages have occurred on human metabolism, and these harmful effects include the production of various types of oxygen, which have oxidative effects, in addition to the accumulation of heavy metal ions such as chromium, nickel, cobalt, and arsenic ions, which leads to an imbalance in antioxidants and affects the activity of some. Hormones and enzymes may cause diseases such as cancer [2]The components of rice husks are 70-90% of organic materials such as cellulose and lignin and other inorganic materials such as silica and alkalis. Rice hulls contain 10-20% of ash, which consists of more than 90-95% of pure, highly porous silica, and the rest is oxides of magnesium, aluminum, calcium, iron and sodium, which account for 1%.

2.Harm of exposure to heavy ions:

Cadmium, if it exceeds 0.005 mg/L, causes kidney damage, while chromium, if exposure to it is higher than 0.005 mg/L, causes skin irritation. Short-term exposure to copper causes gastrointestinal disorders, while long-term exposure causes liver and kidney damage. As for arsenic, if it exceeds 0.01 mg/L, it causes skin damage and circulatory problems and may increase the risk of cancer. As for lead, if its concentration is 0.015 mg/L, it causes delayed physical and mental development in children, while in adults it causes kidney problems and high blood pressure. When nickel is more than 0.2 mg/L, it causes dermatitis, nausea, chronic asthma, and cough. Zinc, when its concentration exceeds 0.8 mg/L, causes depression, lethargy, nervous signs, and increased



thirst. As for mercury, when its concentration exceeds 0.0003 mg/L, it causes rheumatism, kidney disease, the circulatory system, and the nervous system [6].

2.1. Mercury:

Mercury pollution is generated from volcanic and geological activities, as for human activities such as cosmetics, paper manufacturing, thermometers, batteries, and medicines. As for its harmful effects, it causes nerve damage, paralysis, blindness, rheumatoid arthritis, and loss of appetite. The permissible limit in drinking water is 0.001 mg/L and in wastewater is 0.005 mg/L [7-9].

2.2. Arsenic:

It is a very toxic element and its sources are pesticides, herbicides, phosphate fertilizers, and the semiconductor industry. As for the diseases it causes, such as skin, bladder, and kidney cancer, and neuromuscular disorders, the permissible limit is 0.01 mg/L [10,11].

2.3. Cadmium

There are many sources of cadmium pollution, including mining, dyes, metal plating, battery manufacturing, and phosphate fertilizers. It causes diseases including kidney damage and disorder and emphysema[12,13].

The World Health Organization has set the permissible concentration as 0.003 mg/L [14].

2.4. Lead:

It is produced by industrial processes such as batteries, bronze products, pipes, ceramics, and glass.

Poisoning with it causes brain damage, vomiting, anemia, loss of appetite, and blood diseases. According to the World Health Organization, the permissible limit is 0.05 mg/L [15,16].

2.5. Chromium:

Chromium exists in several forms, including tertiary, pentameric, and hexagonal. The toxicity of chromium is very high and is a carcinogen [17]It is contaminated through steel manufacturing processes, dyes and paints, chemical industries, and the wood and ceramic industries [18]. It causes cancer in the digestive system, diarrhea, nausea, vomiting, diarrhea, lung diseases and bleeding (40), and the permissible limit for drinking water is 0.1 mg/L [19].

Copper: 2.6.



Copper is used in many industries such as dyes, tanneries, fertilizers, and paint [20]. Excessive exposure to copper on a continuous basis causes Wilson's disease, liver and kidney damage, vomiting, diarrhea, and lung cancer [21]. The permissible limit is 1.3 mg/L.

2.7. Nickel:

A toxic element released from chemical industries, electroplating, mining, paints, and ink [22] and causes effects such as skin inflammation, nausea, chronic asthma, coughing, and cancer. The US Environmental Protection Agency has set the permissible limit for nickel in drinking water as 0.015 mg/L [23].

2.8. Zinc:

Zinc is found in its +2 oxidation state, which is important, but consuming excessive amounts of it causes damage. Zinc comes from industrial activities such as galvanizing, steel production, burning coal, and refining zinc [24]. An excess of zinc ions causes depression, lethargy, nervous signs, increased thirst and loss of appetite [25], and the permissible limit is 5 mg/L [26].

Composition of Rice Husk(RH) and Rice Husk Ash(RHA):

Rice husk contains 75-90% of organic materials such as cellulose, hemicellulose, lignin, etc., and the rest of the mineral components. Such as silica, alkalis, and trace elements, where cellulose is a polymer of sugars and its basic units (monomer) are beta-glucose, while hemicellulose is a shorter polymer that contains other sugars such as xylose, galactose, mannose, rhamnose, and arabinose, while lignin contains alcoholic aromatic compounds [27-31]. The ash is composed of 87-97% silica, highly porous and lightweight, with a very high percentage External surface area. The presence of a high amount of silica makes it a valuable material for industrial use. As for the ash of rice hulls, it contains more than 90% silica in the amorphous phase, 5% carbon, and the rest is oxides of iron, aluminium, magnesium, potassium, sodium, and sulfur [32].

3. Factors affecting adsorption on rice husk and rice husk ash

3.1. Effect of pH:

The rate of adsorption of heavy ions is greatly affected when changing the pH, as at pH (2-4) we notice that the adsorption is little. It increases with increasing pH, and the reason is attributed to the fact that hydrogen ions H^+ are competitors for adsorption on sensitive sites on the surface where However, at very high pH, more than 5-9, adsorption begins to increase, and this is due to $Co(II) > Cd(II) > Zn(II) > Cu(II)$.



To the disappearance of competing hydrogen ions and the activation of the active sites to be able to adsorption, but when the pH increases, the ions hydroxides OH^- are abundant in the solution, and this leads to the formation of insoluble hydroxides (precipitates), which is also undesirable [33-40].

