

The Adsorption Study of Copper Removal by Chitosan-Coated Sludge Derived from Water Treatment Plant

Meng-Wei Wan, Chan-Ching Wang, and Chien-Min Chen

Abstract—The rapid development of science and technology in recent years created a standard of living that caused serious deterioration in the environment. Heavy metal contamination in the soil, surface water and groundwater is one of the major environmental problems due to their non-biodegradability and toxicity. Thus, how to solve efficiently the heavy metal pollution in groundwater has become the most essential issue around the world. Commercialized adsorbents such as activated carbon are effective in removing heavy metals but remain costly. In this study, the removal of copper (II) from aqueous solutions using a biodegradable material, known as chitosan coated sludge (CCS), was investigated under static conditions. The sludge was obtained from a water treatment plant. Moreover, batch experiments were conducted to investigate the adsorption effect under different initial concentration ($C_0 = 100, 500, 1000$ and 2000 mg/L), solution at pH=3 to pH=4 and contact time (0.5, 1, 2, 4, 6, 12 and 24 h). Results indicated that the data fitted well with Langmuir model at Q_{max} value of 18.83 mg/g CCS for Cu(II) ions at two hours contact time. The kinetic data best fit the pseudo-second order equation, indicating that chemisorption is the rate-limiting step of the Cu(II) adsorption.

Index Terms—Adsorption, chitosan, copper, sludge, water treatment plant.

I. INTRODUCTION

Due to dramatic development of industry, heavy metal pollution has become a global environmental consideration. Heavy metals, such as cadmium, chromium, cobalt, copper, nickel and mercury are common water pollutants [1]. These metals exist in aqueous waste from industries, such as mining, metal plating, and electronics [2]. On the other hand, the presence of heavy metal ions in industrial effluents and drinking water resources is also relevant due to their toxicological properties and potential impacts on human health and environment [3]. Thus, efficient solution to heavy metal pollution in groundwater has become the most essential issue around the world.

Copper (Cu), in particular, is a natural element predominantly used in production industry applications. Copper is also a very common substance that occurs

intrinsically in the environment and spreads through natural phenomena. It is extensively utilized by electrical industries, in fungicides and in antifouling paints. It is toxic to humans, producing oxidative stress when ingested at high concentrations [4]. Among the ionic species of copper, Cu(II) ions can have alarming effects in aqueous solution, attaching easily to organic and inorganic matter based on solution pH [5].

Application of biopolymers such as chitin and chitosan is one of the emerging adsorption methods for the removal of dyes and heavy metal ions, even at low concentrations [6]. Chitosan, a biopolymer prepared through the deacetylation of chitin, which is the major component of crustaceans shells and the second most abundant biopolymer in nature, has been widely used for adsorption of heavy metal ions [7]–[10]. Its chelating properties are attributed to the amino and hydroxyl groups in chitosan chain, that therefore, can act as chelation sites for different metals [11].

The sludge which is found in the bottom of a sedimentation tank in water treatment plants is primarily composed of water. The solids in the sludge are mainly flocs, excess coagulant, such as alum. Alum sludge has a solids concentration of only about 1 % when automatically removed from the basin, or about 2% if manually removed. Many options exist for disposal of sedimentation sludge such as disposal in streams, lagoons and landfills.

Applying permeable reactive barrier for the recovery of metals is a practically environmental remediation technology by building filters along a contaminated stream of groundwater. The remediation of the contaminated waste stream would be costly when chitosan is used alone because construction of filters along the stream requires large quantities of adsorbents. Immobilizing chitosan with a low-cost material results to a lesser amount of chitosan used without affecting the overall metal adsorption capacity [12]. Unfortunately, there are limited references to adsorption studies that provide readily available support for chitosan in spite of its inherent practical advantages.

In this research, the application of an appropriate immobilization material is essential for the utilization of chitosan in industrial applications. Providing a support material (sludge) for the immobilization of chitosan is considered to be both an economical and practical method, which can further enhance its metal binding capacity. The aim of this study is to investigate the removal of heavy metals using chitosan coated sludge (CCS) derived from a water treatment plant. The batch adsorption experimental data were

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used to determine the effectiveness of CCS to uptake copper ions individually from solutions.

II. MATERIALS AND METHODOLOGY

A. Chemicals and Reagents

Chitosan (low molecular weight, CAS No. 9012-76-4) was purchased from Sigma-Aldrich; anhydrous CuSO₄; HCl, fuming 37%; NaOH; ICP Standard Solution, 1000 mg/L Cu(II) were supplied from Merck Company and Sand (EM Science, Gibbstown, NJ). Deionized (DI) water of milli-Q purity was used for all reagent solutions.

