Adsorption of some Metal Ions from Aqueous Solution on Iraqi Rice Bran and Its Relation to the Physical Properties of these Metal Ions

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Abstract:

Adsorption studies were carried out to test the ability of the Iraqi rice bran (Amber type) to adsorb some metals divalent cations (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) as an alternative tool to remove these pollutants from water. The Concentrations of these ions in water were measured using flame and flamless atomic absorption spectrophotometry techniques. The applicability of the adsorption isotherm on Langmuir or Freundlisch equation were tested and found to be dependent on the type of ions. The results showed different adsorptive behavior and different capacities of the adsorption of the ions on the surface of the bran. The correlation between the amounts adsorbed and different cation parameters including (electronegativity, ionic radius, and the second ionization potential) were tested. This study showed the applicability of bran, as a cheap and available waste materials, to remove different cations from solution.

Key words: Adsorption, Rice Bran, Cadmium, Copper, Cobalt, Iron, Nickel, Lead, Zinc.

Introduction:

Adsorption has been used for sequestering the heavy metals from aqueous solutions [1,2]. Many types of adsorbents have been studied for the adsorption of different metals ions solutions [3,4]. Biomass of different origins are known to be capable of sequestering and concentrating heavy metals from aqueous environment. A number of investigations has shown that different metal ions can bind to the cell walls of bacteria [5] fungi [6] and algae [7]

The use of dead biomass for the removal of heavy metals from aqueous solution has been widely studied in the recent years[8] .Dietary fiber is mainly composed of plant cell walls which vary in composition and properties according to the cell type and plant species. In addition to polysaccharides, the walls of some plant cell types contain the hydrophobic polymers lignin or suberin that may produce surface activity[9]. One of these important dietary fibers is rice bran from rice *Oryza sativa L*. It is a by-product of making polished rice from brown rice . Therefore ,rice bran is very cheap , costing about 1 /50 of activated carbon cost . In addition , the use of rice bran is significant from the aspect of effective utilization of waste matter [10.11] .

Biosorption of heavy metals ions is an alternative technology to remove these pollutants from aqueous solutions using inactive and dead biomasses such as agricultural and industrial wastes , algae and bacteria [12] .These alternative methods have been proved to be less expensive than physicochemical processes . They do not need nutrients and are resistant to

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the physicochemical properties of heavy metal solutions[13]. In one study olive milled solid residue was used as a heavy metals adsorbent for its cellulosic matrix ,rich of potential metal binding active sites [12] .The results in many studies indicated that biosorbents are very effective for heavy metals removal in the presence of light metal ions in wastewater[14] .

Experiments were conducted comparing the individual biosorption removal of Cd and Cu from water using Scenedesmus abundans , common green algae . It was shown that , while both living and non-living Scenedesmus .abundans removed Cd and Cu from water ,living algae significantly outperformed non-living algae[15] .

The term adsorption isotherm refers to the relation between the extent of adsorption (Qe) or (X/M) with the equilibrium concentration of the metal ion in solution (Ce) at constant temperature . (X) is the amount of metal adsorbed in milligrams by (M) grams of adsorbent[16]. Two main theories have been adopted to describe adsorption isotherms. The first ,Langmuir adsorption isotherms which is represented by the equation :

$$Ce/ Qe = 1 / ab + Ce / a \quad \text{-------(1)}$$

(where a and b are constant)

The applicability of these equations on the adsorbent – adsorbate system assume the formation of one layer of adsorbate molecules on the surface while the Freundlisch adsorption isotherm consider heterogeneity of the surface and the formation of more than one layer is probable . The linear form of Freundlisch isotherm is :

$$\text{Log } Qe = \log K + 1/ n \log Ce \quad \text{-----(2)}$$

This work deals with the adsorption extent of different metal ions on rice bran and the effects of the physiochemical properties 0f metals on the adsorption process .

