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Research Article

A new low-cost activated carbon produced from tea-industry waste for removal of Cu(II) ions from aqueous solution: Equilibrium, kinetic and thermodynamic evaluation

Ali Gundogdu[1]*, Hasan Basri Senturk[2], Celal Duran[2], Mustafa Imamoglu[3], Mustafa Soylak[4]

[1]*Department of Food Engineering, Faculty of Engineering and Natural Sciences, Gümüşhane University,Gümüşhane,Turkey*
[2]*Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey*
[3]*Department of Chemistry, Faculty of Arts & Sciences, Sakarya University, Sakarya, Turkey*
[4]*Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey*

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ABSTRACT

In this study, a new activated carbon was produced by chemical activation using H_2SO_4 from the wastes generated during black tea production, and its adsorption performance was tested for removal of Cu(II) ions from aqueous solution. A low-cost activated carbon with high adsorption capacity was produced using only a simple laboratory oven without needing a high cost inert atmosphere-carbonization furnace. The adsorption of Cu(II) ions from aqueous solution on the activated carbon was investigated in terms of equilibrium, kinetics and thermodynamics. After the batch mode adsorption tests, the initial solution pH was optimized to 5.0 and the agitation time to 4.0 hours. The adsorption kinetics of Cu(II) ions on activated carbon were fitted with the pseudo-second order kinetic model, and the Freundlich isotherm model was more compatible with experimental data. It was determined that Cu(II) adsorption capacity of the activated carbon was 28.30 mg g^{-1} from the linear Langmuir isotherm, and the adsorption capacity was increased by almost 50% by increasing the temperature from 5 to 40 ^{o}C. From the results, it was proven that the activated carbon produced from tea-industry waste at almost zero cost, which has no use in any field and discharged as waste to the environment, can remove Cu(II) ions from wastewaters with very high performance.

TR

Sulu çözeltiden Cu(II) iyonlarının uzaklaştırılması için çay fabrikası atıklarından üretilen düşük maliyetli yeni bir aktif karbon: Denge, kinetik ve termodinamik değerlendirme

Anahtar Kelimeler:
Aktif karbon,
çay fabrikası atığı,
adsorpsiyon,
Cu(II) iyonları

ÖZ

Bu çalışmada, siyah çay üretimi esnasında ortaya çıkan atıklardan sülfürik asit kullanarak kimyasal aktivasyonla yeni bir aktif karbon üretildi ve sulu çözeltiden Cu(II) iyonlarının uzaklaştırılması için adsorpsiyon performansı test edildi. Yüksek maliyetli bir inert atmosfer-karbonizasyon fırınına ihtiyaç duyulmadan sadece basit bir laboratuvar fırını kullanarak yüksek adsorpsiyon kapasiteli ve düşük maliyetli bir aktif karbon üretildi. Sulu çözeltiden Cu(II) iyonlarının aktif karbon üzerinde adsorpsiyonu denge, kinetik ve termodinamik açıdan incelendi. Çalkalama modunda yapılan adsorpsiyon testlerinden sonra başlangıç çözelti pH'sı 5.0'a ve çalkalama süresi 4.0 saate optimize edildi. Aktif karbon üzerinde Cu(II) iyonlarının adsorpsiyon kinetiği yalancı ikinci mertebeden kinetik modele uyduğu ve Freundlich izoterm modelinin de adsorpsiyon verileriyle daha uyumlu olduğu tespit edildi. Doğrusal Langmuir izoterm modelinden aktif karbonun Cu(II) adsorpsiyon kapasitesinin 28.30 mg g^{-1} olduğu ve sıcaklığın 5 ^{o}C'den 40 ^{o}C'ye yükselmesiyle adsorpsiyon kapasitesinin neredeyse %50 oranında arttığı belirlendi. Bu sonuçlardan, her hangi bir alanda kullanılmayan ve çevreye atık olarak boşaltılan çay endüstrisi atıklarından neredeyse sıfır maliyetle üretilen aktif karbonun, sulu çözeltiden Cu(II) iyonlarını yüksek performansla uzaklaştırabileceği kanıtlandı.

1. Introduction

Activated carbon is a terminological name given to highly porous amorphous materials which can not be characterized by any structural formula or chemical analysis. Activated carbon is a unique adsorbent that is widely used to purify harmful components from gas and liquid solutions, remove color and odor, separate and concentrate for quantitative recovery, and filter. These abilities of activated carbon are due to its high surface area, microporous structures and high surface activity [1].

One of the application areas of activated carbon is, of course, the use as an adsorbent in removal of organic or inorganic pollutants from aqueous media. For this purpose, it is possible to find hundreds of studies in the literature. The adsorption capacity of activated carbon is not only explained by the pore structure, but also by the chemical nature of its surface. The structure of activated carbon contains single atoms and/or many heteroatoms (oxygen, hydrogen, nitrogen and others) in the form of functional groups. Oxygen is the dominant atom in the carbon matrix [2]. Among these surface oxides, the most common are: carboxyl groups, phenolic groups, lactone rings, quinone type building blocks, cyclic peroxides and carboxylic acid anhydrides [3].

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*Corresponding author: a.ramazan.gundogdu@gmail.com
+90 4562337425

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Activated carbon is produced in inert environment (N_2) at temperatures between 500 and 1000 ^oC, simultaneously or sequentially with carbonization and activation processes. The porous structure of activated carbon is provided by activation followed by carbonization [4,5]. There are two types of activation methods to achieve porous and high surface area activated carbon: physical and chemical activations. In physical activation, the surface area of the carbonized structure is expanded using gases such as water vapor or CO_2 following carbonization [6]. In chemical activation, both carbonization and activation are applied simultaneously. Chemical agents such as $ZnCl_2$, KOH, HNO_3, H_3PO_4 and H_2SO_4 are used in the activation process [7–9].

Today, commercial activated carbons are widely used in many areas. All solid raw materials with sufficient carbon in the structure, readily available and low cost can be used in the production of activated carbon. In addition to natural solid raw materials such as coal, wood, fruit husks, coconut and hazelnut shells, a variety of polymer-based synthetic raw materials are also used in the production of activated carbon [10].

Since commercial activated carbons are high cost adsorbents, their effective use is therefore limited. For this reason, production of activated carbon has become widespread in recent years with cheap, effective and different characteristics from agricultural wastes. Agricultural wastes which are lignocellulosic materials, contain three basic structural components; cellulose, hemicellulose and lignin. For this purpose, activated carbons with high porosity and high capacity can be produced from a wide range of agricultural waste by-products such as apricot, almond, cherry and olive seeds, hazelnut, peanut, walnut and various barks.

In this study, a very low-cost activated carbon was produced from waste tea generated during black tea production by chemical activation using H_2SO_4. The removal performance of the activated carbon produced in this work for Cu(II) ions from aqueous solution was assessed from equilibrium, kinetic and thermodynamic aspects. Copper has been preferred as an adsorbate in this work because of its use as a model metal in adsorption studies and its toxic effects at high levels. Many agricultural by-products converted to activated carbon have been used for removal of Cu(II) ions from aqueous phase [11–15].

Copper is actually one of the essential minerals for the body under 1 mg/L in drinking water. Copper is necessary for enzymes which are responsible for renewal of body tissue and stability of bone structure. Copper mineral, which plays a role in energy production and protein synthesis, also contributes to the formation of red blood cells. It is essential for nervous system health and is an important mineral in terms of protection of hair and skin health. On the other hand, overdose of copper can lead to serious mental and physical disturbances such as depression, schizophrenia, dementia, hypertension as well as increased risk of cancer. The sources of copper metal ions at toxic levels are mainly the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard and wood preservative-employing mills, the fertilizer industry, etc. [16–18].

Tons of tea wastes are released from green tea-processing plants in Turkey every year during the production of black tea. Since these wastes can not be evaluated for another purpose, they are discharged directly to the environment or are maybe used as fertilizers. By producing activated carbon from these wastes, their economical recovery will make this work very meaningful. A further advantage of this study is the elimination of environmental pollutants by the activated carbon produced from these wastes.

2. Materials and Methods

2.1. 2.1. Instrumentation

A flame atomic absorption spectrometer (FAAS), ATI Unicam AA-929 (Solar System Analytical Technology, England), was operated for determination of Cu(II) concentration in aqueous solution, having a single element-copper hallow cathode lamp and 10 cm burner head in air/acetylene gas flow. It was also operated under the conditions recommended by the manufacturer. The selected wavelength for copper was 324.8 nm.

Batch mode adsorption experiments were performed by using a mechanical shaker, Edmund Bühler GmbH (Germany). The pHs of the solutions was adjusted with a digital desktop pH meter having a glass combined electrode (HANNA instruments/Romania, model 211). pH meter was first calibrated with buffer solutions (pH 4.0 and 7.0) before use. An ultrapure water system with pre-treatment, arium® 611VF (Sartorius AG, Germany), was used in all adsorption tests.

