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POSSIBILITY OF UTILIZING FROM LEMON PEEL AS A SORBENT IN REMOVING OF CONTAMINANT SUCH AS COPPER IONS FROM SIMULATED AQUEOUS SOLUTION

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ABSTRACT

The potential of natural an inexpensive material as lemon peels was assessed to sorption of copper ions from simulated aqueous solution. Using batch system to study Copper sorption, where the influence of some parameter on sorption process was studied such: pH; contact time; lemon peels amount, and temperature. Equilibrium, kinetic and thermodynamic was assessed. Optimum pH was 6.0; efficiency of removal was 94.84%. Experimental data is processed more satisfactorily with Freundlich model. Thermodynamic analysis has shown that sorption is spontaneous, favorable and exothermic nature. This sorption process was well assessed by a pseudo-second-order process. Addition, analysis of Fourier Transfer Infrared Spectroscopy (FTIR) indicates that Copper reacts with metal oxides and -OH functional group found in lemon peel. These results suggest that this peel can be utilized as a valuable, non-costly sorbent in removing copper from simulated aqueous solution.

Key words: Copper, Sorption, Lemon peel, FTIR, Temperature, Freundlich model.

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1. INTRODUCTION

Currently, one of the most important problems facing humans is environmental pollution. It was increased dramatically in the last few years and reached dangerous levels that threaten living organisms. The term heavy metal points to any chemical element with a comparatively high density and be toxic or poisonous at low concentrations [1].

In environment, located of heavy metal ions from the chain of transmission, like a: Cu; Cd; Ni, and Pb, is the main anxiety because of its toxicity to forms of life [2]. Discharge of heavy metals through water cause harmful effects on health of human, as well as on the environment [3, 4]. Since they are non-degradable, they accumulate inside of organisms, and cause many disorders and diseases.

Addition, minerals presence in unreasonable amounts, due of their toxicity, is contrary to the profitable use of water. Thus, it is necessary to find a way to dispose of heavy metals in wastewater before they are thrown into the environment [3, 4].

Copper is one of the minerals found in the soil at a concentration of about 50ppm, which found in all plants and animals; is a basic food ingredient for humans and animals in small quantities. In environmental, the principle copper sources involve: mining, smelting and refining; manufacture of produced copper-products like a: wires, combustion of fossil fuel, and pipes. Pipes of water are frequently formed of copper; bathing equipment can be form of copper and alloys of bronze containing copper. The main copper source in drinking water occurs as a result of the copper leakage of pipes and fittings of the bath due to acidic water. The remaining blue and green spots on the fixtures of bathroom are a proof of the copper existence in the water [3, 5].

Another copper source in environment is agricultural using versus diseases of plant and treatments utilized to water bodies in order to dispose of algae. From all of above, the copper concentration must be elimination to sensible level through the treatment of effluent from industrial wastewater prior to disposing into river [5].

High quality water is absolutely necessary to life of human; also water with reasonable quality is important for domestic; agricultural; commercial, and industrial uses. From all above, it was observed that all these activities are responsible for water pollution. Every day huge quantities of waste are dumped from these sources into fresh water. The need of water is increasing as all resources of water slowly become unusable because of inappropriate disposal of waste [1]. The mission of providing suitable treatment facility for all sources of contaminated is hard and costly, so there is an urgent need for innovative, low-cost technologies that require low maintenance and energy efficient. Mostlly, the use of different techniques is effective to remove heavy metals from water and wastewater [6, 7, 8]; from these, sorption is efficient and economical [6]. Considered sorption onto activated carbon is a preferable method has been widely utilized in the past few years. Because of the urgent requirement to this treatment to be economic, the researchers intensified their efforts to finding and developing inexpensive alternatives available from various industrial, natural and biological materials or residues [6].

Many researchers utilized numerous of fruit peel as a substitution of activated carbon due to it is high-priced. The use of agricultural-residues as sorbent is attracting attention on large scale because of the availability of large amounts, also a low-prices and belong to the fact that high particulate carbon content and existence of particle structure. The influence of sorbent material depends largely on its biochemical composition, in particular on functional groups in cell wall polysaccharides. Carboxyl groups may have an active function in sorption of metal by algal sorbents [9, 10]. Pectin, a polysaccharide of cell wall of the top plants, is predominantly based on galacturonic acid, contains a considerable number of carboxyl groups; has a familiar capability to contain bi-valence cations. Thus, a material rich in pectin, like citrus peels, from the pectin is removed commercially, has a high natural capability to bind the metal. A many of products rich in pectin have been considered in capabilities to bind metal involve: waste of apple; pulp of sugar beet; orange and banana peels; citrus peels and husks of coffee, and various fruit materials, like a various kinds of citrus peel [9, 10]. This study provides the capability of utilize a natural waste as sorbent such as lemon peels; and its ability to sorption copper in simulated aqueous solution.