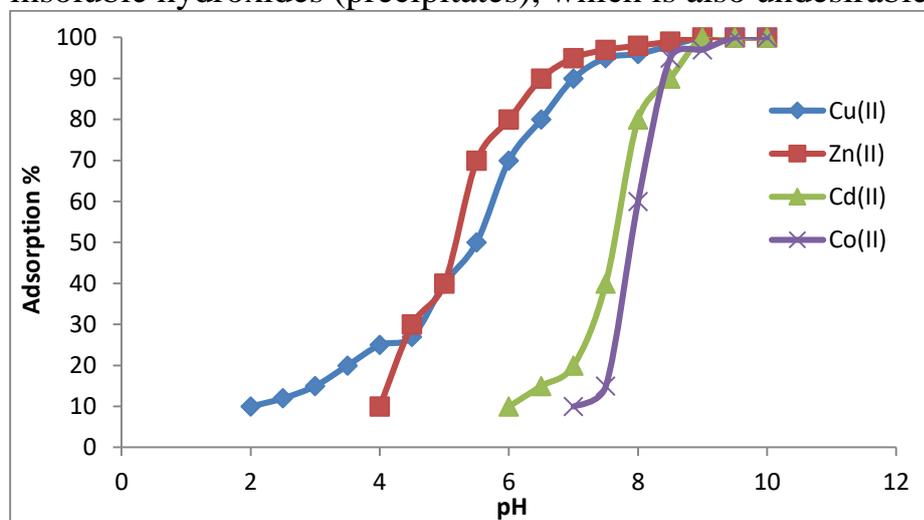


Fig.1. The effect of acid on the adsorption of some heavy ions on the surface of Rice

Husk Ash(RHA).

3.2.Effect of adsorbent concentration: Increasing the amount of adsorbed material increases the adsorption process, as this is attributed to the availability and increase in adsorption sites for metal ions, as the removal of chromium was followed by rice straw, and the optimal dose for adsorption is 8 g/100 ml [41]. Reducing the dose required for adsorption leads to reduced adsorption, and increasing it leads to increased adsorption [42]. The geometric shape of the adsorbent also plays on the concept of mass transfer by adsorption [43]. That is, increasing the amount of adsorbent material leads to easier access to adsorption sites [44]. The capacity of these sites may be different from one element to another[44].

3.3.Effect of initial metal ion concentration: The initial concentration is important to determine the beginning of adsorption, for example, the chromium ion Cr^{3+} is 20 mg/L, as the adsorbent material showed a high adsorption capacity due to the large surface area and sites prepared for adsorption, and when the concentration increases, the movement of ions is hindered [45]. The adsorption process stops when all adsorption sites become covered with metal ions [46].

When the concentration of the adsorbent increases, the adsorption decreases, and this decrease is due to the decrease in sites prepared for adsorption on the surface [47].

Table 1 - Adsorption capacity of rice husk on heavy metal $q_{\text{max}}/(\text{mg/g})$



Adsorbent	Rice Husk
Nickle	2.2
Chromium	2
Mercury	70
Cadmium	23
Zinc	9
Copper	12
Lead	62
Iron	2.5
Cobalt	2.3

3.4.Effect of contact time: The contact time was determined when fixing the concentration of the adsorbed and adsorbed material and the acid value of the solution. It was observed that between the first and second hours the amount of adsorbed material was high. The reason is due to the abundance of adsorption sites on the adsorbent surface on which the ions to be extracted by adsorption settle. When the front sites are occupied at this time, they remain. Remote, isolated, remote, or secondary sites that have not been occupied, and these are few compared to the sites in the front, which are characterized by ease of access and abundance [48,49]. Temperature also has an effect on the amount of adsorbed material, as when increasing temperature causes an increase in kinetic energy, this leads to Easier access to adsorption sites in larger quantities than when the temperature is low, and the reason is due to kinetic energy [50].

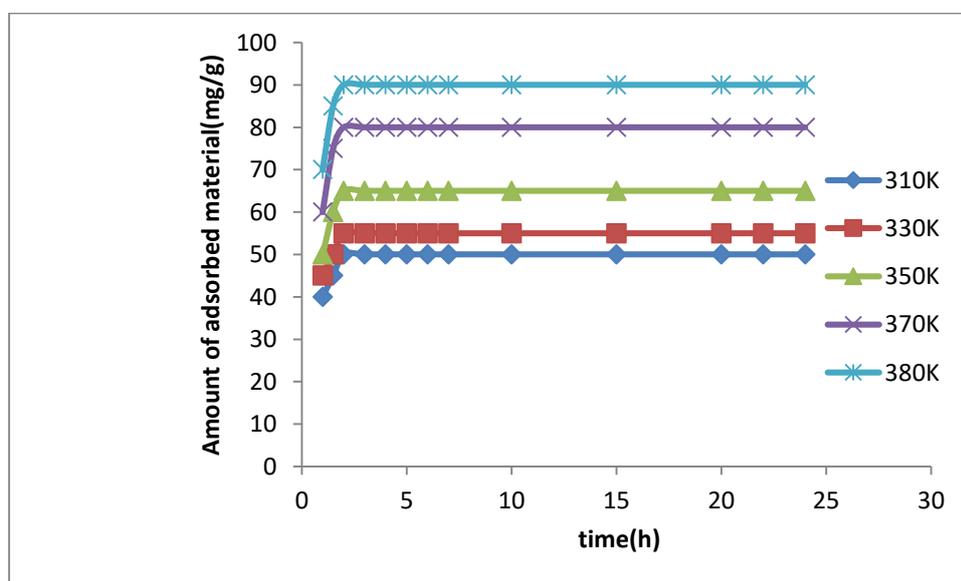


Fig. 2. Effect of contact time on average in adsorption of some heavy ions (Pb^{+2}) on the surface of Rice Husk Ash(RHA). at different temperatures .

For thermodynamic studies, (10,20,30,40,50,60,70,80,90,100) mg/L were taken as the initial concentration of ions () respectively in the acid function (6-8) and 8



g/100 ml of rice husk ash and at times (2-24) The shaking process was continuous at 160 revolutions per minute at a temperature of 25 degrees Celsius[50,51]

$$\text{Removal of heavy ion \%} = \frac{(C_o - C_t)}{C_o} \times 100\% \quad \text{----- (1)}$$

$$q_t = \frac{(C_o - C_e) V}{w} \quad \text{----- (2)}$$

C_o :Inicial Concentration of heavy ion.

C_e: Equilibrium Concentration of heavy ion.

V: volium of soluition (L) .

W: is the adsorbent mass(g).