Materials and Methods:

Commercial rice bran *Oryza sativa L.* was obtained from the local market . It was cleaned , washed with excessive amounts of water , and dried at 50 ^{o}C for two hours and kept in an airtight container . Fifty milligrams of dried rice bran were mixed with 10 ml of each of the following solutions ($CuSO_4 .5H_2O$, $Co(NO_3)_2$, $Pb(CH_3COO)_2$, $FeSO_4$, $ZnCl_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$) (Reidel de Haen) at the following concentrations : (0 , 5 , 10 , 20 , 40 , 60 , 80 and 100 mg / l) . Acidity of the solutions was adjusted to obtain pH = 7, using few drops of 0.1 M HCl or 0.1 M NaOH solutions . The mixtures were shaken using thermostated shaker bath at room temperature (24 ^{o}C) and speed of 60 cycle / minute for 30 minutes. This time was measured experimentally as a time needed for reaching the equilibrium state. After the equilibrium time was elapsed, the mixtures were centrifuged at a speed of 3000 rpm for 10 minutes. The samples then analysed for their ions concentrations after suitable dilution using atomic absorption spectrophotometer (Schimadzu AA-646) with an air –acetylene flame . Hollow cathode lamps were used at the maximum wave lengths and working conditions for each metal supplied by the manufacturer .

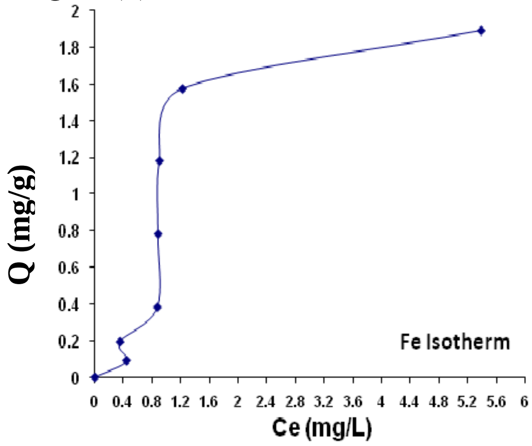
Metal ion adsorption extent (Q) in mg/g was calculated using the following formula :

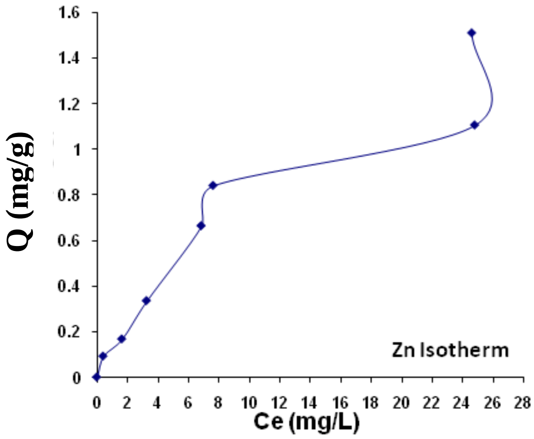
$$Q = V (C_0 – C_e) / M \quad \text{------(3)}$$

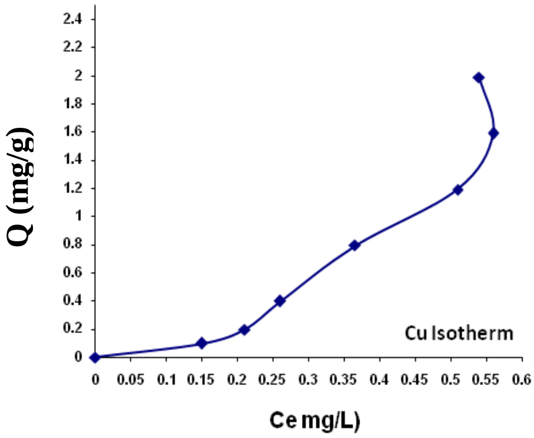
Where C_0 and C_e are the initial and equilibrium metal ion concentration (mg/L) in the solution respectively . (M) is the weight of the rice bran in grams and (V) is the solution volume in liter. Each experiment was repeated three times and the mean value of these results was taken.