2. MATERIALS AND METHODS

2.2. Chemicals and Materials

To obtain a sample of simulated aqueous solution containing the desired concentration of copper which used in this study; by dissolving a specific weight of $CuSO_4.5H_2O$ in distilled water. The mass of these metals was calculated to achieve the desired concentration according to equation (1) assuming total disintegration [11]:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \quad (1)$$

Where: W= heavy metal salt weight (mg); V= solution volume (L); C_i= metal ion concentration in solution (initial) (mg/L); M.wt= molecular weight of metal salt (g/mole); and wt= atomic weight of metal ion (g/mole).

2.2. Apparatus

Atomic Adsorption Spectrometer (AAS) (GBC 933 plus, Australia) that utilized to calculate the soluble copper concentrations. Batch experiments to find optimum values of parameters in this process were executed in 250ml flasks with volume of 100ml at 200rpm in an incubator cum orbital shaker (Heidolph, No.549-59000-0-0, Germany).

2.3. Sorbent Preparation

A biosorbent which used in the removal of copper ions is lemon peel; collected from local juice market. In order to remove surface impurities washed with distilled water; then dried for 24hr at 105°C by oven removing the moisture content. Finally, this dried peel milled and sieved (particles sizes≤0.6mm).

2.4. Sorption Experiments

Batch experiments executed to find the optimum pH; amount of lemon peels; contact time; temperature; equilibrium and kinetics isotherms. Influences of all these factors identified while keeping other variables constant. Synthetic solutions about100ml with concentration of copper 50 mg/L was added into flask with different quantities of lemon peels changing between 0.5 and 2.5g. Adjustments of pH executed by 0.1N HCl, and 0.1N NaOH; then stirred a solution at 200rpm in a predetermined period of time. At ending of agitation time sorbents filtered (Whatman 70mm filter paper) and metal contents of solution were analyzed by AAS.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Lemon Peel

Analysis of FTIR spectral is essential to define the properties of functional groups on the sorbent surface; these are in charge of copper ions sorption. FTIR spectrum of lemon peel has listed to get the information related the stretching and bending vibrations of the functional groups which are include in the adsorbate molecules sorption; which shown in Figure 1a before and Figure 1b after copper sorption. Peak at 3387, 2943.37; 1732.06; 1620.21; 1508.33; 1450.47, and 1373.32cm^{-1} may be assigned to existence of alcohol hydroxyl group (-OH) and acidic hydrogen group (-OH) stretching respectively [12]. This finding indicates that copper reacts with the metal oxides and the functional -OH range found in the lemon peel.

3.2. Effect of pH

Essential parameter which plays role on process of sorption is pH; to study the effect of this parameter in this experiment: 50ppm of copper (II) in 100ml were used; with pH range about (2-10). Put an initial amount of sorbent to all flasks (1gm) with 200rpm agitation speed for 1h at room temperature. The result of efficiency in Figure 2 appears the excess percentage removal with pH raises; lowest sorption was noticed at low pH. A higher concentration and higher mobility of H^+ ions that prefer sorption as compared to M(II) can be indicated; whereas acidic is medium due to high solubility and support of metal ions, the sorbent surface becomes more positively charged with high H^+ concentration such that the attraction between sorbents and metal cations decrease. Conversely, when pH is increased the negatively charged surface area becomes more then facilitates greater metal removal and then at very high pH also decreases in the removal ratio [13].The maximum sorption was achieved at pH 6 (Re% = 87.74) which could be as a partial hydrolysis of metal ions. More increase in pH i.e., above 8 of the solution causes precipitation of metal ions on the surface of the adsorbent by nucleation [14]. The same behavior was noticed by L.F 2016 [3] and Firaset. al.,2015 [13]. To obtain high extraction efficiency without deposition of metal hydroxide, pH6 for Cu(II) was selected for subsequent experiments.