Thermodynamic Study: : Thermodynamic parameters such as the free energy (ΔG° kJ/mol), enthalpy (ΔH° kJ/mol) and entropy (ΔS° J/K.mol) changes during adsorption can be evaluated[53,54]

$$K_c = \frac{q_e}{C_e} \quad \text{----- (3)}$$

$$\Delta G^\circ = -RT \ln K_c \quad \text{.....(4)}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \text{.....(5)}$$

$$\log K_C = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad \text{----- (6)}$$

Table(2) showing the thermodynamic functions for the adsorption of heavy metal ions on rice husk ash.

Cr(III)		ΔG°= (kJ/mol.K)	ΔH°=-21.4(kJ/mol.K) ΔS°=-65.4 J/mol.K
30°C	303K	-1.58	
40°C	313K	-0.93	
50°C	323K	-0.276	
60°C	333K	+0.375	
70°C	343K	+1.0322	
80°C	353K	+1.686	
Zn(II)		ΔG°=(kJ/mol.K)	ΔH°=- 24.81(kJ/mol.K)
30°C	303K	-1.964	



40°C	313K	-1.21	$\Delta S^\circ = -75.4 \text{ J/mol.K}$
50°C	323K	-0.4558	
60°C	333K	+0.3	
70°C	343K	+1.052	
80°C	353K	+1.8062	
Cu(II)		$\Delta G^\circ = (\text{kJ/mol.K})$	$\Delta H^\circ = -27.4 (\text{kJ/mol.K})$
30°C	303K	-3.2206	$\Delta S^\circ = -79.8 \text{ J/mol.K}$
40°C	313K	-2.4226	
50°C	323K	-1.6256	
60°C	333K	-0.8266	
70°C	343K	-0.0286	
80°C	353K	+0.7694	
Co(II)		$\Delta G^\circ = (\text{kJ/mol.K})$	$\Delta H^\circ = -32.4 (\text{kJ/mol.K})$
30°C	303K	-3.524	$\Delta S^\circ = -95.3 \text{ J/mol.K}$
40°C	313K	-2.57	
50°C	323K	-1.618	
60°C	333K	-0.665	
70°C	343K	+0.288	
80°C	353K	+1.241	
Ni(II)		$\Delta G^\circ = (\text{kJ/mol.K})$	$\Delta H^\circ = -31.2 (\text{kJ/mol.K})$
30°C	303K	-2.112	$\Delta S^\circ = -96 \text{ J/mol.K}$
40°C	313K	-1.152	
50°C	323K	-0.192	
60°C	333K	+0.768	
70°C	343K	+1.73	
80°C	353K	+2.688	
Pb(II)		$\Delta G^\circ = (\text{kJ/mol.K})$	$\Delta H^\circ = -37 (\text{kJ/mol.K})$
30°C	303K	-3.67	$\Delta S^\circ = -110 \text{ J/mol.K}$
40°C	313K	-2.57	
50°C	323K	-1.47	
60°C	333K	-0.37	
70°C	343K	+0.73	
80°C	353K	+1.83	

Table (3) shows the relationship between $1/T$ and $\ln K_c$ for adsorption of heavy metal ions on rice husk ash.

1/T	ln K_c					
	Cr(III)	Zn(II)	Cu(II)	Co(II)	Ni(II)	Pb(II)
0.003300	0.000627	0.00077	0.001278	0.001398	0.000649	0.00145
330	2	7	45	89	49	684



0.003194 888	0.000357 4	0.00046 5	0.000938 48	0.000987 594	0.000446 884	0.00098 759
0.003095 752	0.000102 777	0.00016 97	0.000605 34	0.000602 512	0.000071 497	0.00054 74
0.003003 003	- 0.000135 5	- 0.00010 836	0.000298 566	0.000240 2	- 0.000277 40	0.00013 364
0.002915 452	- 0.000362	- 0.00037 030	0.000010 03	- 0.000101	- 0.000606 65	- 0.00025 6
0.002832 812	- 0.000572 77	- 0.00061 543	- 0.000262 16	- 0.000422 85	- 0.000915 89	- 0.00062 354

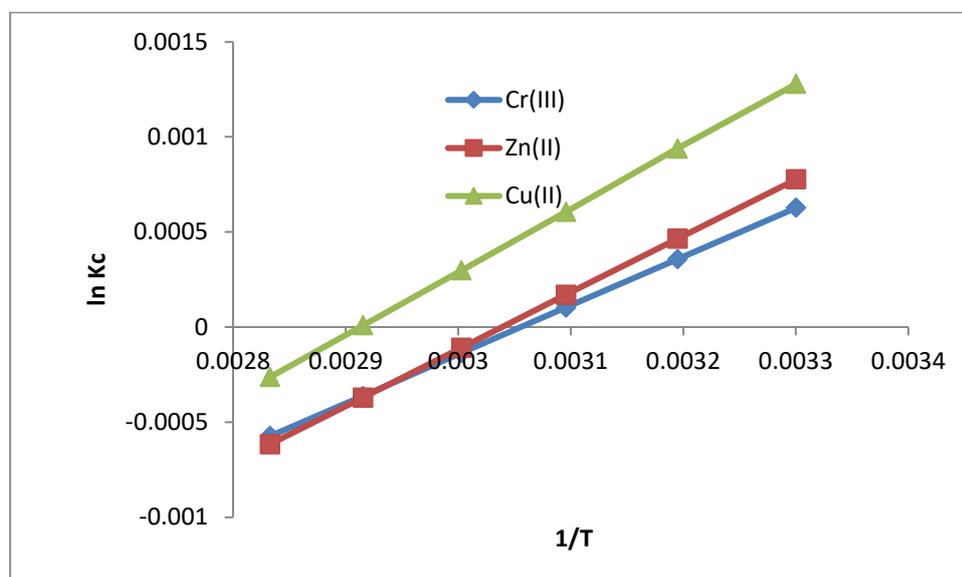


Fig. 3. Plot of ln KC vs. 1/T for estimation of thermodynamic parameters for the adsorption of Heavy metal onto Rice Husk