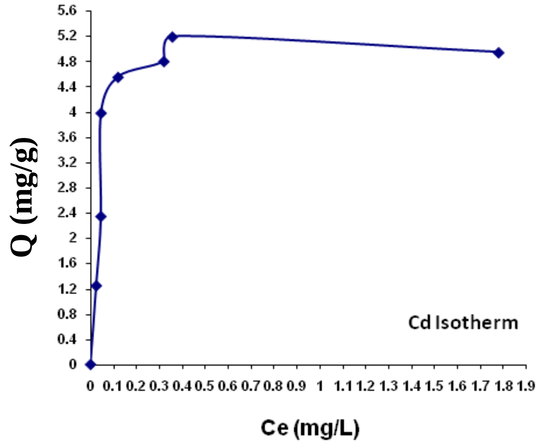
Results and Discussion:

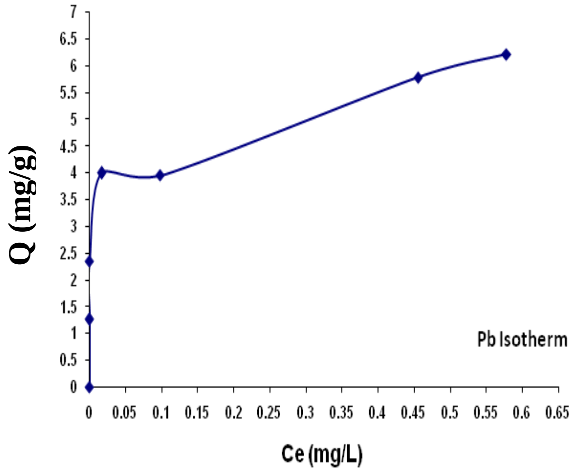
The adsorption isotherms for all the metal ions on rice bran are shown in Figure (1).

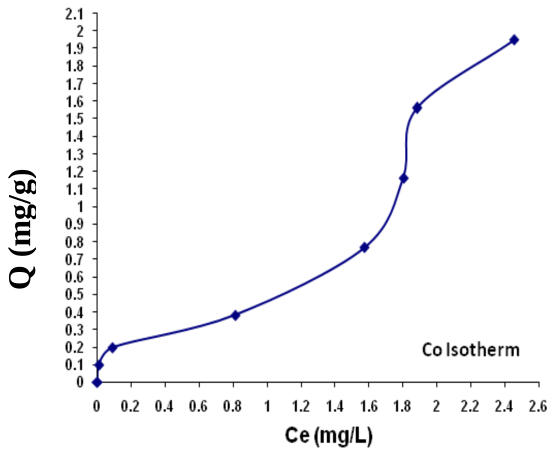












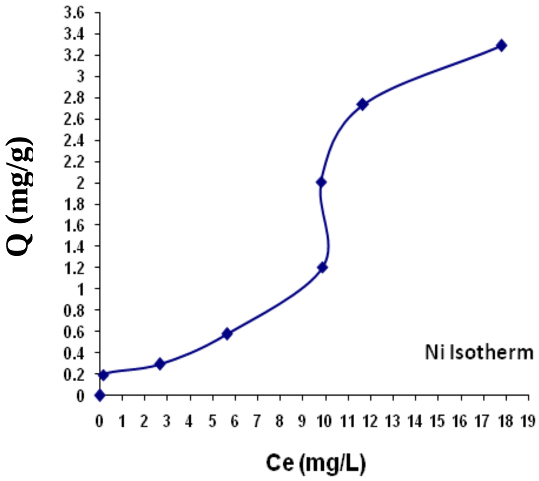


Fig. (1): Adsorption isotherms of Co, Cd, Cu, Fe, Ni, Pb, and Zn metal ions from aqueous solution at 25°C

The applicability of Freundlisch or Langmuir equations for the adsorption isotherm of each metal were examined using the linear form of each equation and the highest correlation coefficient determine whether the adsorption process occur according to Freundlisch or to Langmuir equation . If the r-value of the linear form of equation of one metal is larger than the r-value obtained from the other, then the equation that has a higher r-value was applied . the values of (r) after the application of the two equations are listed in Table (1) . The type of adsorption process according to Gile's classification [17] was obtained and listed in Table (2) . The maximum quantities of ions adsorbed are given in Table (3) .

Table (1): Correlation Coefficients of the linear form of Freundlisch and Langmuir equations.

Metal	r-Value from Freundlisch Equation	r-Value from Langmuir Equation
Cobalt	0.58	0.92
Cadmium	0.29	0.44
Copper	0.91	0.55
Iron	0.60	0.68
Lead	0.64	0.95
Nickel	0.76	0.98
Zinc	0.74	0.94

Table (2): adsorption isotherm types according to Giles Classification.