B. Preparation of CCS

Immobilization of the chitosan was similar to the methods found in the literature [12] with only slight modifications. About 5 g of chitosan and 100 g of dry sludge were stirred in 300 mL of 5% (v/v) HCl for 5 h. 1 N NaOH was added drop by drop until neutralization occurred. The adsorbent was allowed to settle, washed with DI water and was oven-dried for 24 h at 65 °C. After drying and grinding, the materials were sieved, passed through Mesh No. 25 (0.700 mm) and collected on Mesh No. 35 (0.500 mm). The homogenous particle size of 0.500 mm which illustrated the best adsorption efficiency based on previous optimization study of adsorbent's particle size for Cu adsorption was used in the entire experiments. The new adsorbent is called chitosan-coated sludge (CCS).

C. Characteristic Analysis

SEM photographs were taken with a HITACHI S-3000N Scanning Microscope to examine the morphology and surface structure of the adsorbents at the required magnification at room temperature. Thermal gravimetric analyses (TGA) were performed on freeze-dried sludge, chitosan and chitosan-coated sludge (CCS) samples using Rigaku Thermo Plus TG 8120 in the temperature range of 30 – 800°C at a heating rate of 10°C per minute. Surface area of the adsorbents was measured by the single point BET (Brunauer, Emmett and Teller) method using the Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2010).

D. Elemental Analysis by ICP-OES

A Perkin Elmer 2000DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for quantitative determination of metal ion concentration. Standard solutions for the instrument's calibration curve were prepared as indicated: 10 mL of 1000 mg/L of ICP standard diluted to 100 mL with DI water which served as stock solution. Subsequently, different volumes of the stock solution (0.05, 0.1, 0.5, 1.0, 2.0, 4.0, 6.0 and 10.0 mL) were pipetted into 100 mL volumetric flasks and diluted to mark.

E. Batch Adsorption Studies

The adsorption of Cu(II) ions were analyzed in a batch system at room temperature with varied concentrations ranging from 100–2000 mg/L.

1) Single metal ions experiment

The experiments were performed using single solutions of the adsorbates maintained at pH 4.5. The solutions were prepared in DI water using the anhydrous CuSO₄. Thirty mL of single metal ion solution was placed in 100-mL Erlenmeyer flasks and was then combined with 2.5 g of CCS. The equilibration (shaking) time was 24 h at a static speed of 50 rpm. After equilibrium, the solution was filtered using Whatman #40 filter papers. A Whatman #40 filter was selected as a clean-up filter in preparation for ICPOES analysis. The filtrate was analyzed with ICP-OES. The amount of Cu(II) ions adsorbed per unit mass of CCS was calculated using the equation:

$$Q_0 = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ion solution (mg/L), respectively; V is the volume of the solution in liter (L); and m is the amount of CCS in grams(g). The percentage adsorption was determined using the equation:

$$\text{Percentage adsorption (\%)} = \frac{(C_0 - C_e)100}{C_0} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of metal ion solution (mg/L).

III. EFFECT OF C_0 AND CONTACT TIME

In this study, the initial concentration and contact time are two main parameters in the adsorption of Cu(II) ions in aqueous solution. This study determined the capacity of CCS for removing Cu(II) ions in the solution at the equilibrium time. The C_0 concentration were 100, 500, 1000 and 2000 mg/L prepared by diluting the stock solution of Cu(II) ions. The contact times were varied from 0.5, 1, 2, 4, 6, 12 and 24 h.

A. Effect of Solution pH

The C_0 of 100 mg/L was adjusted to the required pH value using 1 N HCl and 1 N NaOH. CCS (2.5 g) were equilibrated at the desired pH of the specified volume of the adsorbates (30 mL) for 24 h at a static speed of 50 rpm. The final pH of the filtrate was determined and its metal ion content was analyzed using ICP-OES.

B. Kinetics of Adsorption

In order to investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo second-order kinetics were applied in the data. This includes the mass transfer and chemical reactions due to the large number and variation of different chemical groups on chitosan chains [13].

1) Pseudo first-order kinetics

The pseudo first-order kinetics can be expressed as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

where k_1 is the rate constant of pseudo first-order adsorption

(min^{-1}); q_e and q_t are the amount of metal ion adsorbed per gram of chitosan-coated sludge (mg/g CCS) at equilibrium and at any time t , respectively. A straight line for the plot of $\log(q_e - q_t)$ versus t would give the first-order rate constant k_1 and equilibrium adsorption capacity q_e , from the slope and the intercept of the line.