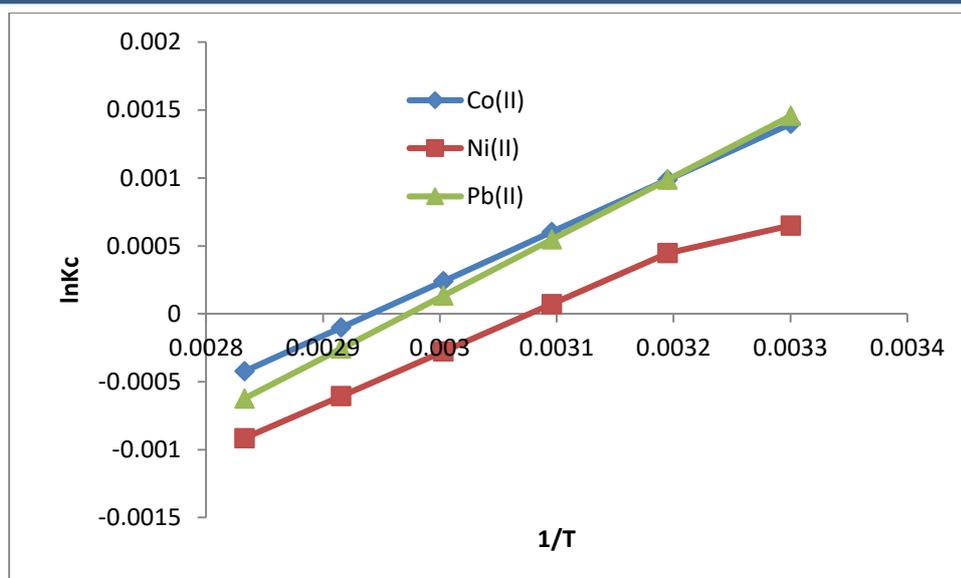


Fig.4. Plot of $\ln K_C$ vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of Heavy metal onto Rice Husk Ash .

4. Adsorption Isotherms: The isotherm is an explanation of adsorption and the amount of adsorbed material over time when the temperature is constant, where the adsorption is initially rapid and large. Then it begins to decrease and gradually approaches stability and equilibrium, which is the state in which the amount adsorbed on the surface is equal to the amount leaving [55,56].

The difference between chemical and physical adsorption is that chemical adsorption is in one layer and the free energy is greater than 20 kJ/mol, It is difficult to liberate adsorbed particles because the bond between the adsorbent and the adsorbed material is strong. As for physical adsorption, it has a low free binding energy, that is, less than chemical adsorption, and the bonding takes place in several layers, meaning that only the first layer of particles is attached to the surface, while the other layers are linked to each other, and therefore these particles are easily separated from the surface. The surface is high and is affected by temperature and pressure. Adsorption was classified by Giles into several categories, such as (S, L, H, and C), where type S takes a shape similar to the letter S, and the adsorbed particles are either vertical or inclined towards the surface, while type L is concerned with Langmuir adsorption, and the orientation of the adsorbed particles is horizontal with the adsorbent. Class H refers to adsorption with very dilute solutions, as well as to high-molecular-weight and giant molecules such as polymers, while class C to the possibility of chemical adsorption[57,58].

4.1. Langmuir equation for adsorption:



This equation was formulated by Irving Langmuir to describe the adsorption of particles on solid surfaces. The adsorption occurs in one layer on the surface, and the adsorption is rapid at first, as it occurs on a surface that contains a specific number of adsorption sites. Then the adsorption begins to decrease as a result of the decrease in adsorption sites until we reach a state of equilibrium in which it is... The number of adsorbed particles is equal to the number of particles leaving the surface, and the Langmuir equation can be described as follows[59-62]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e \text{ -----(7)}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max}} \cdot \frac{1}{C} \text{ -----(8)}$$

Where:

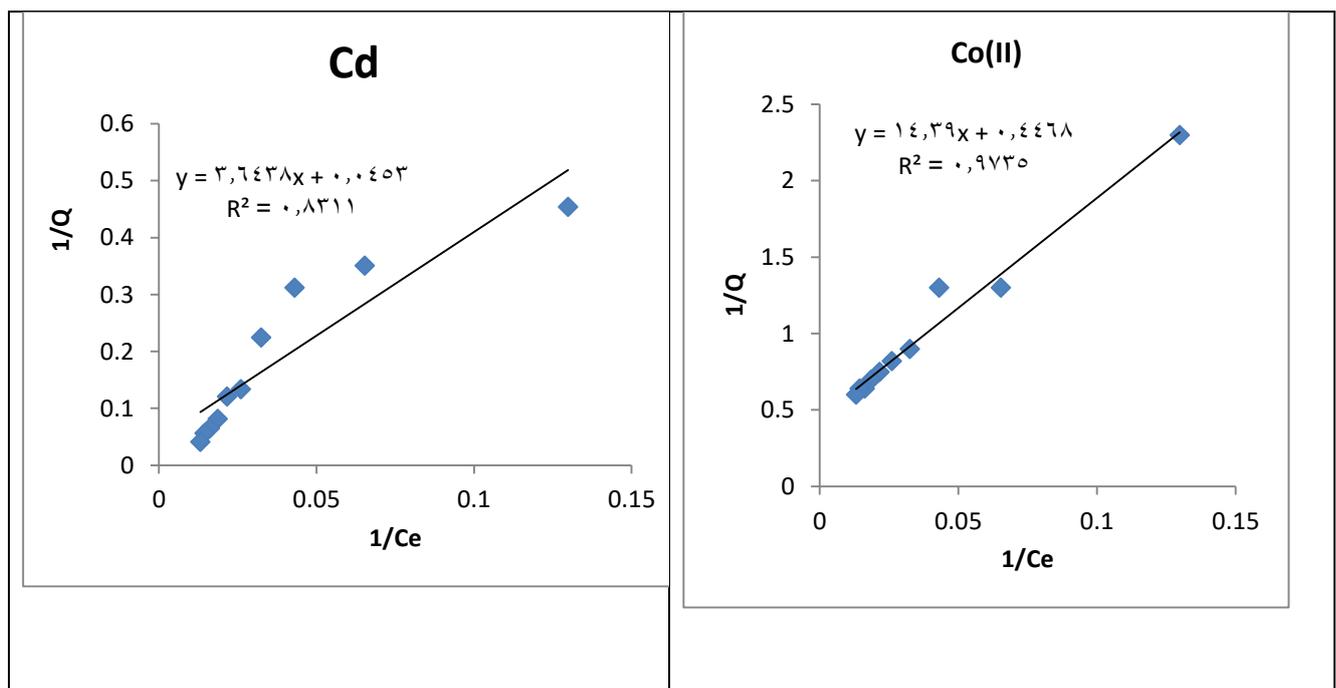
Ce: the concentration of the solution at equilibrium (mg/L).