2.2. Chemicals and solutions

The chemicals used in this study were of analytical purity and obtained from Merck (Darmstadt, Germany) and Fluka (Darmstadt, Germany). The salt copper(II) nitrate trihydrate, $Cu(NO_3)_2{\bullet}3H_2O$, was used for preparing 1000 mg L^{-1} Cu(II) stock solution. Working solutions were prepared by diluting this stock solution at appropriate ratios for using in adsorption tests. 0.1 mol L^{-1} HCl and NaOH were used for adjusting the pH of Cu(II) working solutions.

2.3. Tea-industry waste and production of activated carbon

Tea-industry waste (TIW) used as a starting material (precursor) in the production of activated carbon was obtained from tea factories in Of, Trabzon-Turkey. The tea wastes were dried at 105 °C for 20 hours and stored in a desiccator.

20 g of TIW was taken and thoroughly mixed with 20 g of concentrated H_2SO_4. The mixture was left in an oven set at 200 ^oC for 24 hours. The carbonized sample was thoroughly washed with boiled pure water to remove any acid residues. The resulting activated carbon (TIW-AC, Tea-Industry Waste – Activated Carbon) was then treated with 1% $NaHCO_3$ for 24 hours to completely neutralize the acid residues. TIW-AC was filtered and then thoroughly washed with ultrapure water and finally dried at 105 °C for 24 hours. The obtained TIW-AC was used after grinding to a particle size of <150 µm [9, 19–21].

TIW-AC produced in this study was produced without needing for any high cost carbonization furnace. The cost of activated carbon produced using a simple oven available in every laboratory is also very low.

2.4. Characterization

Activated carbon produced from TIW was characterized by various parameters: Proximate-ultimate, the surface acidic functional groups, pH–pHpzc (point of zero charge), SEM (Scaning electron micrograph), BET surface area and pore structure, FT-IR and MB (Methylene Blue)–Iodine numbers analyses. Detailed information for characterization has been given in our previous work [9], and additional information, figures and tables were also given in the supporting information (SI) file (Table S1 and Fig. S1 and S2).

2.5. Adsorption test

In this work, Cu(II) ions were prefered as an adsorbate in order to test the asorption performance of TIW-AC from aqueous solution. Copper is often used as a model adsorbate to test the performance of any adsorbent in adsorption studies. Thirty mg of TIW-AC was weighed into a series of polypropylene tubes with a volume of 15 mL. 10 mL of 100 mg L^{-1} Cu(II) solution having initial pH adjusted between 2–12, were separately added into the tubes. After agitating tube contents on a mechanical shaker (Edmund Bühler GmbH, a max. speed of 400 rpm) for 12 h at room temperature, they were filtrated through 0.45 µm nitrocellulose membrane.

From the concentrations of adsorbate remained in the filtrate (Ce), the metal contents were measured by FAAS. Adsorption percentage (%) was calculated by following formula (1), subtracting equilibrium concentration (Ce) from initial concentration (Co).

$$\text{Adsorption}\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

The quantity of Cu(II) adsorbed by one g of TIW-AC was determined in mg g^{-1} by the following equation:

$$q_e = \frac{(C_o - C_e)\times V}{m} \tag{2}$$

Each test was performed for three times and the mean values of the results are presented in this work.

2.6.Adsorption kinetics

The time dependence of the adsorption process is called adsorption kinetics. The time-dependent kinetic events of adsorption process are as follows: (i) the adsorbate ions or molecules are diffused to the boundary of the film layer on the adsorbent surface, (ii) the adsorbate travels towards the pores of the adsorbent, (iii) the adsorbate travels through the pore spaces of the adsorbent to reach the adsorption surface and (iv) adherence of the adsorbate to the pore surface of the adsorbent.

Many equations have been derived to explain adsorption kinetics. These are the most commonly used ones; pseudo-first order kinetic model, pseudo-second order kinetic model and intra-particle diffusion kinetic model.

Pseudo-first order kinetic model was introduced by Lagergren in 1898 [22]. This model does not apply to the total duration of adsorption in most cases. It can usually be applied for the first few minutes of the adsorption process, that is, when the equilibrium has not yet been reached [23]. The kinetic equation of this model is as follow:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{3}$$

If the equation is integrated according to the boundary conditions; $t = 0$, $q = 0$, $t = t$ and $q = q_t$, the equation becomes linear as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) indicate adsorbate quantities retained on the adsorbent at equilibrium and at time t, respectively. k_1 (min^{-1}) is the pseudo first-order rate constant. ln(qe–qt) vs t graph is linear and gives an idea about whether the kinetic model is compatible with the adsorption data. q_e and k_1 can be found from the intercept and slope of the linear graph.

Pseudo-second order kinetic model, in contrast to pseudo-first order kinetic model, is compatible with the mechanism of rate control step during the entire adsorption process. Pseudo-second order kinetic model is estimated by the following formula [24]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

When this equation is rearranged, becomes a linear equation as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{6}$$

k_2 (g mg^{-1} min^{-1}), is the rate constant for pseudo second order kinetic model. If a plot of t/qt versus t is linear, it indicates the compatibility between kinetic data and pseudo-second order model. q_e and k_2 can be easily determined from the slop and intercept of the linear graph, respectively.

If the diffusion mechanism cannot be clearly explained by pseudo-first and pseudo-second order equations, intra-particle diffusion model may be applied to the kinetic data. The equation of intra-particle diffusion model is as follow:

$$q_t = k_{id} t^{1/2} + C \tag{7}$$

k_{id} (mg g^{-1} $min^{-1/2}$) is here the rate constant for intra-particle diffusion, and C (mg g^{-1}) is a constant number that characterizes the boundary layer thickness. The values k_{id} and C can be determined from the slope and intercept of a graph plotted between q_t and $t^{1/2}$. Multilinear lines can be obtained from the graph of q_t versus $t^{1/2}$. The first sharp line in the graph indicates film diffusion and/or adsorption. The second line is the further step of adsorption, that is, the part where the intra-particle diffusion is the rate control step. The third part shows that the adsorption process has been reach the equilibrium position, and intra-particle diffusion in this step starts to slow down because the concentration of the solution decreases considerably [25,26]. If the intercept (C) representing the intra-particle diffusion in the second part passes through the origin, it is cocluded that the adsorption rate is only controlled by intra-particle diffusion. If it does not pass through the origin, it can be said that the adsorption process has more complex mechanism and the rate is probably controlled by more than one mechanism [27–29].

2.7. Adsorption equilibrium

Adsorption equilibrium is expressed by adsorption isotherms. At constant temperature, the relationship between the adsorbate concentration (Ce) remaining in the aqueous solution after reaching the equilibrium and the adsorbate amount (q_e) adsorbed per unit weight of the adsorbent is known as adsorption isotherms. Adsorption continues until equilibrium is established between the concentration of the adsorbate on the surface of the adsorbent and the concentration of adsorbate remaining in the solution. If the system temperature is kept constant, a graph showing the equilibrium state between Ce and q_e can be plotted. This graph is the adsorption isotherm [30].

The most well-known approaches for expressing adsorption isotherms with mathematically suitable formulas are Langmuir, Freundlich and Brunau-Emmet-Teller (BET) isotherms. To understand which adsorption process is better represented by which isotherm, a graph is drawn after applying the experimental data to all isotherm equations. The isotherm type in which the data form a linear graph and the correlation coefficient R^2 is greater than 0.95 is the most suitable for that adsorption. But one or more isotherms may also be appropriate.

According to the Langmuir isotherm model, adsorbate ions or molecules that move toward the active site on the adsorbent surface retain these sites. Since each active group in these sites on the adsorbent surface can only be occupied by one adsorbate ion or molecule, the adsorbed layer is considered to be monomolecular, that is to say a homogeneous layer formation. In order to explain these phenomena, Irving Langmuir, based on theoretical considerations, introduced a new model called Langmuir isotherm [31,32]:

The mathematical equation for the non-linear Langmuir isotherm is as follows:

$$q_e = \frac{bC_e}{1 + bC_e} \tag{8}$$

when the equation is linearized, the following new equation is derived:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{maks}} + \frac{1}{bq_{maks}} \tag{9}$$

where q_e is the quantity of adsorbate retained on one g of adsorbent (mg g^{-1}), q_{max} represents the max. quantity of the capacity related to single layer adsorption (mg g^{-1}), Ce is the adsorbate quantity remaining in the aqueous phase at equilibrium (mg L^{-1}), and b is a constant related to the system energy (L mg^{-1}).