Metal	Type of isotherm according to Giles Classification
Cobalt	L4
Cadmium	L2
Copper	S3
Iron	L2
Lead	H2
Nickel	L4
Zinc	L3

Table (3): The Maximum quantity adsorbed by each gram of rice bran.

Metal	Maximum quantity adsorbed by each gram of rice bran Qe (mg/g)
Cobalt	1.95
Cadmium	4.95
Copper	1.99
Iron	3.69
Lead	7.4
Nickel	3.29
Zinc	1.51

From the results in Tables (1) and (2) , it can be concluded that cobalt,lead ,nickel and zinc ions ,obeyed Langmuir equation , while the adsorption of copper obeyed Freundlisch adsorption isotherm. Cadmuim and iron do not obey either of these two equations .It can be supposed that biosorption phenomenon occur by a general ion exchange mechanism combined with a specific complexation reaction for copper ions . Moreover ,a preliminary investigation of the active sites, showed the presence of two different site affinities depending on the metal concentration, according to the hypothesis of two kinds of uptake mechanisms for metal ions biosorption[12] .

Adsorption of copper ions obeyed Freundlisch adsorption equation indicating that the forces that are responsible for adsorption are heterogeneous depending on the concentration of metal ions. Adsorption isotherms of Co and Pb were of H-type which indicates strong forces between these metal ions and rice bran surface. The adsorption at low concentrations of Co and Pb was almost complete . In one study[18] ,the metal interaction with the cellular structures of the marine algae have been investigated for better understanding of the adsorption of dissolved metals by biomaterials . Copper was efficiently sorbed by the algae sites, and the binding affinity order of these metal ions was $Cu^{+2} > Cd^{+2} > Co^{+2}$

These results are different from those obtained in this study using rice bran which could be attributed to the differences in the structure and active sites on the surface of rice bran in addition to the differences in the affinities of metal ions to the specific sites. The order of the capabilities of the ions to adsorb on the surface of rice bran was as follows:

$Pb^{+2} > Cd^{+2} > Fe^{+2} > Ni^{+2} > Cu^{+2} > Co^{+2} > Zn^{+2}$

This order of ions adsorption can be explained by the solubility factor i.e.,the less soluble is the most adsorbed and vice versa . This finding is very important in the pollution with Pb and Cd because these metals are very toxic when compared with other metals (under study). Therefore their adsorption on cheap adsorbents is of economic and health importance.

Adsorption investigation of metal competition for the algae binding sites suggested the presence of carboxylate , amino , and hydroxyl groups[19] .

It was found that the carboxyl groups in the structure of polysaccharides present within the algae matrix display high sorption capacity for lead and copper . The negative surface charge of algae particles results in an electrostatic interactions and coordination between the metal ions and adsorbent surface [20] .

The metal uptake is dependent on the type of biosorbent with different accumulation affinities towards the tested elements . The rate of the uptake of the different metals was fast in the first two hours ; after that the increase in metal uptake was insignificant [18] .

The adsorption forces may include other processes different from adsorption such as complexes formation or precipitation of insoluble complexes on the surface of algae. The mechanism involved in Cd accumulation on Tetraselmis chuii was restricted to surface phenomena, while on Spirulina maxima Cd was accumulated on different layers of the surface [21] .

Regarding the nature of the surface , other results indicated that the adsorption of metal ions occurred on the surface active sites that approximately have identical energy and geometry [22]. However, the homogeneity of the biomass surface is unlikely if the structure of rice bran is taken into consideration. The body of rice bran consists of long filaments of cellulose and linan arranged end to end and characterized by high surface area per unit of weight due to the very low density of the bran. Moreover, the facts about the structure exclude the homogeneity of the active sites, but there is a good indication that the major fraction of the active sites has narrow ranges of energy and same affinity towards ions .

To explain the results in Figures (2) ,(3) and (4) for the adsorption quantities according to the physical properties of the adsorbed ions . It can be seen that there is a positive correlation between the maximum quantities adsorbed (Q) and each of the ionic radius and electronegativity . At the same time there is a negative correlation with the second ionization energy. The strongest correlation was with the electronegativity. The correlation coefficients of these parameters were 85.1 , 68.8 , and 60.7 respectively . Results in Figures 2 ,3 and 4 indicate also that there is an electrostatic interaction between some of the biomass cell components and metal ions and there is an effect of steric interaction (concluded from the ionic radius correlation) between metal ions and the active sites on the surface of biomass cells . Energy of ionization also has an effect on the adsorption process . However , the picture of the forces that control the adsorption of metal ions on plant surfaces still needs more work to clarify .