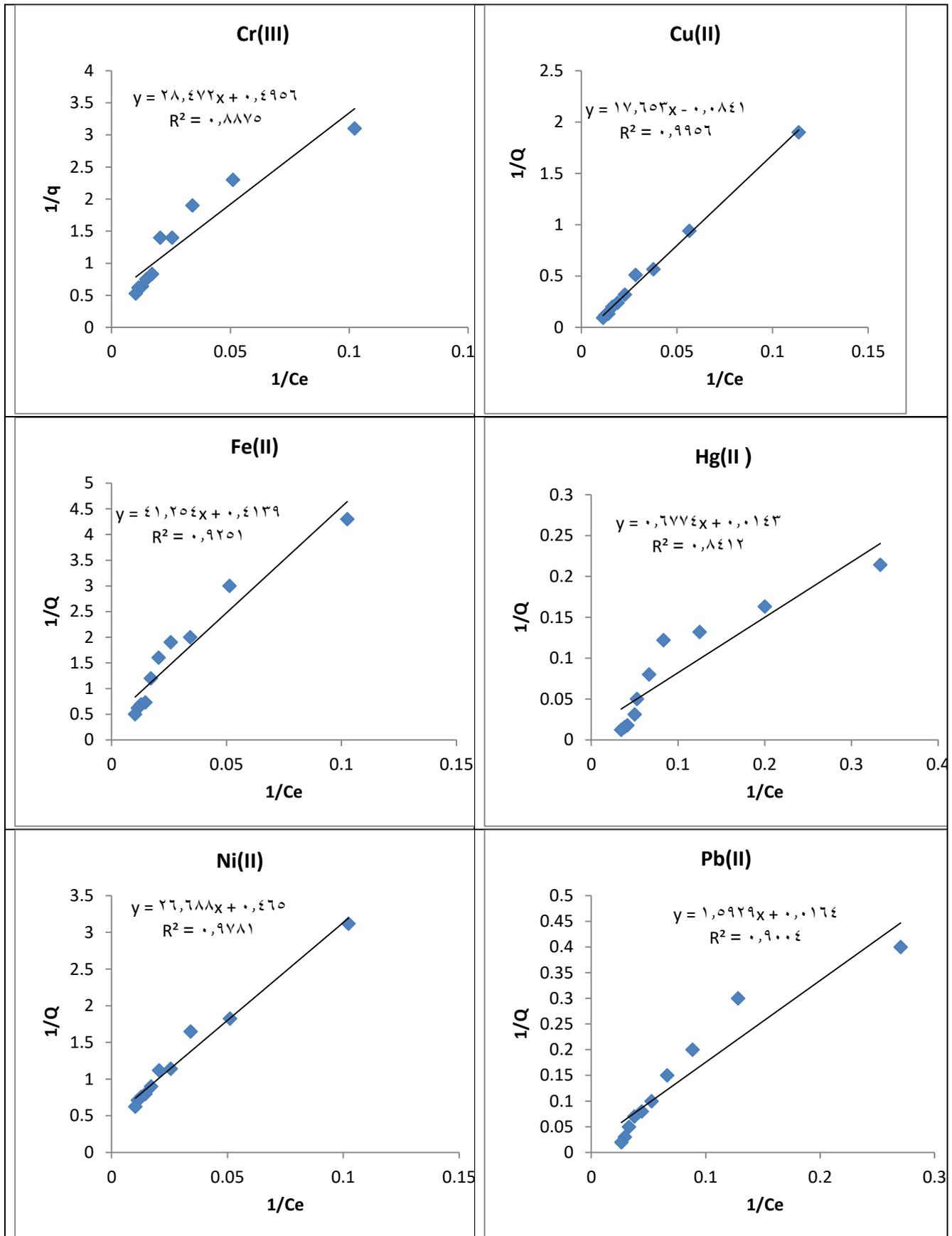
qe :amount of adsorbent (mg/g)

qmax : max amount of adsorbent (mg/g)

b: Langmuir adsorption constant related to the energy of adsorption (L/mg).

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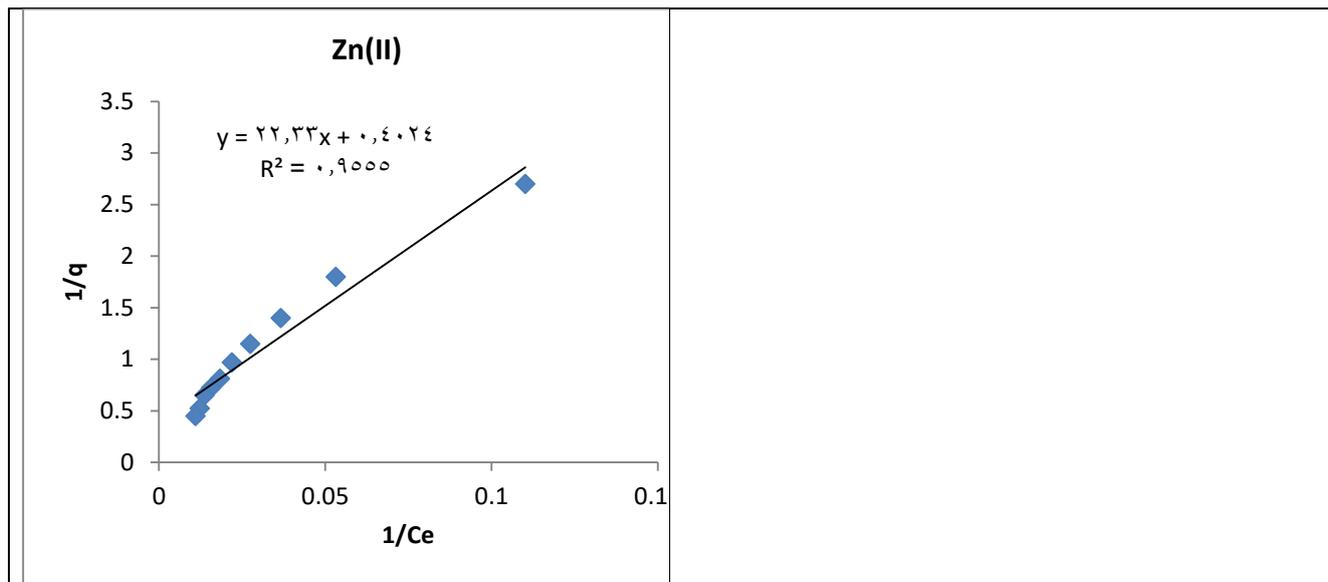