If Ce/q_e versus Ce graph is linear, this gives a clue as to whether the adsorption is compatible with the Langmuir model. q_{max} and b can be easily found from the slope and the intercept of the graph, respectively.

Another isotherm model that is best known and applied together with Langmuir is the Freundlich isotherm model. Freundlich argued that adsorption takes place on nonhomogeneous surfaces with different energies and characters. The quantity of matter (q_e) adsorbed by the adsorbent increases rapidly with the effect of pressure or concentration, but the adsorption rate slows down as the solid surface is filled with adsorbed molecules. The non-linear form of the Freundlich isotherm is given by the formula [33]:

$$q_e = K_f \times C_e^{1/n} \tag{10}$$

Where Kf (mg g^{-1}) is a constant with respect to adsorption capacity. n is a constant related to the adsorption density and indicates the strength of the bond from the interaction between adsorbent and adsorbate. The high values of Kf indicate that adsorbent and adsorbate are very close to each other so that the adsorption can easily take place. The n value varies with the heterogeneity of the adsorbent for the suitability of the adsorption process. If n value is in the range of 1–10, it indicates that the selected adsorbent-adsorbate pair is quite suitable for adsorption. The 1/n value is the heterogeneity factor and, unlike the n value, it takes values in the range 0-1. The more heterogeneous the surface, the closer the value of 1/n is to zero. The accuracy of this isotherm model is better than that of Langmuir isotherm in heterogeneous adsorption systems.

If the form of the Freundlich isotherm shown in formula 10 is rearranged, the following linear form is obtained:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{11}$$

There is a linear relationship between lnCe and lnq_e, and the graph to be plotted is a straight line. Kf and 1/n can be found from the intercept and slope of the line, respectively.

2.8. Adsorption thermodynamics

The dependence of an adsorption process on temperature is related to three critical parameters: the total energy of a system, "Enthalpy (H)", the energy available to the system "Gibss free energy (G)" and the unavailable energy "Entropy (S)". Absolute values of these 3 criteria can not be determined. However, energy changes occurring in the system can be determined. The relationship between these three factors and the system temperature is given by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

Where ΔG°, ΔH° and ΔS° are the standard Gibbs free energy change (kJ mol^{-1}), the standart enthalpy change (kJ mol^{-1}), the standart entropy change (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively.

To estimate the Gibbs free energy of an adsorption event taking place at a specific temperature, it is first necessary to calculate the equilibrium constant (Kd) of the system. Kd can easily be found by the ratio of the adsorbate concentration retained in the unit mass of the adsorbent to the adsorbate concentration remaining in the solution:

$$K_d = C_a / C_e \tag{13}$$

Where K_d, Ca and Ce are the adsorption equilibrium constant, the adsorbate concentration retained in the unit mass of the adsorbent (mg L^{-1}) and the adsorbate concentration remaining in the solution, respectively.

Gibbs free energy value can easily be found for the corresponding adsorption process if the calculated value of K_d is placed in the following equation:

$$\Delta G^\circ = -RT\ln K_d \tag{14}$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}). From the equation 12 and 14, the following Van't Hoff equation can be derived:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

A graph plotted between lnK_d and $1/T$ is linear. It is possible to find ΔH° from the slope and ΔS° from the intercept. Thus, information on reaction progress can be obtained. If the value of ΔH° is positive, the adsorption process is endothermic, if not exothermic. Negative values of ΔG° also reveal that adsorption occurs spontaneously, that is, the feasibility of the adsorption process can be easily explained by the fact that the enthalpy and Gibbs free energy are negative. Positive ΔSo values refer an increase in randomness between the adsorbent and solution interfaces [34].

3. Results and Discussion

3.1. Effect of pH on adsorption of Cu(II) ions from aqueous solution by TIW-AC

Adsorption of metal ions from aqueous solution on an activated carbon is much more complex than adsorption of organic molecules and is particularly influenced by the solution pH. With the change of pH, metal ions form different species in the aqueous solution [35].

With increasing pH, most metal ions in cationic form in solution have high adsorption potential on activated carbon. However, the further increase of the pH, especially at higher concentrations, the metal ions such as Al^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Fe^{3+} and Ni^{2+} either tend to precipitate into hydroxides or to form anionic hydroxide complexes [36–38]. For this reason, it is very important to determine an optimum pH value when working with metal ions.

Fig. 1(a) shows the change in pH-dependent adsorption behavior of Cu(II) ions on TIW-AC. At low pH values, TIW-AC is surrounded by H_3O^+ ions, so the functional groups of TIW-AC are positively charged. H_3O^+ ions therefore prevent the adsorption of the same positively charged Cu(II) cations to TIW-AC surface. As shown in Fig. 1(a), therefore, the adsorption yield of Cu(II) ions in cationic form is very low at low pH values [39]. The increase in pH increases the adsorption efficiency of Cu(II) ions on TIW-AC, that is, the reduction of total positive charges on the adsorbent surface allows Cu(II) ions to gain competition between H_3O^+ ions and Cu(II) ions. At this point, electrostatic interactions between TIW-AC surface and Cu(II) ions increase, and the adsorption rate increases rapidly [40].

Higher pH values are more favorable for adsorption of cationic species since the surface charge of TIW-AC is a more negative. However, since Cu(II) ions tend to precipitate as hydroxides at increasing pH values, and because of the possibility of formation of negatively charged hydrolysis products, the pH must be optimized to an appropriate value.

Fig. 1(b) shows the distribution of Cu(II) species in the aqueous solution by the change of pH [41,42]. The predominant species for adsorption of +2 valent metal cations on the activated carbon from aqueous solution are Cu^{2+}, $Cu(OH)^+$ ve $Cu_2(OH)_2^{2+}$. These species are particularly dominant at pH range of 4 and 8. However, after pH 6, Cu(II) ions start to precipitate as hydroxides (Fig. 1(b)). Therefore, the choice of the optimum pH value is highly critical. The adsorption of such cationic forms on activated carbon occurs as in the following reactions [42]:

$$R{-}COOH + M^{2+} \leftrightarrow R{-}COOM + 2H^+ \tag{16}$$

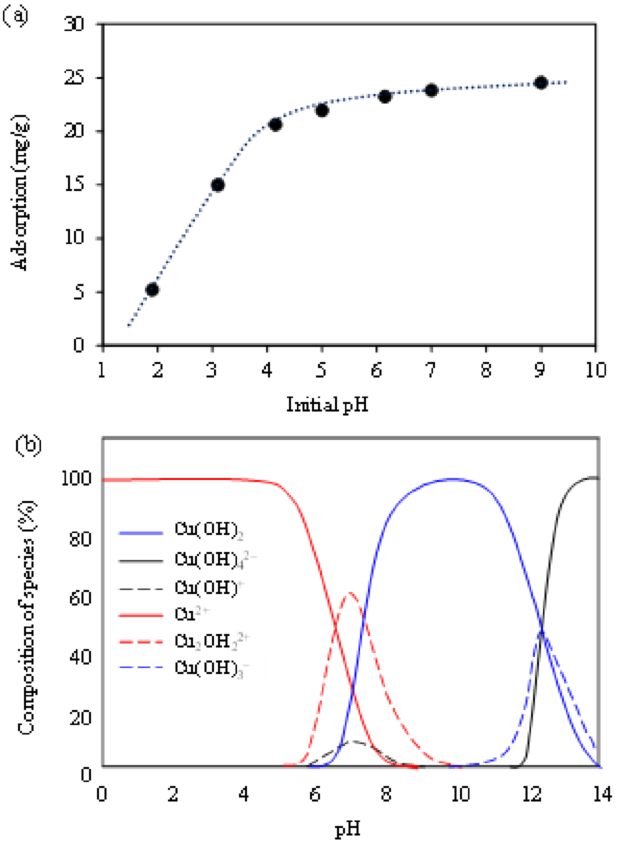

Fig. 1. (a) Effect of initial pH on adsorption of Cu(II) ions (Initial Cu(II) ion conc.: 100 mg L^{-1}, TIW-AC quantity.: 3.0 g L^{-1} (30 mg TIW-AC in 10 mL metal ion solution), contact time: 4.0 h, temperature: 25.0 °C), (b) Speciation diagram for Cu(II) ions (Initial Cu(II) conc.: 30.0 mg L^{-1}) mg L^{-1}.

$$R{-}COOH + M(OH)^+ \leftrightarrow R{-}COOM(OH) + H^+ \qquad (17)$$

In view of the above description, the pH 5.0 value for adsorption of Cu(II) ions on TIW-AC was optimally chosen, and the subsequent parameters were carried out at this pH.

