ADSORPTION OF COPPER ON SURFACES OF FEASIBLE MATERIALS (PLANT WASTE, SLUDGE AND BENTONITE) METAL)

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ABSTRACT

Extraction of Copper ion from its water solutions using plant waste (compost), sludge and Bentonite metal as cheap natural adsorbed materials. It was found that Copper ion extraction was based on concentration of Copper and amount of the adsorbed materials. Highest amount of adsorption was obtained at 180 µg Cu ml^{-1} as Bentonite, plant waste and sludge respectively. Thermal equilibrium of the system was studied by Langmuir equation, R^2 gave a good linear relationship in succession. Maximum regulatory capacity and regulatory capacity at equilibrium is 1.0 , 0.99 and 0.96 to plant waste, sludge and Bentonite respectively, as the preference coefficient constant calculated by the Langmuir equation indicate that adsorption is preferable and irriversible for plant waste and sludge while not preferentially and reversible for bentonite. ∆G adsorption reactions were automatic for the Bentonite metal, while for plant waste and sludge non-spontaneous reaction and needs extra activation energy. It is clear from the above that the use of natural materials in the extraction of copper ion is a very effective method and it is an inexpensive and friendly methods enviroomen t.

Keywords : preference coefficient, ∆G for adsorption reactions, natural adsorbents.

مجلة العلوم الزراعية العراقية -2022 :53(3):654-659 الحياني واخرون

امتزاز النحاس على سطوح مواد رخيصة الثمن (مخلفات نباتية والحمأة ومعدن البنتونايت)

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المستخلص

تم دراسة استخلاص أيون النحاس من محاليله المائية باستخدام مخلفات النباتات (كمبوست) والحمأة ومعدن البنتونايت كمادة مازة طبيعية رخيصة الثمن. وجد أن استخلاص أيون النحاس يعتمد على تركيز أيون النحاس وكمية المادة المازة ، إذ تم الحصول على أعلى كمية إمتزاز عند التركيز 180 مايكروغرام Cu مل $^{-1}$ مع استخدام معدن البنتونايت ثم المخلفات النباتية ثم الحمأة. تم دراسة الاتزان الحراري للنظام باستخدام معادلة لانجماير ، إذ أعطى النظام معامل تحديد (R^2) علاقة خطية جيدة بلغ 1 و 0.99 و0.96 للمخلفات النباتية والحمأة ومعدن البنتونايت بالتتابع مما يدل على ملائمة النموذج للنظام تحت الدراسة.، إذ يشير ثابت معامل التفضيل المحسوب بواسطة معادلة لانجماير إلى أن الإمتزاز يكون مفضلاً وغير عكسي بالنسبة للمخلفات النباتات والحمأة بينما غير مفضل وعكسي للبنتونايت ، للنظام المدروس. كانت الطاقة الحرة (∆G) لتفاعلات الإمتزاز لمعدن البنتونايت تلقائية ، بينما كانت تفاعلات المخلفات النبات والحمأة غير تلقائية وتحتاج إلى طاقة تنشيط إضافية. مما سبق يتضح أن استخدام مواد مازة طبيعية في استخلاص أيون النحاس تعد طريقة فعالة جدا ، ومن مميزاته أنه يعتبر من الطرق غير المكلفة والصديقة للبيئة.

الكلمات المفتاحية: معامل التفضيل، الطاقة الحرة لتفاعلات الإمتزاز (∆G)، المواد المازة الطبيعية

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INTRODUCTION

Water pollution caused by industrial and human activities is considered as one of the major problems in the world, as it is the leading cause of 80% of diseases worldwide (7), and due to United Nations Organization reports , there is almost 1.1 billion people that can not get potible water mostly from poor and developing countries (1). There are thousands of chemical compounds that are discharged daily directly or indirectly to water sources without any treatment (16). Among these substances are the most dangerous and harmful heavy metals, even when present and in low concentrations, because they accumulate inside living tissues (14,17). Some heavy metals such as Iron, Copper and Zinc are necessary to maintain vital activities in living organisms, while Others, such as Lead and Cadmium, play no role in these activities and are therefore classified as toxic elements, but at high concentrations, all heavy elements, whether necessary or unnecessary, cause toxicity to organisms (6). There are many methods used to remove heavy metals such as chemical deposition, membrane separation, ion exchange, liquid extraction, electrodialysis, and adsorption (15,18, 10) . The use of powders such as activated Carbon, Silica, Alumina, etc., is excellent in removing heavy but costly elements and their manufacturing process is accompanied by the production of environmental pollutants, leading to the use of alternative materials (natural powders) that are available in large quantities or unused or present in wastes (13,19) . Therefore, much research is conducted on various types of natural materials that have proven to be effective in extracting heavy metals (Bentonite and Silicate clay minerals) and many organic materials (3,4,5, 11) . The use of plant residues (compost), sludge and Bentonite is considered a natural mezzanine, as it is a cheap material for the recovery of heavy metals, including Copper ion. To this end, plant residues (compost), sludge and bentonite were used to study their ability to extract this ion from their aqueous solutions as a method used to treat copper-contaminated water and solutions and to determine the maximum adsorption capacity and binding capacity of the adsorbed ion.=