3.4. Effect of Lemon Peels Quantity

The quantity of sorbent is one of the substantial criteria for obtaining a quantity of metal ion. The effect of amount executedby varying the banana peels amount (0.5-2.5g), whereas the other parameters as: pH 6, initial metal concentration 50mg/l, agitating time 2h and stirring speed 200 rpm stayed remain. As the sorbent amount increased sorption of metal ions increased, too. This was predictable because the increasing concentration of the catalyst provides greater concentration on the surface area or the absorption site, for a constant initial concentration of metal [3, 12, 13]**.** The higher removal efficiency was achieved by using 2.0g/100ml sorbent dosages (Re% = 94.64) (Figure 3).

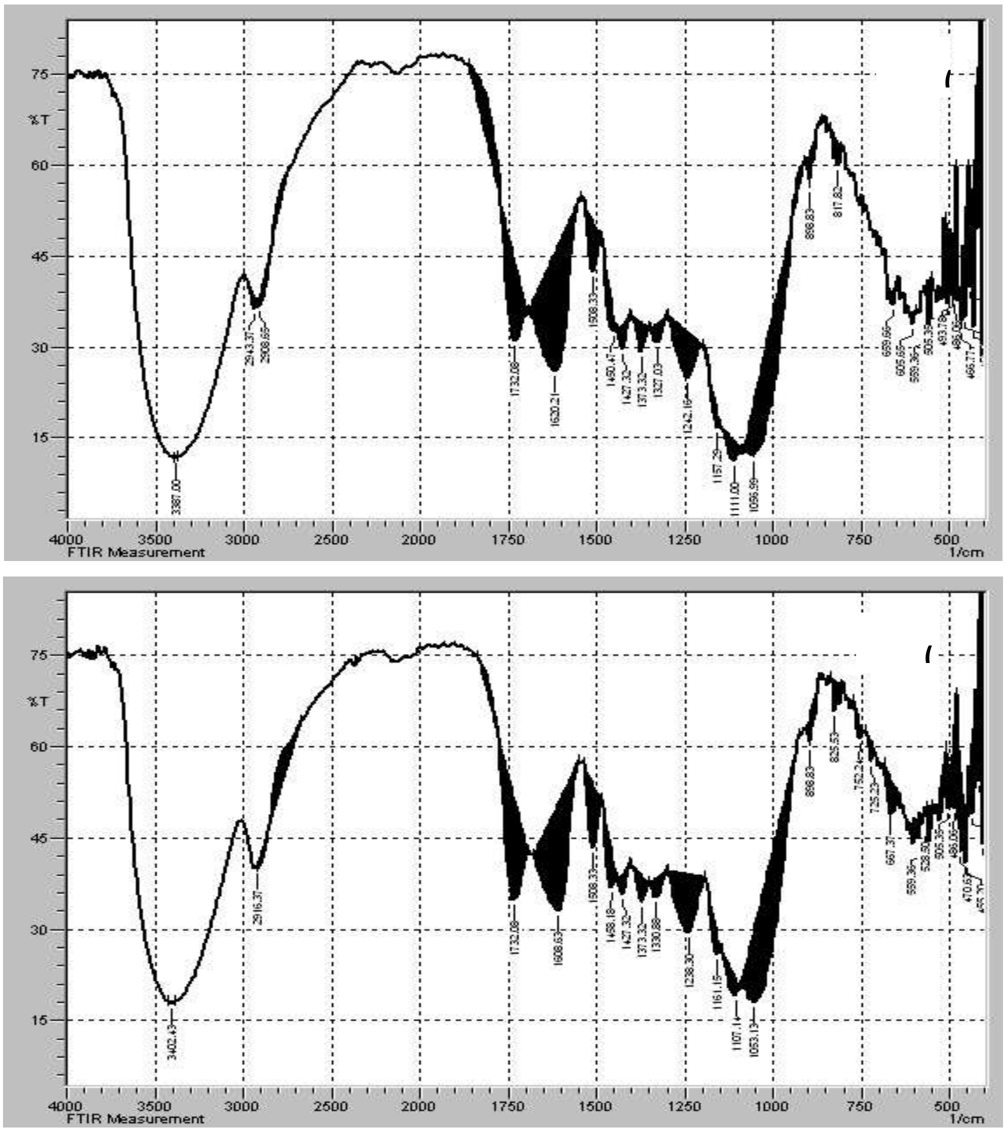

Figure 1 FTIR spectrums of lemon peels (a) before; (b) after

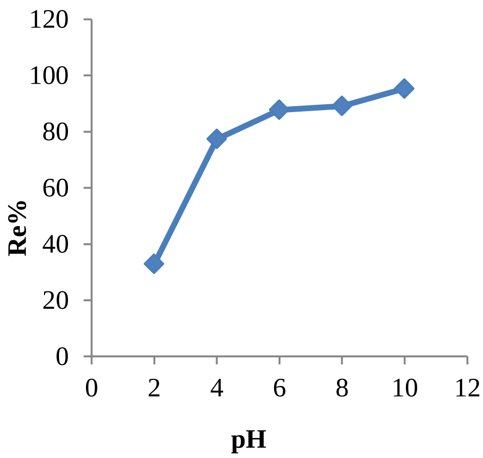

Figure 2:Effect of pH on of Cu (II) uptake.

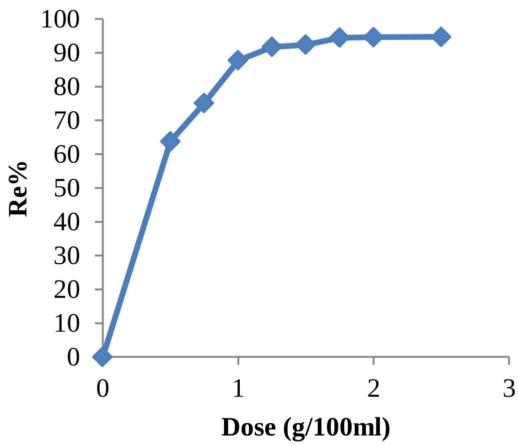

Figure 3: Effect of sorbent dose on Cu (II) uptake.

3.4. Effect of Contact Time

Removing of copper ions increases over time and reaches saturation within 90min. the effect of this parameter was studied with taking 2.0g sorbent with 100 ml of a metal solution in various flasks; vibrating at different period of time. Figure 4 appears contact time effect on the removal rate of copper ions, the removing of sorbate is fast, but step by step decreases over time till it reaches equilibrium. The