3.2. Effect of contact time on adsorption of Cu(II) ions by TIW-AC

The effect of the time to reach equilibrium for the adsorption of Cu(II) ions on TIW-AC was investigated. A series of Cu(II) solutions (10 mL of 100 mg/L) adjusted to pH 5.0 and 50 mg TIW-AC were treated at different time intervals. The amount of Cu(II) adsorbed by 1 g TIW-AC was calculated after the metal ion concentrations remaining in the solution were determined by FAAS.

As can be seen from the graph of time vs adsorbed Cu(II) amount in Fig. 2(a), the adsorption of Cu(II) ions on TIW-AC reached equilibrium after from the 2 hour shaking period. The short period of the equilibrium is especially important in terms of economical cleaning of the wastewater without taking too much time [43]. It seems that the first minutes of the adsorption is quite fast, then slows down and finally reaches equilibrium. Hence, it is understood that the adsorption rate is controlled essentially at three stages [44]. From these results, the time to reach equilibrium was optimized to 4 hours. Three different kinetic models were used to investigate the adsorption kinetics in more detail: Pseudo-first order, pseudo-second order ve intraparticle diffusion kinetic models. From the pseudo-first order kinetic equation (Equation 4), the k_1 rate constant and q_e(exp.) values were found from the $t - \ln(q_e - q_t)$ graph (Fig. 2(b)). In the same way, k_2 and q_e(exp.) The values were calculated with the graph of t versus t/q_t for the pseudo-second order kinetic model. Looking at the graphs in Fig. 2(c) and the values in Table 1, it appears that the adsorption of Cu(II) ions on TIW-AC is in accordance with the pseudo second-order rate expression due to the magnitude of R_2 values and

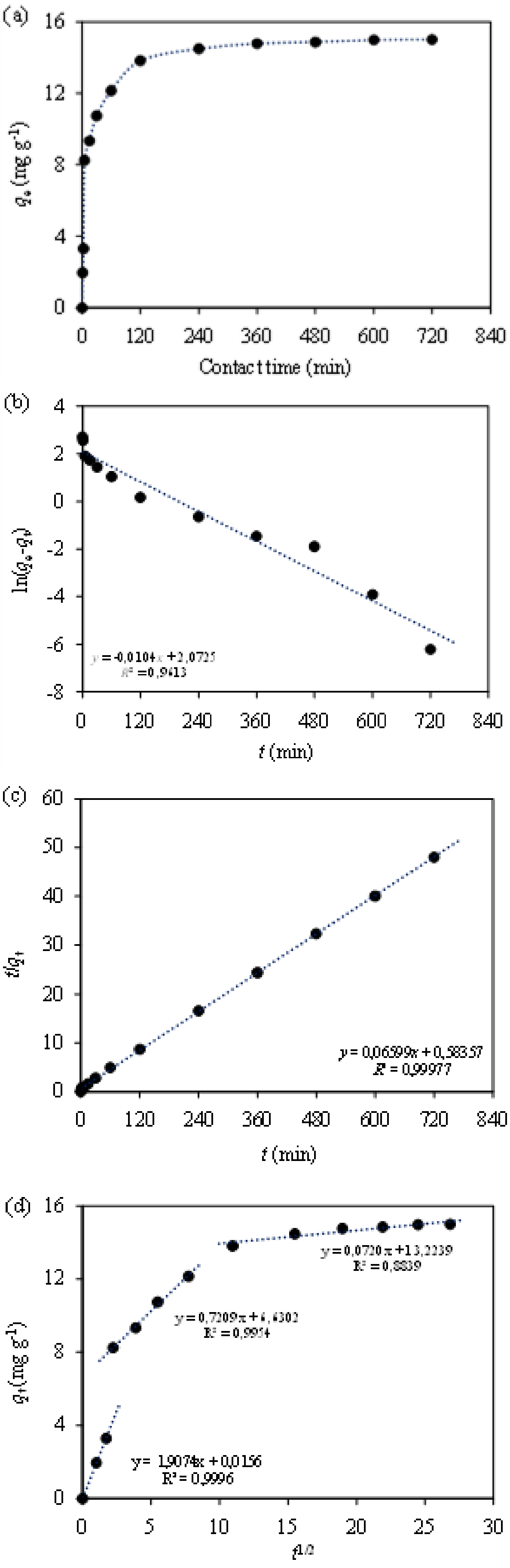

Fig. 2. Adsorption kinetics of Cu(II) ions: (a) effect of contact time on Cu(II) adsorption, (b) preudo first order kinetic model, (c) pseudo second order kinetic model, (d) intraparticle diffusion kinetic model (initial pH: 5.0, initial Cu(II) conc.: 100 mg L^{-1}, TIW-AC quantity, 5.0 g/L, temperature: 25.0 °C).

Table 1. Kinetics constants for Cu(II) adsorption on TIW-AC

	Pseudo-first order			Pseudo-second order			Intra-particle diffusion		
q_e(exp.) (mg g^{-1})	q_e(cal.) (mg g^{-1})	k_1 (min^{-1})	R^2	q_e(cal.) (mg g^{-1})	k_2 (g $mg^{-1}min^{-1}$)	R^2	k_{id} (mg $g^{-1}min^{-1/2}$)	C (mg g^{-1})	R^2
15.00	7.94	-1.04×10^{-2}	0.9613	15.15	7.46×10^{-3}	0.9998	0.7209	6.63	0.9954

the closeness between q_e(exp.) and q_e(cal.).

Due to the rapid filling of the film layer on the exterior surface of TIW-AC with Cu(II) ions, the adsorption rate at the beginning is quite high. After the outer surface is filled, the adsorbate ions slowly move towards the pores. Due to the rapid filling of the film layer of the exterior surface of TIW-AC with Cu(II) ions, the adsorption rate at the beginning is quite high. After the exterior surface is filled, the adsorbate ions slowly move towards the pores. This is the step that limits the rate of adsorption and can be thought of as the diffusion of the adsorbate molecules into the particle interior. The last step is the step where adsorption reaches equilibrium. As saturation is reached at this stage, the adsorption rate is very slow and much less adsorbate molecule is adsorbed [45]. As shown in Fig. 2(d) for the intra-particle diffusion model, the $t^{1/2} - q_t$ graph contains three different lines whose slopes are different from each other. This indicates that more than one process affects the adsorption rate of Cu(II) ions onto TIW-AC. The second line on the graph represents intra-particle diffusion. The constants obtained from the graph are also given in Table 1. If the adsorption rate is only controlled by intra-particle diffusion, the line must pass through the origin. If it does not pass through the origin, the adsorption rate is controlled not only by intra-particle diffusion but also by boundary layer diffusion.

3.3. Effect of adsorbent quantity on adsorption of Cu(II) ions by TIW-AC

To investigate the effect of different amounts of TIW-AC on the adsorption of Cu(II) ions from aqueous solution, TIW-AC quantities between 10-150 mg and 10 mL of 250 mg/L Cu(II) solutions adjusted to pH 5.0 were agitated for 4 hours. As the total surface area and adsorption sites increase with the increase of TIW-AC amount, the amount of Cu (II) ion adsorbed from the solution is also increased. However, this increase is non-linear, that is, the amount of metal adsorbed by per gram of adsorbent decreased with the increase of TIW-AC amount (Fig. 3(a)). This can be mathematically explained by the new equation derived by combining equations 1 and 2:

$$q_e = \frac{\%\text{Ads.} \times C_o \times V}{100 \times m} \tag{14}$$

As can be seen from the equation (14), there is an inverse relationship between q and m provided that C_o and V are constant. That is, as the amount of adsorbent increases, there is a decrease in the amount of adsorbate adsorbed on 1 g of adsorbent [46]. It is also possible to explain this situation for the following two reasons [47–49]: (i) the increased amount of adsorbent in the fixed adsorbate concentration leads to the formation of unsaturated surfaces on the adsorbent surface, (ii) The aggregation of high amounts of adsorbent particles results in a reduction in the total surface area of the adsorbent. The capacity of the adsorbent therefore also decreases.

3.4. Effect of adsorbate concentration on adsorption of Cu(II) ions by TIW-AC

To investigate the effect of the initial Cu(II) concentration on adsorption by TIW-AC, a series of Cu(II) solutions with concentrations of 50–1000 mg L^{-1} and adjusted to pH 5.0 were agitated with 50 mg TIW-AC for 4 hours. After centrifugation at 3000 rpm, the remaining metal concentrations unadsorbed in the solution were determined by FAAS. Then the amounts of Cu(II) adsorbed on TIW-AC were calculated with the Equation 1 and Equation 2.