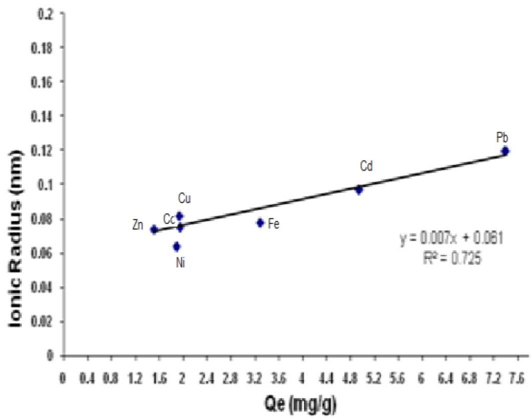


Fig. (2): Correlation between the maximum quantity adsorbed (Q) and second ionic radius of the metal used.

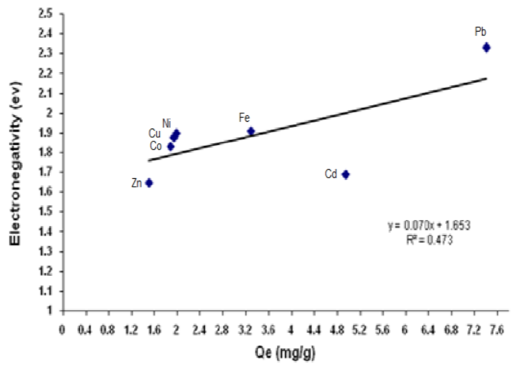


Fig. (3): Correlation between the maximum quantity adsorbed (Q) and ionic electronegativity of the metal used.

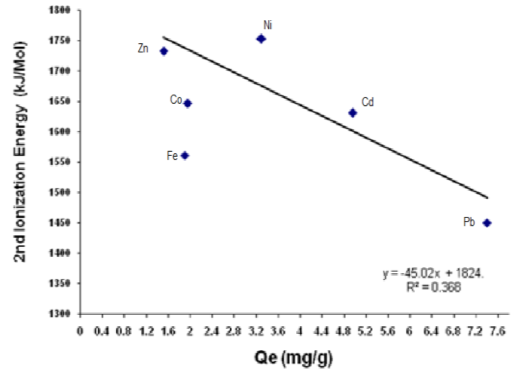


Fig.(4): Correlation between the maximum quantity adsorbed (Q) and second ionization energy of the metal used

So the main conclusions can be achieved from the results of this study are :

The adsorption of these cations is directly proportional to their ionic radius and electronegativity , but negatively proportional to their second ionization energy . It can be concluded also that the less soluble cation in aqueous solution is the more adsorbed one .

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امتزاز ايونات بعض المعادن من محاليلها المائية على سطوح نخالة الرز العراقي وعلاقته ببعض الخواص الفيزيائية لهذه الايونات

سمير محمود جاسم

*قسم الكيمياء والكيمياء الحياتية / كلية الطب / جامعة النهرين

الخلاصة:

اجريت دراسة الامتزاز هذه لمعرفة قابلية نخالة الرز العراقي (نوع العنبر) على امتزاز ايونات بعض المعادن الملوثة للماء(Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+})
تم قياس تراكيز الايونات باستعمال مطياف الامتصاص الذري . تشير النتائج الى ان خضوع امتزاز هذه الايونات الى معادلات لانكماير او فرندلج يعتمد على نوع الايون وان الكميات الممتزة من هذه الايونات وسلوكيات امتزازها تختلف باختلاف تلك الايونات . كما تمت دراسة العلاقة بين كميات الايونات الممتزة وبعض الخواص الفيزيائية لتلك الايونات مثل السلبية الكهربائية ، انصاف اقطار الايونات و جهود التاين.
اظهرت الدراسة امتلاك نخالة الرز لقابلية جيدة في ازالة هذه الايونات الملوثة من الماء.