MATERIALS AND METHODS

Preparation of the material

Plant waste (compost), sludge and Bentonite were used as natural adsorbents as their properties are listed in tables 1 and 2 .

Table 1. Some chemical properties of some environmental media

environmental media	pH	EC dS m^{-1}	% Water holding capacity	N	P	K
Plant waste(compost)	7.2	4.8	680	1.44	0.31	0.97
Sludge	7.9	1.8	140	0.98	1.36	0.52

Table 2 . Metal composition of Bentonite

Total	L.O.I	Fe_2O_3	Na_2O	K_2O	MgO	CaO	Al_2O_3	SiO_2	constituent
99.66	12.49	5.12	1.11	0.60	3.42	4.48	15.67	56.77	% W

Chemical treatment

Media samples (plant waste, sludge and bentonite) were taken, dried, grinded, passed through a sieve of 2 mm opening diameter, a mass of 2 g was taken from each sample, and placed in a 50 cm^3 centrifuge tube and 6 copper nitrate levels added ($Cu(NO_3)_2.3H_2O$) are 60, 80, 100, 120, 140 and 180, at a ratio of 1: 10 (the volume of the added solution 20 cm^3) and with three replicates, (copper concentrations were prepared using 0.03 standard of calcium nitrate ($Ca(NO_3)_2.4H_2O$), as an electrolytic solution to reduce changes in Ionic strength). The tubes were shaken by an electric shaker for 6 hours at 25°C. The balanced solution was separated from the centrifuge precipitator at a speed of 3000 rp m^{-1} for 10 minutes. The concentration of copper in 10 cm^3 of the equilibrium solution was determined by using an atomic absorption device(C_{in}, and final concentration (C_{fin}, µg ml^{-1}), in each flask

$$Cu^{2+} - ad. = \frac{V(C_{in} - C_{fin})}{W} \quad ... (1)$$

Where:

Cu^{2+}-ad. : Amount of copper adsorbed in µg g^{-1}, V: volume of copper solution in flask in ml, W: dry weight of adsorbent in g. The adsorption results and the equilibrium concentrations of the copper ion were subjected to linear formulas of the Langmuir single-surface equation in order to obtain the adsorption criteria (maximum adsorption capacity, binding capacity, maximum regulatory capacity, regulatory capacity at equilibrium, free energy and preference factor.

$$\mathbf{X = \frac{KbC}{(1 + KC)}} \dots (2)$$

Where:

X: the amount of copper adsorbed in µg g^{-1} soil, C: represents the copper concentration in the equilibrium solution in µg ml^{-1}, and b: represents the maximum adsorption in µg g^{-1} and K: the binding factor of the element on the soil surface. energy coefficient in ml $µg^{-1}$unit.

The values of constants are calculated after plotting the relationship between C / X values and C values to get a straight line, so the slope of the line is 1/b, and the intersection with the y-axis Intercept is 1/Kb.

$$\mathbf{\frac{C}{X} = \frac{1}{Kb + C/b}} \dots (3)$$

Maximum Buffering Capacity (MBC)

This value is expressed mathematically by multiplying the maximum adsorption capacity of the surface (Xm) in the binding energy (K) of the Langmuir equation, which is a characteristic of ion adsorption. The Langmuir equation, as noted by Yassen & Fakher (20) and Al-Hassoon *et al*. (4,5), are as follows:

$$\mathbf{MBC = \frac{dx}{dc} = (K\,Xm)} \dots (4)$$

Equilibrium Buffering Capacity (EBC)

It expresses the gradient of the adsorption curve when the ion concentration in the solution approaches a certain concentration, and is mathematically represented by the tangent slope of the adsorption curve at this concentration in the Langmuir equation.

$$\mathbf{EBC = \frac{K\,Xm}{(1 + KC)^2}} \dots (5)$$

Thermodynamic parameters

The preference coefficient (separation) (RL) was calculated from the following equation:

$$\mathbf{R_L = \frac{1}{(1 + K_L)C_0}} \dots (6)$$

where:

K_L = binding energy, and C_0 = copper concentration in the equilibrium solution.