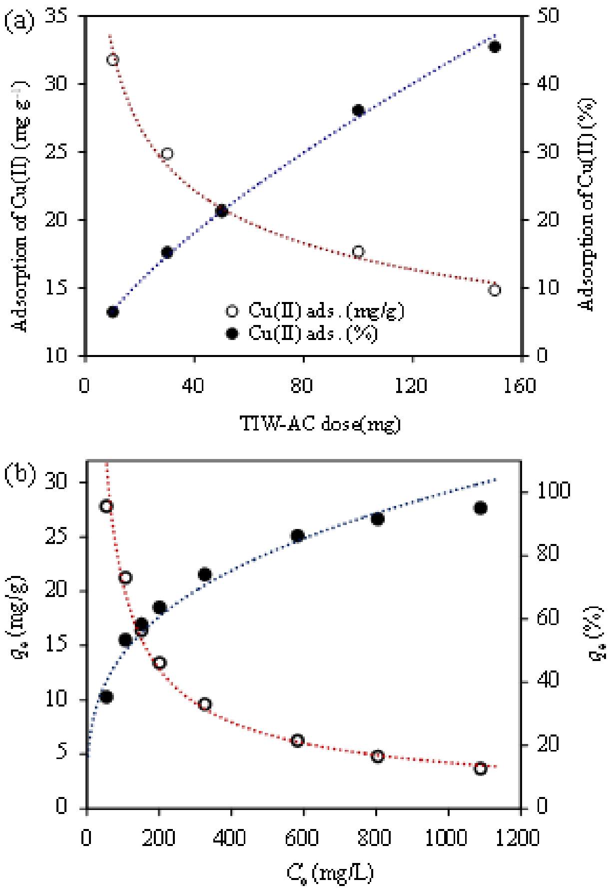

Fig. 3. (a) Effect of adsorbent quantity on adsorption of Cu(II) ions by TIW-AC (Initial Cu(II) conc.: 250 mg/L, initial pH: 5.0, contact time: 4.0 h, temperature: 25.0 °C), (b) Effect of adsorbate concentration on adsorption of Cu(II) ions by TIW-AC (Initial Cu(II) conc.: 50–1000 mg L^{-1}; initial pH: 5.0; TIW-AC dose: 5.0 g L^{-1}; contact time: 4.0 h, temperature: 25.0 °C).

The relationship between the increasing concentrations of initial Cu(II) solutions (Co) and Cu(II) quantities (qe) adsorbed by the fixed amount of TIW-AC is shown in Fig. 3(b). At the beginning, it is seen that there is an increase in the adsorption rate for low C_o values and then there is a decrease in the adsorption rate due to the slow filling of the surface of TIW-AC. Thus, the percentage of adsorption as a consequence of increased Cu(II) concentration appears to decrease.

Both non-linear and linear Langmuir and Fruendlich adsorption isotherms were plotted to explain the adsorptive behavior of TIW-AC with increasing initial Cu(II) concentration in more detail (Fig. 4), and corresponding constants are determined from these graphs (Table 2). In order to plot the adsorption isotherms, the relationship between Cu(II) concentrations (Ce) remaining in the solution after adsorption process and the Cu(II) quantities (q_e) adsorbed on TIW-AC was taken into account. First, the graphs of qe versus Ce were plotted (Fig. 4(a)), then linear graphs of Langmuir and Freundlich isotherms were obtained (Fig. 4(b) and (c)).

From the linear graphs, it can be said that the adsorption of Cu(II) ions on TIW-AC is compatible with both isotherm models since the R_2 values in Table 2 are high (>0.95). However, it may be more appropriate to plot non-linear Langmuir and Freundlich graphs to determine which model is better. For this purpose, q_{max} and b constants obtained from the equations of linear graphs (Table 2) were

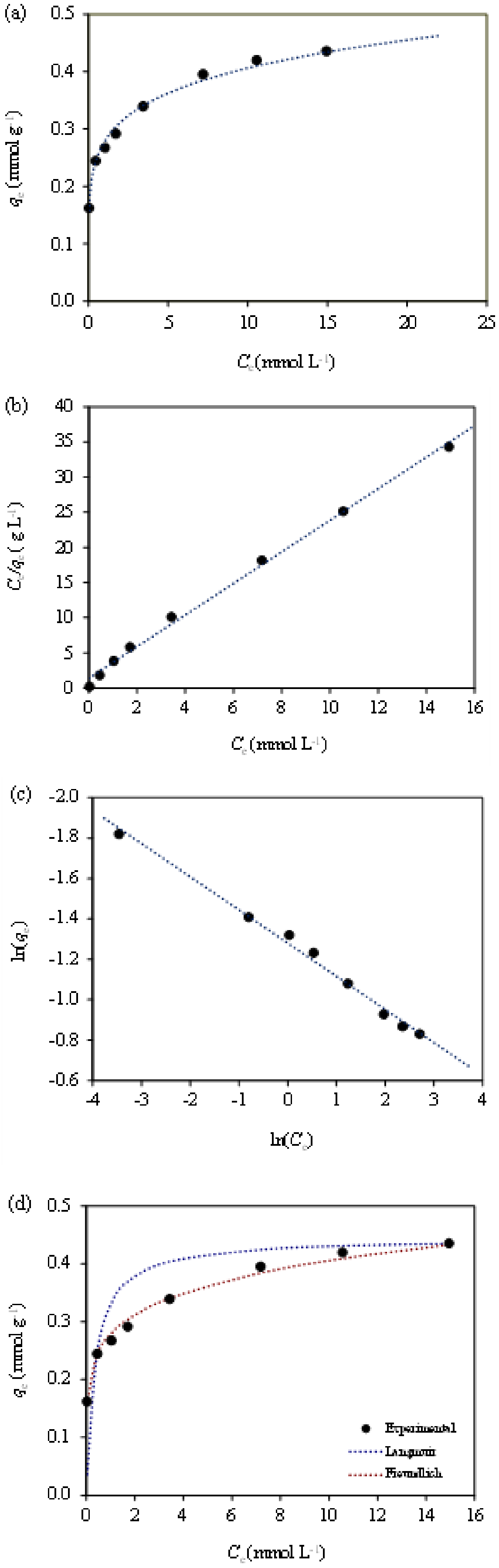

Fig. 4. Relationship between Cu(II) ions at equilibrium and Cu(II) ions adsorbed on TIW-AC: (a) Ce vs q_e graph, (b) Lineer Langmuir isotherm; *Ce* vs *Ce/qe* graph, (c) Linear Freundlich isotherm; ln*Ce* vs ln*qe* graph, (d) Non-linear Langmuir and Freundlich isotherms

put in place in the non-linear equations of the isotherms (Equations 8 and 10). Because *Ce* values are already known, new q_e values were calculated, and q_e versus *Ce* curves were plotted (Fig. 4(d)). It is apparent from Fig. 4(d) that the Freundlich isotherm better describes the adsorption of Cu(II) ions on TIW-AC than Langmuir since the experimental points are best represented by Freundlich curve.

From the obtained isotherm results, it can be said that TIW-AC has a heterogeneous surface for the adsorption of Cu(II) ions. Highly enriched active adsorption sites (functional groups) with different character and type occur in the activated carbon produced by sulfuric acid activation at relatively low temperatures.

From the Langmuir isotherm in this study, the Cu(II) adsorption capacity of TIW-AC was found as 28.30 mg g^{-1} (0.445 mmol g^{-1}). Together with the other optimization conditions, the capacity value obtained in this study was compared with other studies in the literature. Table 4 shows that this value is comparable with the values obtained from the methods using many different activated carbons reported in the literature. The adsorbent quantities used (g L^{-1}) should be taken into account when making a comparison between the results. Because, as the amount of adsorbent decreases, the amount of metal adsorbed by per one g of adsorbent increases, so the capacity increases.

3.5. Effect of temperature on Cu(II) adsorption by TIW-AC

In order to investigate the effect of temperature on the adsorption of Cu(II) ions in aqueous solution by TW-AC, experiments were carried out at four different temperatures (5, 15, 25 and 40 °C). The initial Cu(II) concentration was selected as 150 mg L^{-1} and adsorption tests were carried out under optimum conditions.

From the temperature–adsorption graph plotted with the obtained results, it is seen that the adsorption effiency of Cu(II) ions on TIW-AC increase with the increase of the temperature (See the SI file, Fig. S3(a)). As the temperature increased from 5 °C to 40 °C, the adsorption efficiency increased from 31.8% to 62.7%. From these results, it seems that the adsorption mechanism of Cu(II) ions on TIW-AC is endothermic. The positive effect of temperature increase on adsorption can be attributed to the fact that interaction between TIW-AC and Cu(II) ions more increases with temperature, passive sites become more active, and/or particle diffusion plays a more active role when the pore structure of TIW-AC expands [61–63].

For the determination of the thermodynamic parameters ΔG, ΔS and ΔH, the graph of lnK_d vs *1/T* were plotted (See the SI file, Fig. S3(b)).. The values calculated from the graph are given in Table 3. With increasing temperature, the ΔG values on the table are more negative. Therefore, this indicates that the adsorption takes place spontaneously. The ΔG value is positive if the lnK_d value is negative at temperatures below 50% of the adsorption. The suitability of adsorption for the selected initial Cu(II) concentration is possible at high temperatures. At low Cu(II) concentrations, room temperature is enough for spontaneous formation of adsorption.