Fig. 5. Plot of 1/q vs. 1/Ce Langmuir Adsorption of heavy metals on Rice Husk Ash.

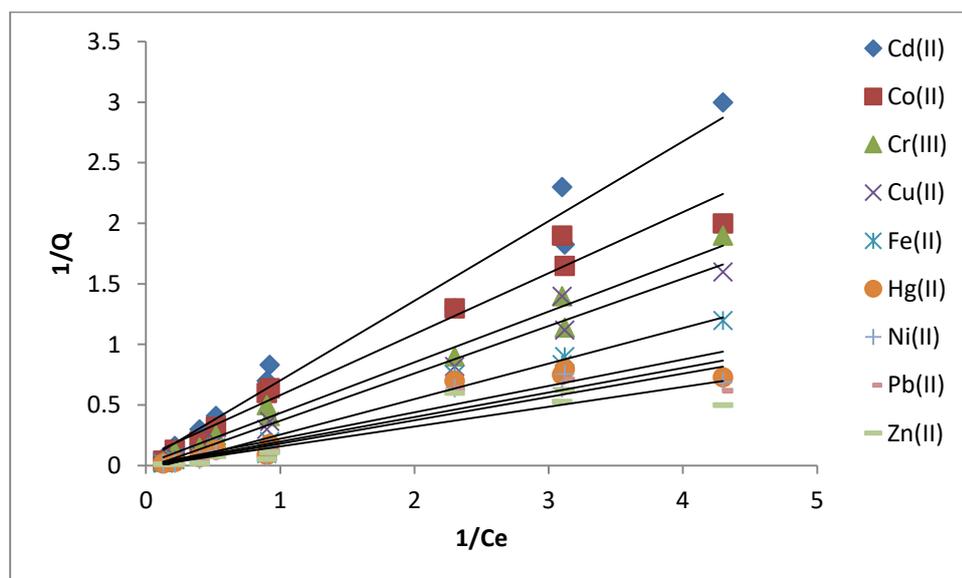


Fig.6.. Plot of 1/q vs. 1/Ce Langmuir Adsorption of heavy metals on Rice Husk Ash.

Table (4) shows the maximum amount of adsorbent and Langmuir constants for the adsorption of heavy ions on rice husk ash.

Heavy ion	slope	q_{max}	b	R^2



Zn ²⁺	8.848	9	0.012557	0.9555
Co ²⁺	14.39	2.238	0.155534	0.9735
Cr ³⁺	28.472	2.0177	0.017561	0.8875
Pb ²⁺	1.5929	60.975	0.0103	0.9004
Fe ²⁺	41.254	2.416	0.010033	0.9251
Ni ²⁺	26.688	2.15	0.017424	0.9781
Cu ²⁺	4.3956	12.12	0.01877	0.9956
Cd ²⁺	7.7558	33.8	0.005417	0.8311
Hg ²⁺	0.6774	69.93	0.0211	0.8412

4.2.Freundlich adsorption equations

It is one of the important isothermal equations used in the case of adsorption from a solution. This equation was developed by the German scientist Herbert Max Finaly Freundlich in 1926 [55]. Since most surfaces are heterogeneous, that is, the potential energy changes are irregular, and the reason for this is that the adsorption sites occur at different energy levels Which leads to a change in the adsorption isotherm. Therefore, the Freundlich equation was developed to represent the change in the amount of the adsorbent per unit area or mass of the adsorbent with the equilibrium concentration. The first use of the Freundlich equation is to describe the adsorption of the gas phase and the adsorption of solute from the solution. The Freundlich equation can be written as follows

$$Q_e = K_F C_e^{1/n} \dots\dots\dots(9)$$

. Where: Q_e: the amount of solute adsorbed

C_e: concentration of the solution at equilibrium.



n, K_F: Freundlich constants.

The linear equation takes the following form:

$$\ln Q = \ln K_F + \frac{1}{n} \ln C_e \dots\dots\dots(10)$$

When plotting log Q_e against log C_e, we get a straight line with a slope equal to 1/n, and its intersection equals the value of log K_F.

It is worth noting that the most important defect in the Freundlich equation is that it does not show the maximum limit for adsorption. The Freundlich equation applies more to cases of adsorption of solutions on heterogeneous surfaces than the Langmuir equation [58,60,61,63].