The Preference Factor (ΔG) was calculated from the following equation (Woodruff Equation :

$$\mathbf{\Delta G = -RT \ln K} \dots (7)$$

where:

ΔG: free energy (kJ mol^{-1} $kelvin^{-1}$), R: constant gases, T: absolute temperature (kelvin), K: binding energy.

RESULTS AND DISCUSSION

Results in Table 3 indicate the effect of the concentration of the primary copper ion added and its concentration in the dynamic equilibrium solution in plant waste (compost), sludge and bentonite metal. This table shows that there is a steady increase in the amount of copper in the equilibrium solution with the added primary concentration. Average concentration of copper followed the arrangement of :

Sludge > Plant waste > Bentonite

The reason for the low concentration of copper balanced with bentonite is due to the high capacity of this metal in the adsorption of copper because it has a large surface area working to draw the largest amount of added concentration and thus the reduction of residual (18).

Table 3. Copper Concentration in Dynamic Equilibrium Solution

Primary Copper added µg ml^{-1}	Copper concentration in dynamic equilibrium solution µg ml^{-1}		
	Plant waste	Sludge	Bentonite
60	0.2146	0.4986	0.0584
80	0.2960	0.5947	0.0649
100	0.3626	0.7487	0.0766
120	0.6756	0.8957	0.0881
140	0.7007	1.065	0.0922
180	0.7990	1.2228	0.1004
Aevrage	0.5081	0.8376	0.0801

Effect of the initial concentration of copper ion on the amount adsorption

The results show in table 4 reveal that the adsorption of the adsorbent increased with the concentration of the added Copper solution. This indicates that there are a large number of active sites on the surface of the adsorbent (responsible for adsorption of the ion), therefore, the removal of Copper ions from the solution of plant waste and sludge continues until the filling of all these sites, and the maximum adsorption at a concentration of 180 µg ml^{-1}, Bentonite and plant waste and sludge reached 1799.00,1792.01 and 1787.77 µg g^{1}.

Table 4. Amount of Copper adsorbed on the materials used

Primary Copper added µg ml^{-1}	The amount of Copper adsorbed on the materials used µg g^{-1}		
	Plant waste	Sludge	Bentonite
60	597.85	595.01	599.42
80	797.04	794.05	799.35
100	996.37	992.51	999.23
120	1193.24	1191.04	1199.12
140	1392.99	1389.35	1399.08
180	1792.01	1787.77	1799.00
Average	1128.25	1124.96	1132.53

Study of thermal equilibrium

The study of thermal equilibrium of the adsorption process is important to understand how the dissolved material is linked to the adsorbent in order to determine the best conditions in which the substance is adsorbed. Copper grabs and retains more in plant waste and Bentonite due to the high affinity of Copper to adsorped on its compared with sludge