metal ratio removal is initially higher because of the availability of a considerable surface area for the metals sorption. The binding sites after brief period of time become limited and it is difficult to take the remaining vacant surface positions by copper ions due to the formation of the centrifugal forces between the copper on the solid surface and the liquid phase [3, 14, 15].

3.4. Effect of Temperature and Thermodynamic Parameters

The temperature effect of copper uptake on banana peel was executed by taken 50mg/L of initial metals ion concentrations at 298, 308 and 318 K (25, 35, and 45 ^{o}C); when increasing the temperature ratio, the ratio of heavy metals increased, that means that sorption process was endothermic in nature. The results are plotted in Figure 5.The thermodynamic parameters were calculated by these equations below [16] [17]:

$$lnK_d = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad \text{... (2)}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ} T \quad \text{... (3)}$$

Where K_d is coefficient of distribution; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant (8.314 J/mol K) and Gibbs free energy change ΔG^0. These parameters are presented in **Error! Unknown switch argument.** and Table **2**, respectively.

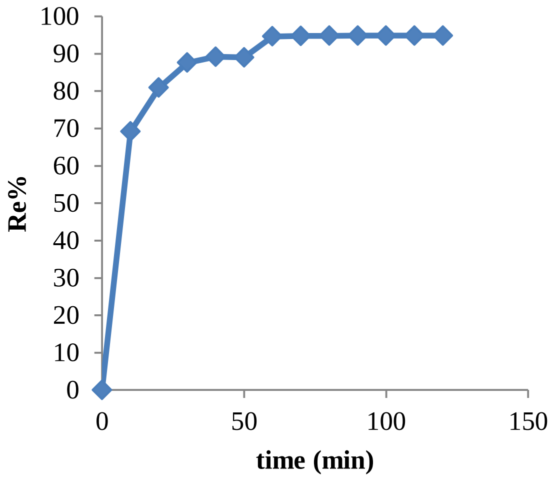

Figure 4: Effect of time on Cu (II) uptake.

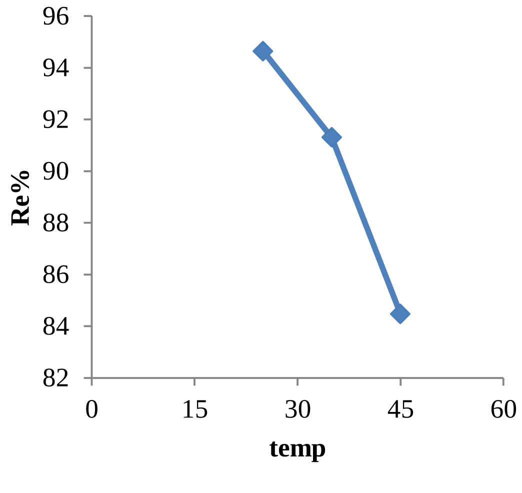

Figure 5:Effect of temperature on of Cu (II) uptake.