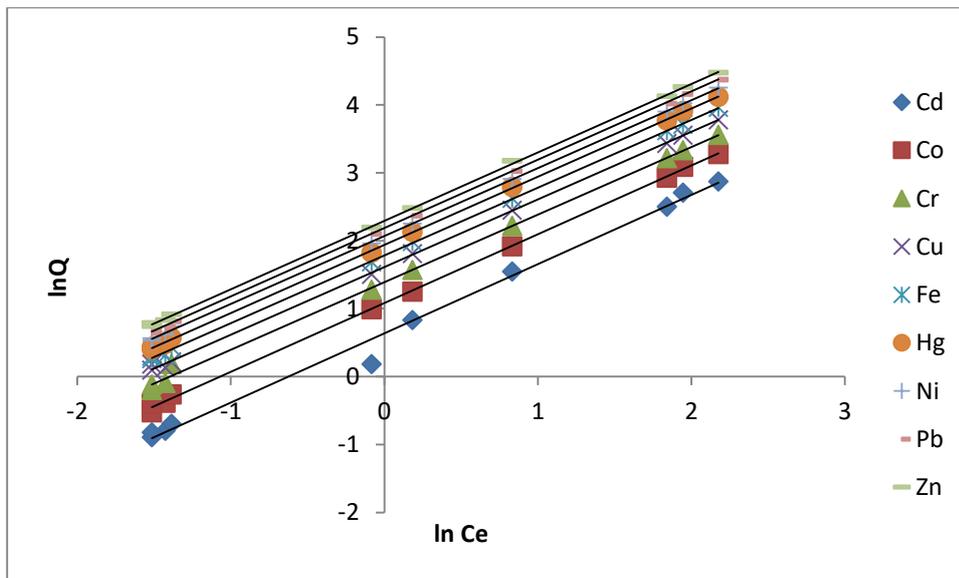
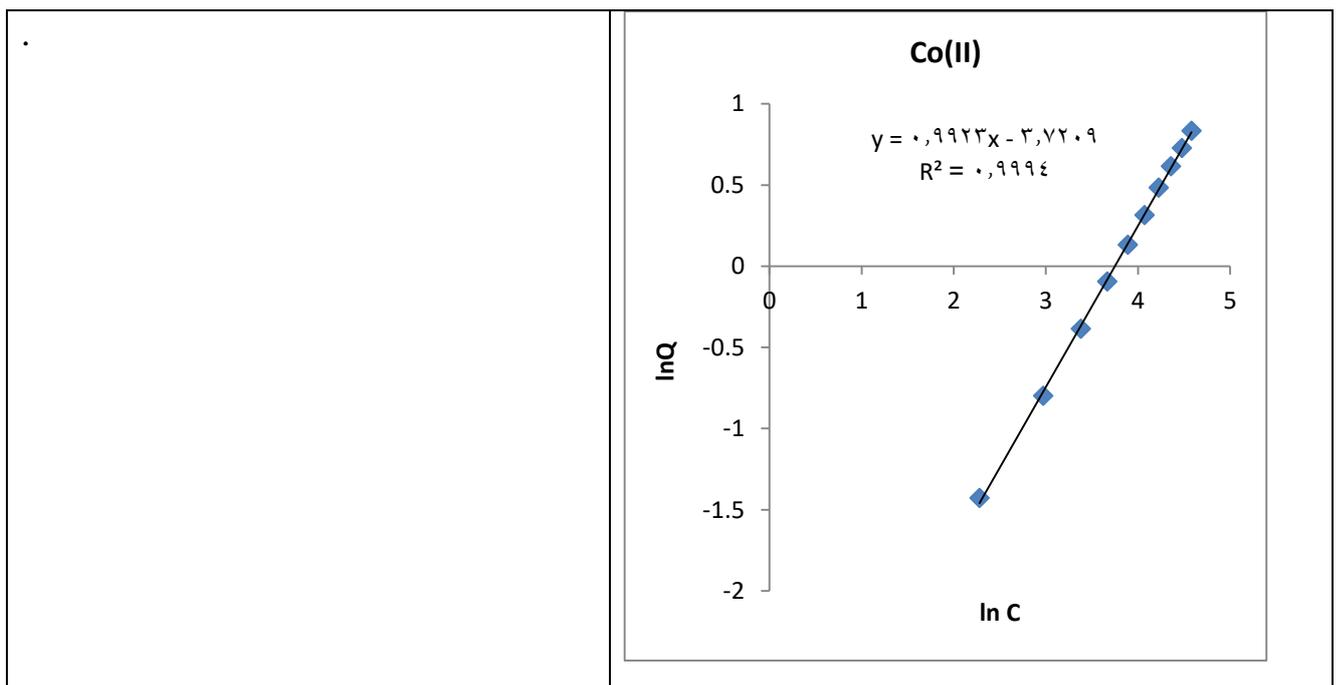
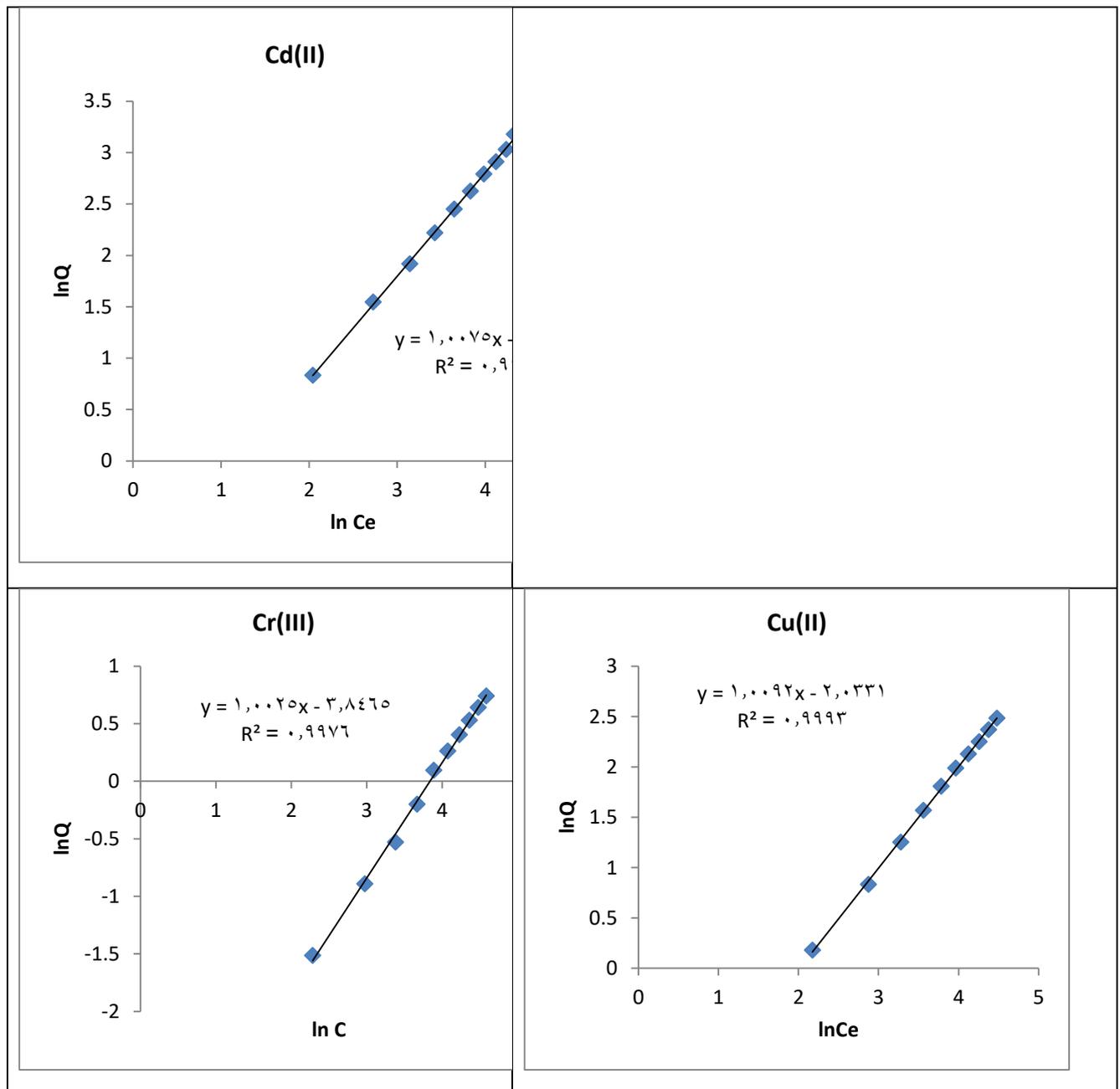