2) *Pseudo second-order kinetics*

The pseudo second-order kinetics can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 (g/mg min) is the rate constant of pseudo second-order adsorption. The plot of t/q_t versus t would give the pseudo second-order rate constant k_2 and q_e . The pseudo second-order kinetic model is based on the assumption that the rate-limiting factor maybe chemisorption involving valence forces through sharing of electrons between the amino group and metal ions [14].

C. *Equilibrium Isotherms Studies*

Adsorption isotherm models describe the relationship between adsorbates and adsorbents at equilibrium. The two most wellknown isotherm models are the Langmuir and the Freundlich. In this study, equilibrium isotherms were used to determine the adsorption mechanism of CCS for Cu(II) ions. The adsorbents were combined with fixed volumes (30 mL) of metal ion solutions varying the initial concentrations (100, 500, 1000, and 2000 mg/L) at 4 h contact time. The relation between the amount of adsorbed metal and the remaining concentration of metal ions in solution is described by the isotherm studies.

1) *Langmuir isotherm model*

The Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites, can be expressed as:

$$Q_0 = \frac{Q_{\max} k_L C_e}{1 + b C_e} \quad (5)$$

where Q_{\max} (mg/g) is the maximum amount of the metal ion per unit weight of CCS capable of forming complete monolayer coverage on the surface, bound at a high equilibrium concentrations C_e ; Q_0 is the amount of metal ion adsorbed per unit weight of CCS at equilibrium; k_L and b are the Langmuir constants, where b is related to the affinity of binding sites [15]. According to the Langmuir equation, the maximum adsorption capacity was derived from the following equation:

$$Q_{\max} = \frac{k_L}{b} \quad (6)$$

where k_L and b can be determined from the linear plot of $1/Q_0$ against $1/C_e$.

2) *Freundlich isotherm model*

Another widely used empirical equation, the Freundlich equation, was based on adsorption on a heterogeneous surface. The equation is represented by:

$$Q_0 = k_f C_e^n \quad (7)$$

where k_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. A linear form of the Freundlich equation will yield the constant k_f and $1/n$.

$$\ln Q_0 = \ln k_f + \frac{1}{n} C_e \quad (8)$$

Therefore, k_f and $1/n$ can be determined from the linear plot of $\ln Q_0$ versus $\ln C_e$. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The obtained values of $n > 1$ signify favorable adsorption conditions [15].

IV. RESULT AND DISCUSSION

A. *Characteristic Analysis*

Sludge, chitosan and CCS bioadsorbents were characterized and among these three, the CCS illustrates higher surface area and pore volume when compared to the other two adsorbents. Obviously the metal uptake capacity of this adsorbent is higher due to its free adsorption sites. SEM/EDS analysis was exploited to illustrate the variation of morphology, mineralogical and chemical composition for each adsorbent.

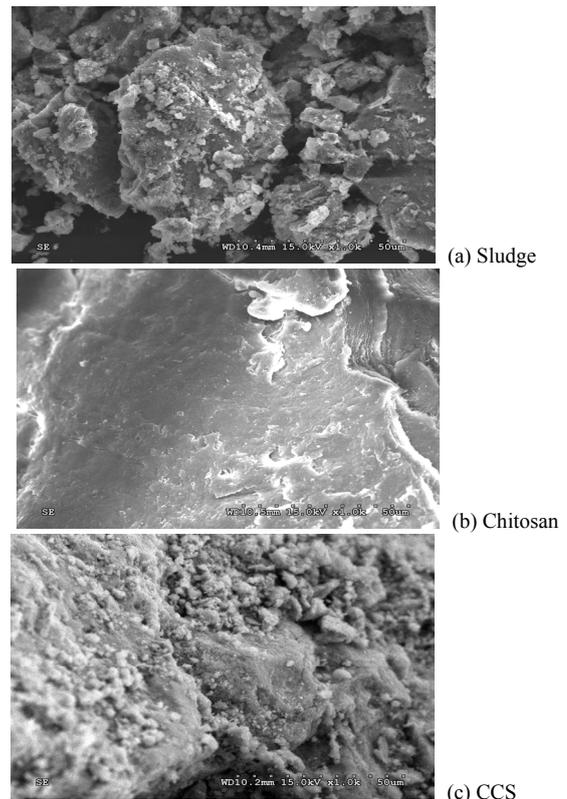


Fig. 1. SEM pictures of different adsorbents

The SEM images of the surface on sludge, chitosan and CCS are shown in Fig. 1. Fig. 1(a) and 1(b) indicates that sludge displays a rough structure on surface with a large surface area while chitosan displays a relative smooth structure on surface with a lesser surface area. Fig. 1(c) confirmed the presence of many pores and some cracks on

the surface of the CCS adsorbent.