The positive value of ΔH indicates that the adsorption of Cu(II) on TIW-AC is an endothermic process. ΔH can also help to decide whether the adsorption is chemical or physical. Adsorption may take place either through chemical interaction between the chemical groups on the activated carbon surface and the adsorbate molecules in the aqueous solution, or by different physical interactions such as electrostatic interactions, hydrogen bonding, Van der Waals interactions, ion exchange and hydrophobic interactions [64]. The enthalpy of physical adsorption is generally not greater than 1 kcal mol^{-1} (4.2 kJ mol^{-1}). On the other hand, it is not smaller than 5.0 kcal mol^{-1} (21.0 kJ mol^{-1}) for chemical adsorption. Taking the value of ΔH in Table 3, it can be considered that the adsorption of Cu(II) ions on TIW-AC proceeds more chemically. However, it is difficult to come to a definite conclusion because this value is almost at the limit.

The positive ΔS value increases the likelihood of random occurrence of adsorption equilibrium occurring at the solid and liquid phase interface during adsorption process. More specifically, it indicates an increase in the amount of unused energy, that is, an increase in the irregularity of the system.

Table 2. Constants of Langmuir and Freundlich isotherms for adsorption of Cu(II) ions by TIW-AC

	Langmuir constants					Freundlich constants			
	q_{max}		b		R^2	K_f		n	R^2
TIW-AC quantity (g L^{-})	(mmol g^{-1})	(mg g^{-1})	(L mmol^{-1})	(L mg^{-1})		(mmol g^{-1})	(mg g^{-1})		
5.0	0.445	28.30	2.852	0.04488	0.9960	0.278	31.30	6.13	0.9919

Table 3. Thermodynamic parameters for adsorption of Cu(II) ions on TIW-AC at different temperatures

T (°C)	K_d	ΔG (kj mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kj mol^{-1})
5	0.47	1.76	88.71	26.12
15	0.89	0.29		
25	1.30	– 0.64		
40	1.68	– 1.35		

3.6. Desorption of Cu(II) ions from TIW-AC and reuse of the adsorbent

Desorption experiments are highly important in terms of explaining the adsorption mechanism and helping to recover adsorbate and adsorbent. [65,66]. Moreover, the use of suitable desorption solutions which allow for regeneration of the adsorbent without damaging, enables the efficiency of the selected method, reuse of the adsorbent, and thus the process becomes more economical.

In this study, the HCl solution used for this purpose in the literature was selected as the desorption solution and its concentration was optimized so as not to damage the adsorbent. Satisfactory desorption of Cu(II) ions adsorbed on TIW-AC with HCl means regeneration without damaging of TIW-AC. For this reason, besides the type of desorption solution to be selected, its concentration is also of great importance [66,67].

The desorption process was studied in two stages. In the first step, a series of Cu(II) solutions with an initial concentration of 100 mg L^{-1} and a 10 mL volume were treated with 50 mg TIW-AC separately under optimal conditions, and then the amounts of metal adsorbed on TIW-AC were determined. In the second step, Cu(II) ions adsorbed on TIW-AC were desorbed with 10 mL of HCl solutions in the concentration range of 0.01–1.00 mol L^{-1}. The desorption percentages of Cu(II) ions were calculated after the concentrations of metal ions passing into the HCl phase were determined (See the SI file, Fig. S4(a)). From the results obtained, it can be seen that Cu(II) ions can be effectively desorbed with 0.25 mol L^{-1} HCl. For this reason, this concentration of HCl was optimized. Desorption of Cu(II) ions adsorbed on TIW-AC with 0.25 mol L^{-1} HCl was achieved with a yield of 96.6%. It was observed that the desorption efficiencies did not change much in the studies conducted with more concentrated HCl solutions.

3.7. Reuse of TIW-AC after regeneration

Reuse of the used adsorbent after regeneration is of great importance in terms of economy and preference. At this stage after the adsorption-desorption transformation, the change in adsorption ability was investigated by reprocessing the used adsorbent with Cu(II) ions in aqueous solution.

For this purpose, Cu(II) solutions with an initial concentration of 95 mg L^{-1} were first treated with TIW-AC under optimum conditions. The metal-loaded adsorbent was then agitated with the desorption solution, 0.25 mol L^{-1} HCl for regeneration. The regenerated adsorbent was washed thoroughly with pure water until no HCl residue remained and then again treated under the optimum conditions with the same Cu(II) solution. Then desorption was again carried out with HCl solution. In this way the adsorption-desorption cycle was repeated 5 times.

When looking at the column graphs drawn with the obtained

Table 4. Comparison of Cu(II) Langmuir adsorption capacity of TIW-AC with the other activated carbon in the literature together with other optimization values

Precursor	Activation	pH	Contact time (h)	Temp. (°C)	AC dose (g L^{-1})	Capacity, q_{max} (mg g^{-1})	Ref.
Hazelnut husk	Potassium acetate	5.0	2.0	25	1.0	105.3	12
Grape bagasse	Phosphoric acid	5.0	3.0	45	2.0	43.47	13
Capsicum straw	Potassium hydroxide	5.0	3.33	25	1.0	21.93	14
Medicinal plant (*Salvadora persica*)	Phosphoric acid	4.0	5.0	25	1.0	74.30	50
Sugarcane bagasse	Zinc chloride	6.0	-	-	5.1	13.24	51
Pecan nutshell (*Carya illinoinensis*)	Sodium chloride	5.0	24.0	30	2.0	23.37	52
Jengkol shells (*Pithecellobium Jiringa*)	Ultrasonic assistance	4.5	1.25	30	10.0	104.167	53
Corncob	Carbon dioxide	-	-	30	1.0	81.97	54
Pigeon peas hulls	Sulfuric acid	5.0	1.0	40	4.0	20.83	55
Green vegetable waste	Potassium hydroxide	3.5	1.5	25	0.6	75.0	56
Hazelnut husks	Zinc chloride	5.7	1.0	-	12.0	6.645	57
Ceiba pentandra hulls	Water steam	6.0	1.0	30	5.0	20.8	58
Pulse crop (*Phaseolus aureus*)	Water steam	7.0	1.0	30	6.5	19.5	59
Peanut shells	Water steam	4.8	24.0	-	10.0	50.4	60
Rubber wood sawdust	Phosphoric acid	6.0	4.0	30	5.0	5.729	61
Tea-industry waste	Sulfuric acid	5.0	4.0	25	5.0	28.30	This work

results ((See the SI file, Fig. S4(b))., it is seen that TIW-AC can be reused after every cycle without losing its feature. As a result of this parameter, it is seen that TIW-AC can be used repeatedly for the adsorption of Cu(II) ions without loss of adsorption property after regeneration. Studies that reduce the process cost by reusing the various adsorbents used with adsorption-desorption cycles are found in the literature [44,67].

3.8. Effect of foreign ions on adsorption of Cu(II) ions by TIW-AC

Real water samples contain many foreign ions besides metal ions. In order to be able to effectively use activated carbons in the purification of industrial or domestic wastewaters, it is necessary to investigate whether the existing foreign ions have negative or positive effects on the adsorption of metal ions.

Adsorption efficiency of Cu(II) ions on TIW-AC in the presence of foreign ions in the medium was investigated. Each foreign ion in the concentration of 100 mg L^{-1} was added to the medium individually or mixed, and the general procedure was applied. From the graphs obtained, the foreign ions showed a small negative effect on adsorption of Cu(II) ions by TIW-AC (See the SI file, Fig. S5).. The effect of cationic foreign ion species on the adsorption of Cu(II) is greater than that of anionic species. Among the cationic species, Ca^{2+} ions have more negative effects than others. Numerous studies have been found in the literature regarding the suppression of the adsorption of metal ions on activated carbon or on many adsorbents by alkaline and alkaline earth cations [44,65,67,68]. +2 valent alkaline earth cations suppressed Cu(II) uptake more than +1 valent cations. The Ca^{2+} ion suppresses Cu(II) uptake by 13.9%. It can be said that +2 valent ions like Ca^{2+} were adsorbed on TIW-AC, and thus the Cu(II) uptake was suppressed because of the decrease of TIW-AC capacity. The solution in which Cu(II) ions and other ions coexist has highest negative effect (20% decrease) on Cu(II) uptake by TIW-AC (See the SI file, Fig. S5).