In Table 2 various calculated thermodynamic parameters, using the above-mentioned relationships (eqs. 2, and 3); shown negative value of ΔH refers to the exothermic nature of the sorption process. The negative value of ΔS refers to a larger order within the sorption process. This may explained by the fact that within the sorption procedure the co-ordinate molecules of water which displayed by copper ions achieve less translational entropy than is wasted by copper types, leading to a decrease in randomization. A similar negative entropy change has also been reported elsewhere (Unnithan et al., 2002 [18], and Sunil et ai., 2010) [15]. Moreover, this result indicates that the low temperature prefers to remove copper molecules by sorption onto lemon peel as the process of sorption is exothermic in nature. The reduction in removing because at high temperature the thickness of the boundary layer decreases because of high trend to the molecules to get-away from the surface of sorbent to the solution phase, lead to low capacity of sorption as temperature is increased [19]. Comparable results were noticed before by Sunil et ai., 2010 [15].

Table 1 The distribution coefficients at various temperature.

Metal	k_d			R^2
	298k	**308k**	**318k**	
Copper(II)	17. 65672	10.49425	5.435006	0.992

Table 2 The parameters of thermodynamic of adsorption of Cu(II) ions on banana peel.

Metal	**ΔH(J/mol)**	**ΔS (J/mol K)**	**ΔG(kJ/mol)**		
			298K	**308K**	**318K**
Copper(II)	-46.3339	-131.361	39.0993	40.41292	41.72653

3.5.1. Isotherm Models

Langmuir and Freundlich models were applied to establish sorption-activity. Sorption-isotherms estimate the relation between the pressure stabilization or concentration and adsorbate amount which adsorbed by the adsorbent unit mass at a constant temperature. The model of Langmuir is [16, 20]:

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \quad (4)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the highest ability of sorption for monolayer coverage (mg/g), b is the constant related to attraction of binding site (L/mg), and C_e is metal ions concentration in the solution at balance (mg /L). And Freundlich model is [16, 20]:

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad \text{(Linear form)} \quad (5)$$

Where: K= constant indicate that proportional sorption ability of the adsorbent (mg/g), 1/n = constant expressive of the strength of the adsorption (both K and n be expressive at range of adsorption and at grade of nonlinearity between solution and concentration, respectively). The results of both models are presented in Table 3.

Table 3 Langmuir, Freundlich isotherms Parameters

Langmuir model	**Copper (II)**	**Freundlich model**	**Copper (II)**
R^2	0.875	R^2	0.911
q_m(mg/g)	7.407	1/n	1.639
b (1/mg)	0.221	K (mg/g)(l/mg)$^{1/n}$	1.239

3.5.2. Kinetic Models

Adsorption mechanism of dye is explained by the adsorption kinetics models; these are pseudo-first-order and pseudo-second-order. Studies of these models show the behavior of sorption of dye on egg-shells; the pseudo-first order and pseudo-second order-models, respectively [17, 20]:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \quad (7)$$

Where q_{eq} and q_t (both in mg g^{-1}) are the amount of dye adsorbed at equilibrium and at time correspondingly. K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the kinetics rate constants for the pseudo first- and second order-models, correspondingly. Table 3 showed the results below:

Table 3 Values of kinetic models.

Metal	$q_{eexperimental}$ mg/g	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	$q_{e\ calculated}$ mg/g	R^2	k_2g/mg.min	$q_{e\ calculated}$ mg/g	R^2
Copper	2.371	-0.086	1.972	0.889	0.1399	2.439	0.997

4. CONCLUSIONS

The function of lemon peel as a available sorbent in removing copper from simulated aqueous solution by batch technique was evaluated. pH 6.0 chosen as optimum value with equilibrium time of 90min; the best fit with the Freundlich isotherm model was provided. Sorption kinetics followed pseudo-second-order model. Analysis of thermodynamic indicates that the procedure was a spontaneous and exothermic in nature. This study indicates that lemon peel is inexpensive as a waste material obtainable in the world; as well it may supply an easy, efficient and low-cost way to remove copper form polluted water.

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