B. Batch Adsorption Experiment

1) Effect of C_0 and contact time

As shown in Fig. 2, it is remarkable that an increase in the initial concentration (C_0) for both Cu(II) ions led to an increase in the adsorption capacity of chitosan-coated sludge (CCS) at various contact times. This can be attributed to the mass transfer effects and the driving force of the concentration gradient being directly proportional to the initial concentrations. Fig. 3 demonstrated that the higher adsorption rates were examined at the beginning. The plateau values indicated that the adsorption equilibrium was gradually attained. Retention of Cu(II) ion was noted to be inversely related to C_0 . At the lowest (100 mg/L) and the lower (100~500 mg/L) concentrations, the equilibrium adsorption capacities were related to the ionic size. At the higher C_0 (1000~2000 mg/L), the equilibrium adsorption capacities were attributed to the hardness of the metal ions.

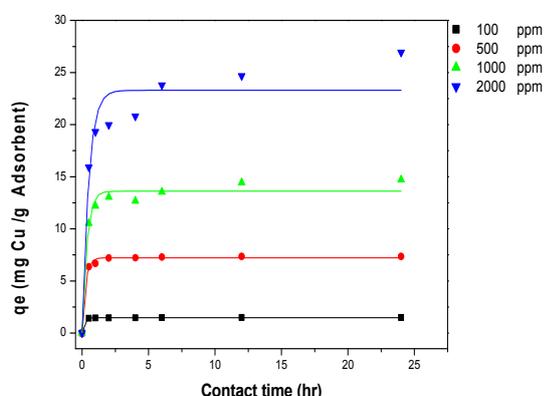


Fig. 2. Effect of initial concentration and contact time on equilibrium adsorption of Cu(II) ions onto chitosan-coated sludge.

Masel (1996) expounded that hardness is inversely related to the ability of the molecule to share electrons [16]. It follows that when the hardness is small, and the number of shared electrons will be large and vice versa. Therefore, more numbers of electrons were shared, which resulted in stronger covalent interactions with the chitosan at a higher C_0 . In this case, the maximum adsorption capacity was achieved after the binding ability of the adsorbent approached saturation at equilibrium time.

As shown in Fig. 3, an exposure time of 24 h was used during batch studies to achieve the equilibrium. It demonstrated that CCS can potentially remove more than 50% of Cu (II) ions at the highest concentration and reached the equilibrium at 1 h regardless of the initial concentrations (C_0). Moreover, when adsorbate concentrations were raised, binding capacity of the adsorbent reached saturation instantaneously, which resulted in diminishing the overall % adsorption of Cu ions.

2) Effect of pH

To prevent precipitation, experiments were carried out at $pH < 6$ to ensure the solubility of metal ions [14], [17], [18]. At high pH, precipitation usually occurred with the metallic ions attached to hydroxide ions forming $Cu(OH)_2$ at $pH > 8$.

To clarify the influence of solution pH on the adsorption capacity, chitosan-coated sludge (CCS) was subjected to

different pH values ($pH = 2, 3, 4$) at an oscillating time of 1 hour. The choice of the oscillating time was in accordance to CCS adsorption equilibrium experiments. The results of experiments are shown in Figure 4. The CCS illustrates good adsorption phenomena at pH 4 and pH 3. However, it demonstrated the downward trend as the pH value decline.

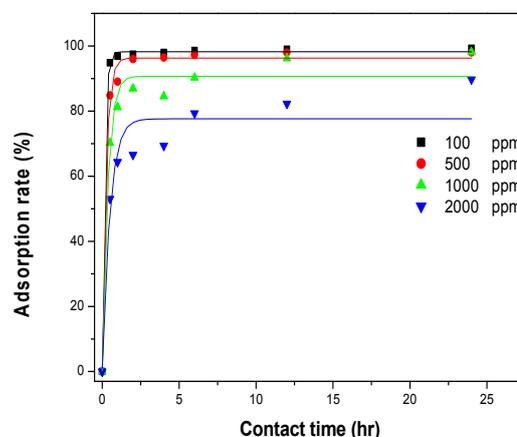


Fig. 3. Adsorption percentage at different concentrations and contact time of Cu(II) ion onto chitosan-coated sludge.