4. Conclusion

In this study, a new low-cost activated carbon was produced from tea-industry waste at laboratory conditions using a simple oven without needing a high-cost carbonization furnace, and its adsorption performance was tested for the removal of Cu(II) ions from aqueous solution in terms of equilibrium, kinetics and thermodinamics. As a result of adsorption tests, TIW-AC showed high performance in removing Cu(II) ions from aqueous media when compared with the literature.

Three reasons that make this study meaningful come to light: (i) A new activated carbon has been produced that can be used effectively in many fields, from wastes that are not used in any purpose and discharged directly to the environment. (ii) Thanks to the production of an activated carbon, the possible environmental pollution from these wastes can be eliminated. (iii) By using the activated carbon from these wastes, another environmental pollution can be eliminated. Thus, these wastes can be also re-gained by economy.

Obtaining new materials that can be used in many areas from such agricultural wastes or by-products that are not used for any purpose should be highly encouraged both economically and environmentally.

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SUPPORTING INFORMATION (SI)

Research Article

A new low-cost activated carbon produced from tea-industry waste for removal of Cu(II) ions from aqueous solution: Equilibrium, kinetic and thermodynamic evaluation

Ali Gundogdu[1*], Hasan Basri Senturk[2], Celal Duran[2], Mustafa Imamoglu[3], Mustafa Soylak[4]

[1]*Department of Food Engineering, Faculty of Engineering and Natural Sciences, Gümüşhane University, 29100–Gümüşhane/Türkiye*

[2]*Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080–Trabzon/Türkiye*

[3]*Department of Chemistry, Faculty of Arts & Sciences, Sakarya University, 54187–Sakarya/Türkiye*

[4]*Department of Chemistry, Faculty of Sciences, Erciyes University, 38039–Kayseri/Türkiye*

***Corresponding author e-mail:** a.ramazan.gundogdu@gmail.com

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1. RESULTS AND DISCUSSION

1.1. Characterization Results

The results of the physicochemical characterization of the activated carbon (TIW-AC) produced by sulfuric acid activation from the tea-industry waste (TIW) as starting material are given in Table S1.

Because it is not heat treated, the volatile matter content of TIW is higher than the TIW-AC, as expected, while the carbon content is lower than that of TIW-AC. The ash content of TIW-AC is higher than TIW. Ultimate analysis results show that the TIW-AC, which is subjected to carbonization and activation at a relatively low temperature, is particularly rich in S content. This caused the ash contents to rise high. The H and O content of TIW-AC is lower than that of TIW due to the loss of H_2O at the carbonization temperature. The C/H ratio also increased with increasing C percentage. The increase in the C/H ratio indicates the aromatization of the structure, thus indicating the formation of regular structure. Furthermore, the increase in the C/H ratio indicates an increase in graphitization.

Table S1. Physicochemical characteristics of TIW and TIW-AC

	TIW	TIW-AC
Proximate analysis (%)		
Humidity	6.62	9.13
Volatile	77.2	51.7
Fixed carbon	11.4	33.8
Ash	4.73	5.44
AC yield	–	84.2
Ultimate analysis (%)		
C	47.89	56.27
H	5.86	3.12
N	2.39	3.70
S	0.30	1.93
O[a]	43.55	34.98
C/H[b]	0.69	1.51
BET surface area (m^2/g)		
S_{BET}	35.2	45.5
Iodine number (mg/g)	253.0	167.9
Methylene blue number (mg/g)	27.8	39.1
pH	5.32	6.00
pH_{pzc}	4.90	5.25
Surface acidic groups (mmol/g)		
Total	2.47	5.93
Carboxylics	1.03	2.58
Phenolics	0.98	1.93
Lactonics	0.46	1.42

[a] By difference

[b] Mol ratio

SEM images taken for TIW as the starting material in production of activated carbon show that the surface of the material is very rough and has recess-protrusions, but there are no obvious pore structures, channels or gaps on the surface (Fig. S1(a) and Fig. S1(b)). The SEM image of TIW-AC activated with sulfuric acid at relatively low temperature shows that the porous structure is not very clear (Fig. S1(c) and Fig. S1(d)). The BET surface area of TIW-AC produced by subjecting to carbonization and activation at relatively low temperatures is lower when compared to the activated carbons in the literature. However, an activated carbon with relatively low surface area but high adsorption capacity and rich surface functional groups was produced in this work using a simple laboratory oven without needing a high cost inert atmosphere-carbonization furnace (see the adsorption results). From the SEM images of Cu(II) loaded TIW-AC obtained after adsorption, it can be said that the surface is partly covered (Fig. S1(e) ve Fig. S1(f)). This indicates that TIW-AC has adsorbed Cu(II) ions.

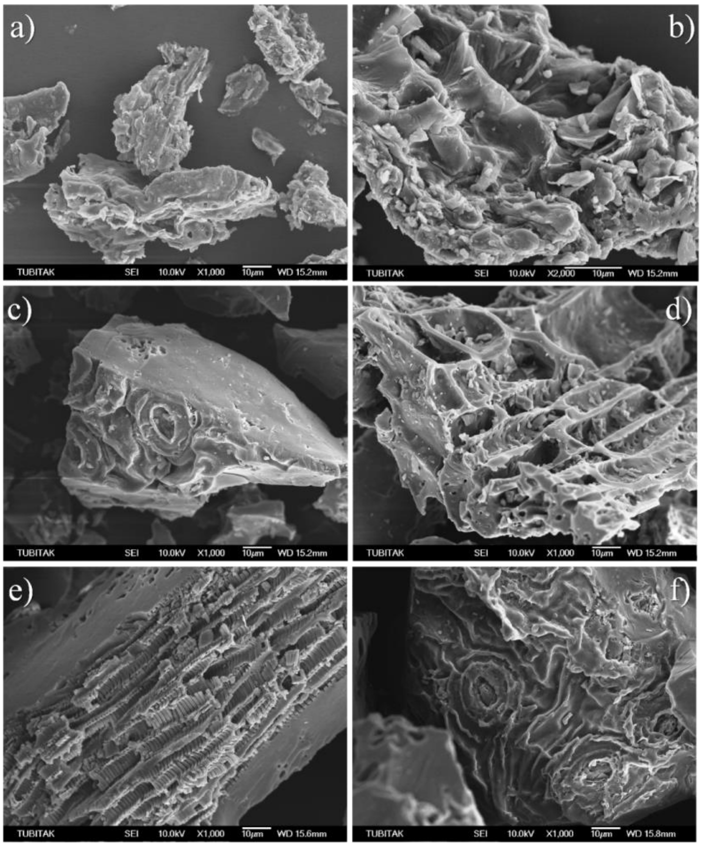

Fig. S1. SEM images a) and b) for TIW, c) and d) for TIW-AC, e) and f) for Cu(II) loaded TIW-AC

The parameters that give an idea about the porosity of an activated carbon in laboratory conditions; methylene blue number for large molecular structures, iodine number for small molecular structures. According to these two test results, it can be decided which adsorption process should be carried out with which kind of activated carbon. From the MB and iodine number results given in Table S1, it can be said that both TIW and TIW-AC have higher ability to adsorb small molecules than large molecules. When looking at the pH values, it can be said that the adsorbents are acidic. Values of pH$_{pzc}$ < 7 indicate that acidic groups are more dominant than basic groups. When the pH$_{pzc}$ values are considered, it can be concluded that the surface charge of the adsorbents are neutral at around pH 5, so this value may be effective especially for the adsorption of metal ions.

According to the Boehm titration results given in Table S1, TIW-AC appears to be quite rich in terms of surface acidic functional groups. Surface acidic groups are enriched in activated carbon produced by sulfuric acid activation at low temperatures. The most important feature of these activated carbons is that they have extremely high surface activity rather than their surface area. In this case, the adsorption of small ions such as metal ions in the aqueous solution is realized by these activated carbons with high performance. If the activation temperature is set between 200-400 °C, acidic surface oxides are enriched in the resulting activated carbon. High amounts of acidic oxides play an extremely active role in the adsorption of metal ions from aqueous solution. This is one of the most important factors that increase the capacity of the relevant adsorbent.

Fig. S2 shows IR spectra of TIW and TIW-AC. Due to the fact that it is not subjected to heat treatment, a large number of volatile components are present in the TIW. For this reason, it has functional groups in many different types and quantities. The slightly broad peak at 3396 cm^{-1} is due either to moisture or to hidoxyl (–OH) groups present in the sample. Hydroxyl containing structures; phenols, alcohols and carboxylic structures. The peak appearing at 1454 cm^{-1} also comes from the phenolic OH group in the structure. As the phenolic structures deteriorate at high temperatures, the peaks in this region disappear. The three peak aliphatic C–H peaks at 2918, 2852 and 1372 cm^{-1}. The peak at 1734 cm^{-1} is the C=O stretching peak originating from the carbonyl groups. The peak at 1051 cm^{-1} belongs to the C–C bond, while the peaks at 1051–1237 cm^{-1} indicate the presence of S=O groups in the structure. The relatively long peaks at 1646 and 1051 cm^{-1} are the C=C and C–O streching peaks. The peak at 892 cm^{-1} also points to the group C–O–H.