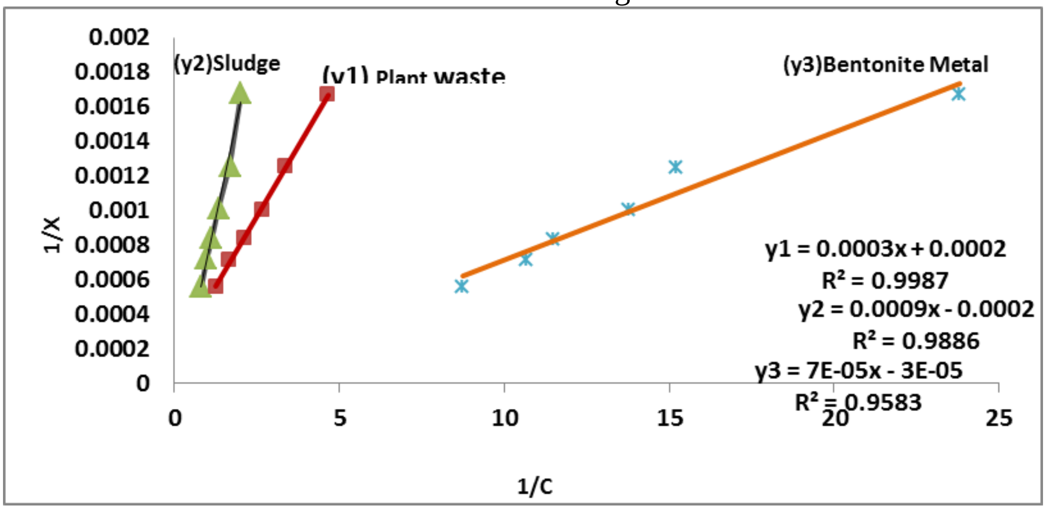

Figure 1. Langmuir 's linear equation for thermal equilibrium on Copper

The Langmuir equation assumes that the maximum adsorption occurs when the primary layer is saturated with solute ions. Constants are as follows: The highest binding capacity of sludge was 4.5 µg g^{-1}, the maximum adsorption capacity of Bentonite 2000000 µg g^{-1}. is shown in table 5, and the highest determination coefficient (R^2) for plant waste was 1.00, as shown in Figure 1, but generally represents good linear relationship to sludge and Bentonite as well (2).

Table 5. Thermal equilibrium constants in the Langmuir equation for Copper adsorption on Plant waste, sludge and Bentonite

Tre.	Bonding energy ml µg^{-1}	Maximum adsorption µg g^{-1}(X_m)	determination coefficient R^2
Plant waste	1.5	3333.33	1.00
Sludge	4.5	1111.11	0.99
Bentonite	0.0001	2000000	0.96

Maximum regulatory capacity (MBC) and regulatory capacity at balance (EBC) : Table 6 shows the maximum regulatory capacity and the regulatory capacity at equilibrium for Copper. The maximum regulatory capacity values for plant waste, sludge and Bentonite were 4999.995, 4999.995 and 200 ml μg^{-1} respectively. Regulatory capacity values for plant waste, sludge and Bentonite were 1610.216, 218.818 and 200 µg g^{-1} respectively. The difference in the regulatory capacity values between the adsorbents is due to the different adsorption nature of Copper, and the variation of the maximum adsorption values and the binding energy at the high energy sites caused the ion readiness difference at the different locations of the adsorption curve, as copper adsorption does not differ in nature on all adsorbent surfaces, but the difference is in the nature of the adsorbent surface. The binding of the ion in such materials clearly means that it is easily released from the adsorption surfaces into the solution, causing increased diffusion rates of this ion and subsequent increased absorption by the plant (7). Li *et al*. (9) explained the importance of MBC values in describing soil contamination by Lead and other heavy metals and that increasing their values indicates that the ionic adsorbent type of the heavy element has a low binding capacity, which facilitates its movement and migration (Heavy Metals Migration) towards the depths of the soil and on the type of heavy element and its movement in the soil.. The soil has a self-purification capacity and high regulation capacity to cope with pollution.

Thermodynamic standards

The main advantage of Langmuir equation is to calculate the preference constant (RL), which can be calculated from the equation, as its value gives a good indication of the nature and form of adsorption. If its value is greater than 1, this indicates that adsorption is not preferred, and adsorption is linear if its value is 1, and adsorption is preferred if its value is between 0- 1, and adsorption is not reversed if its value is 0. Through this study and by applying Langmuir equation, it was found that the value of the preference coefficient constant for plant residues, sludge and Bentonite 0.78, 0.22, 12.50, respectively, which indicates that adsorption is preferable and non-reversible for plant residues and sludge, unfavorable and inverse for Bentonite for the studied system. . Table 6 also shows that the adsorption reactions were spontaneous with Bentonite, indicating that the free energy value was negative and that the reaction was negative while the free energy values of Copper adsorption of plant waste and sludge were shown. It clearly shows that this reaction is not automatic and requires additional activation energy, and that these values are in line with the values of the preference factor (separation coefficient, R_L) (20).

Table 6. Maximum regulatory capacity, regulatory capacity at equilibrium, free energy and preference factor

Tre.	MBC (ml μg^{-1})	EBC (ml μg^{-1})	ΔG KJ mol^{-1} $Kelvin^{-1}$	R_L
Plant waste	4999.995	1610.216	0.06	0.78
Sludge	4999.995	218.818	0.21	0.22
Bentonite	200	200	-1.30	12.48

Achnowledhment

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