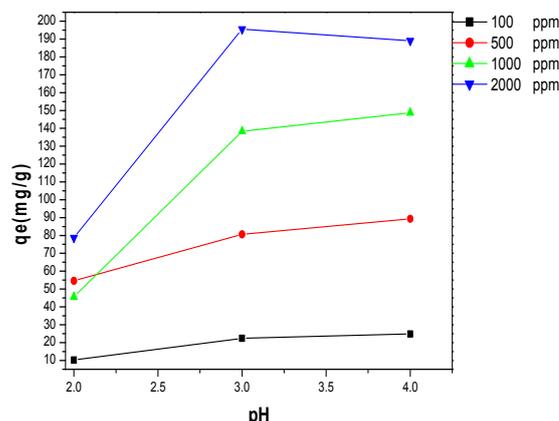
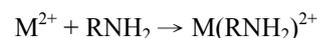


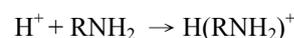
Fig. 4. The pH effect of CCS on equilibrium adsorption

The CCS adsorption capacity is influenced significantly by the pH value. The chitosan attached to the water treatment plant sludge provides larger contact surface resulting to an increase in adsorption capacity. However, in acidic condition, there is competition between H^+ ions and the heavy metals in terms of binding with the basic NH_2 groups of chitosan. Metal adsorption percentage decreased since most of the NH_2 groups of CCS are in the protonated form (NH_3^+) [19].

Taboada et al., (2003) and Wan et al. (2010) described the similar phenomena as the following competing reactions, where M^{2+} represents the divalent metal ion and R is the polymer structure of chitosan [19], [20].



The amino group of chitosan may react with hydrogen ions (H^+) according to:



Conversely, there was an improvement in the metal adsorption percentage while the pH value was increased. CCS exhibited enough binding capacity. The adsorption percentage of different Cu (II) concentrations increased with

pH range from 2 to 4. However, the influence on retention time was minimal for the succeeding values (pH 3-4) regardless of contact time. This effect suggested that the amino group was deprotonated. The chelation mechanism outranked the adsorption one where more metal ions chelating with chitosan.

C. Kinetics of Adsorption

To investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo second-order kinetic equations were both examined. Table I shows the adsorption kinetic studies of Cu(II) ions onto CCS at different C_0 . The pseudo first-order kinetic model did not adequately describe the adsorption results with a low

correlation coefficient for the entire data (0.1855–0.6038). However, the pseudo second-order kinetic model provided an impressive and comparable correlation for the adsorption of both ions in contrast to the pseudo first-order model (0.9977–0.9998).

The pseudo first-order rate model has been widely used for sorption of metals [14], which was widely used for reversible reactions with an equilibrium being established between liquid and solid phases. In many cases, the pseudo first order do not fit well to the whole range of contact time and is generally applicable over the initial stage of adsorption process [21].

TABLE I: ADSORPTION KINETIC STUDIES OF CU (II) IONS ONTO CHITOSAN-COATED SLUDGE (CCS)

Cu(II) (C_0 , ppm)	Pseudo-first order kinetic model			Pseudo-second order kinetic model			
	k_1	q_e	R^2	q_e	q_e^2	k_2	R^2
100	0.00005	2.08	0.1855	1.49	2.23	0.26588	0.9998
500	0.00005	6.95	0.309	7.37	54.39	0.03043	0.9996
1000	0.00016	11.81	0.5439	14.90	222.10	0.00289	0.9995
2000	0.00023	16.81	0.6038	273.97	75060.99	0.00001	0.9977

Ho (2006) illustrated that the pseudo second-order reaction was used to distinguish the kinetic equation based on the concentration of a solution from the adsorption capacity of a solid [22]. In this study, the rate constant k_2 was determined experimentally by plotting the slopes and intercepts of t/qt against t . The high correlation coefficient shown in Table I illustrated an agreement of experimental data with the pseudo second-order kinetic model (Eq. (4)) for different Cu(II) ion concentrations. The overall adsorption rate for both ions appeared to be controlled by the chemical process. This conclusion is based on the assumption that chemisorption involved sharing or exchange of electrons as covalent forces between the transition metal cations and adsorbent and ion exchange [22].