Fig.7. Fig. 5. Plot of ln Q vs. ln Ce Freundlich Adsorption of heavy metals on Rice Husk Ash





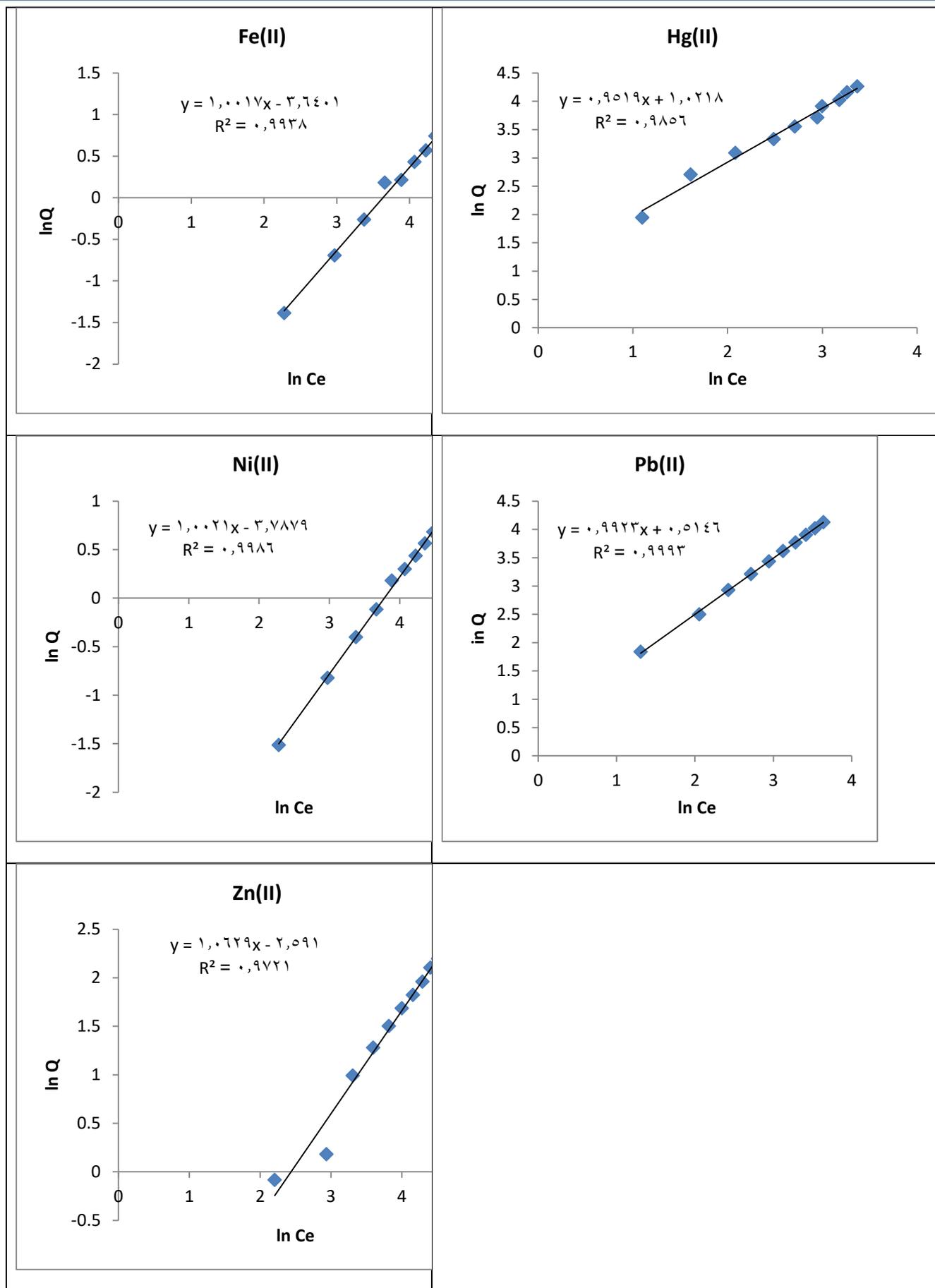




Fig.8. Fig. 5. Plot of $\ln Q$ vs. $\ln C_e$ Freundlich Adsorption of heavy metals on Rice Husk Ash

Table (5) Freundlich constants for adsorption of heavy metal ions on rice husk ash

Heavy ion	n	k_f
Zn ²⁺	0.94082	0.075
Co ²⁺	1.00776	0.0242
Cr ³⁺	0.9975	0.021354
Pb ²⁺	1.00776	1.673
Fe ²⁺	0.998303	0.2625
Ni ²⁺	0.99791	0.022643
Cu ²⁺	0.99088	0.1309
Hg ²⁺	1.05053	2.77812
Cd ²⁺	0.99255	0.2935

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