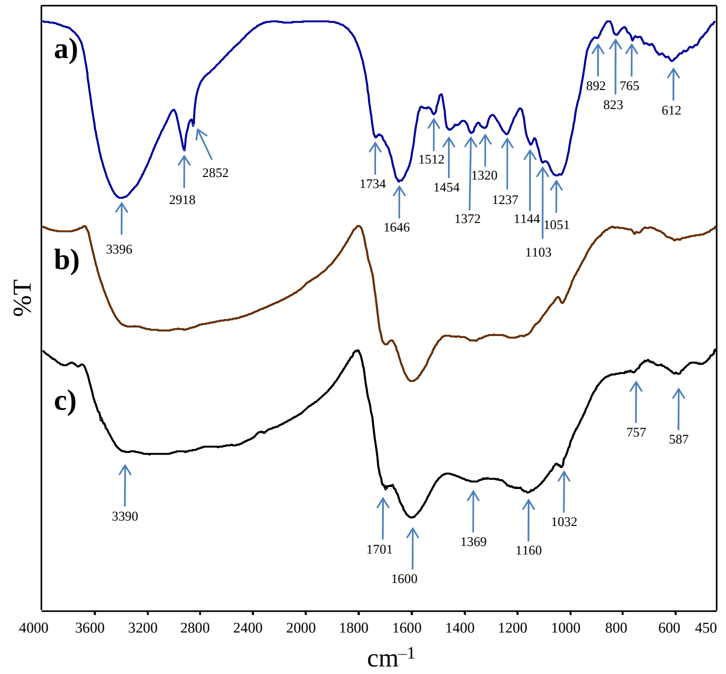

Fig. S2. IR Spectrum for a) TIW, b) Cu(II) loaded TIW-AC and c) TIW-AC

Since TIW-AC is carbonized at low temperature, many of the groups in the starting material (TIW) are retained in the structure. Fig. S2 shows the IR spectra of TIW-AC taken before adsorption and after adsorption. Looking at the IR spectrum, it is seen that the principal peaks are at 3390, 1701, 1600, 1369, 1160 and 1032 cm^{-1}. These peaks belong to the groups –OH, C=O, C=C, C–H, S=O and C–O groups, respectively. In the IR spectra obtained after adsorption, there is no change in the frequency and number of functional groups, but the transmittance values are increased. Since some of the functional groups after adsorption are occupied by adsorbate ions, an increase in the transmittance is a normal result. This result is also evidence of the adsorption of Cu(II) ions from aqueous solution by TIW-AC.

1.2. Effect of temperature

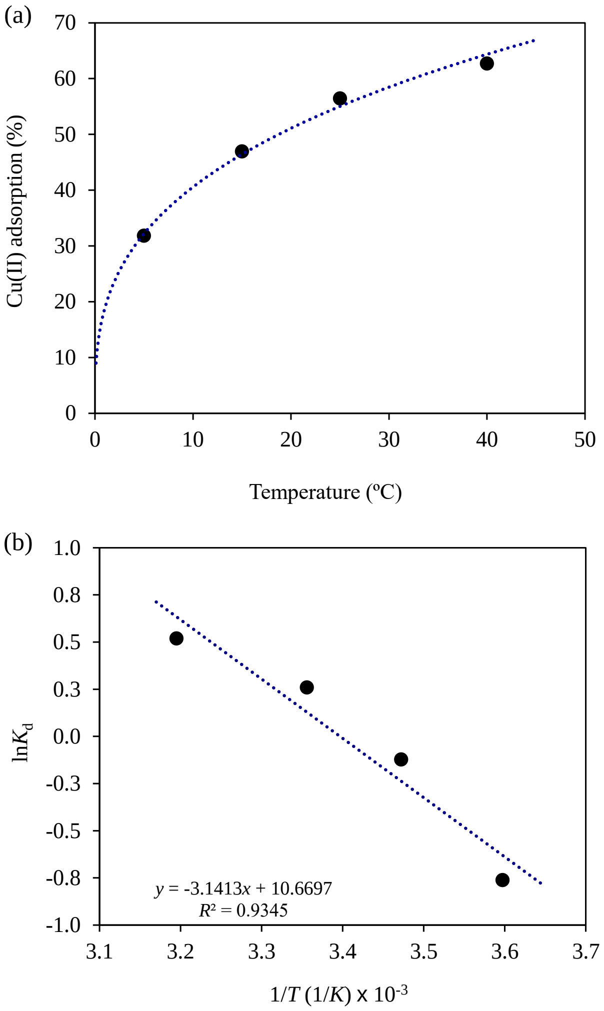

Fig. S3. (a) Effect of temperature on Cu(II) adsorption by TIW-AC, (b) The graph of lnK_d vs 1/*T* for thermodynamic parameters (initial Cu(II) conc.: 150 mg L^{-1}, initial pH: 5.0, TIW-AC dose: 5.0 g L^{-1}, contact time: 4.0 h)

1.3. Desorption of Cu(II) ions from TIW-AC and reuse of the adsorbent

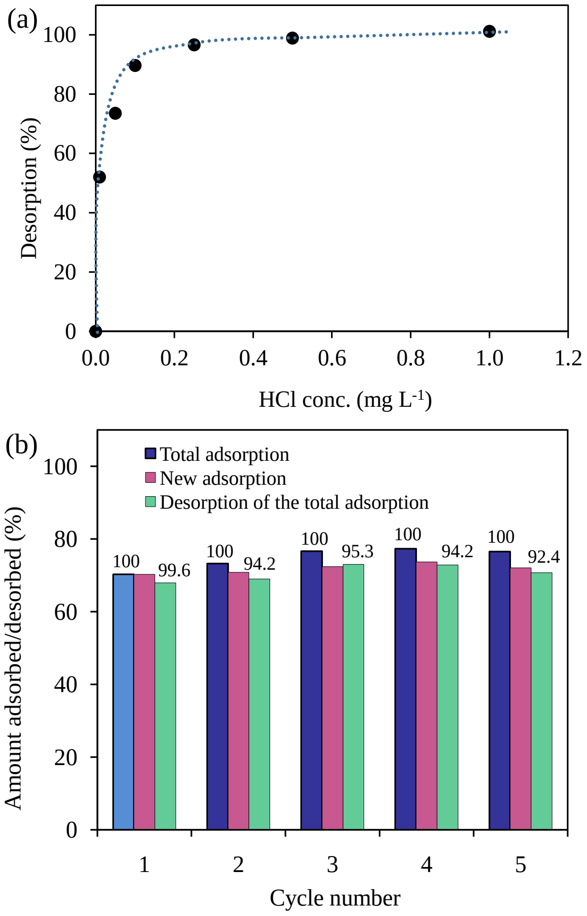

Fig. S4. (a) Desorption of Cu(II) ions adsorbed on TIW-AC (Initial Cu(II) conc.: 100 mg L^{-1}; TIW-AC dose: 5.0 g L^{-1}; Cu(II) quantity adsorbed on TIW-AC 13.5 mg g^{-1}, temperature: 25.0 °C), (b) Reuse of TIW-AC after regeneration (initial Cu(II) conc.: 95 mg L^{-1}, desorption solution: 0.25 mol L^{-1} HCl, temperature: 25.0 °C)

1.4. Effect of Foreign İon

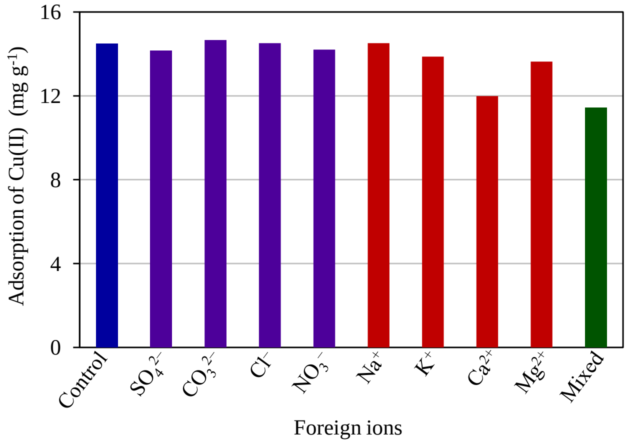

Fig. S5. Effect of foreign ion on Cu(II) adsorption by TIW-AC (initial pH: 5.0; Each ion conc.: 100 mg L^{-1}, Cu(II) conc.: 100 mg L^{-1}; TIW-AC dose: 5.0 g L^{-1}; contact time: 4 h, temperature: 25.0 °C)