Based on the equation, the adsorption rate dq/dt is proportional to the second-order of $(q_e - q)$. High adsorption equilibrium capacity, q_e , results in fast adsorption rates and short equilibrium times. Short equilibrium times coupled with high adsorption capacity indicates a high degree of affinity between Cu(II) ions and CCS. Moreover, several studies for adsorption of divalent metals on heterogeneous sorbents reported that the majority of the metal sorption kinetics follows the pseudo second-order mechanism [22].

D. Adsorption Isotherm

The experimental adsorption data were examined by using the Langmuir and Freundlich isotherm model to indicate the possible adsorption mechanism. In this study, the regression coefficients were selected to indicate good linearity, which confirmed that the Cu(II) ions followed the two theories of adsorption, as shown in Table II. The results show that at different equilibrium time, the calculated data of Langmuir

isotherm which exhibited the highest regression correlation for both ions ($> 98\%$) described a better fitting model than that of Freundlich isotherm, the R^2 value can be higher than 0.99.

Langmuir isotherm model is most suitable for monolayer adsorption based on the assumption of finite numbers of adsorption sites. All sites are equivalent and there is no interaction between adsorbed ions. The result indicates the applicability of monolayer coverage on the surface of CCS in spite of the surface modification [19]. Moreover, the maximum adsorption capacities of Cu(II) ions were obtained by using Langmuir isotherm model, which are 11.88, 12.56, 18.83, 16.50, 16.61, 17.45, and 17.54 (mg-Cu/g-CCS) at different times (0.5, 1, 2, 4, 6, 12, and 24 hours) respectively. This results also indicate that CCS reached the saturated adsorption after 2 hours, where the maximum amount of the adsorption is 18.83 mg/g. A single copper layer ions are adsorbed (uniform monolayer adsorption) for each active site. The adsorbent presents many adsorption active sites (repeating amine group), each with the same pro-active position forcing the adsorption of copper ions from the solution. However, longer adsorption time resulted to a slight desorption of copper ions. This phenomenon is caused by the water purification sludge itself which contains some metal elements desorbing into the solution forming positively charged ion resulting into competitive adsorption of Cu(II) ions.

No value of the CCS calculated by the Freundlich isotherm model is greater than 1, which reveals the phenomena of favorable metal adsorption. Thus, CCS adsorbent illustrated high adsorption potential for heavy metal removal in aqueous solution.

TABLE II: SUMMARY OF ADSORPTION ISOTHERMS STUDIES FOR Cu(II) IONS ONTO CHITOSAN-COATED SLUDGE (CCS)

Contact time (hrs)	Langmuir isotherm				Freundlich isotherm		
	K_L	B	Q_{max} (mg/g)	R^2	n	K_F	R^2
0.5	0.29	0.025	11.88	0.9957	2.08	0.6636	0.9846
1	0.49	0.039	12.56	0.9964	2.14	0.8972	0.9776
2	0.58	0.031	18.83	0.9994	2.06	1.1293	0.9379
4	0.75	0.045	16.50	0.9992	2.23	1.3110	0.9325
6	1.10	0.066	16.61	0.9987	2.14	1.5025	0.9512
12	1.58	0.091	17.45	0.9983	2.15	1.9099	0.9265
24	2.32	0.132	17.54	0.9928	1.92	2.1498	0.9470

V. CONCLUSION

Bioadsorbent, chitosan-coated sludge (CCS), has demonstrated high efficiency in removing Cu(II) ions from aqueous solution. The amount of Cu(II) ions adsorbed increased with increasing pH. The equilibrium studies were described using both Langmuir and Freundlich isotherm models. The Langmuir isotherm illustrated the best description of the metal adsorption mechanism. The maximum adsorption capacity of Cu (II) ions was 18.83 mg/g after 2 hours contact time. Moreover, the equilibrium kinetics agreed well with pseudo second-order kinetics, which indicated that the adsorption was controlled by chemisorption.

This study has illustrated the possible adsorption behavior of CCS to remove copper ions from water. In conclusion, these preliminary results indicate the possibility of using sludge derived from water treatment plant to establish an inexpensive large-scale filter as a permeable reactive barrier for metal removal, the goal of waste recycle and reuse.

APPENDIX

b	Langmuir constant, related to the energy or the net enthalpy of adsorption process
C_e	equilibrium concentration, mg/L
C_o	initial concentration, mg/L
K_f	Freundlich constant, an indicator of adsorption capacity
K_L	Langmuir constant incorporating the enthalpy of adsorption
k_1	rate constant of pseudo-first order, min^{-1}
k_2	rate constant of pseudo-second order, g/mg min
n	Freundlich constant
q_e & q_t	amount of metal adsorbed at equilibrium and at any time, mg/g
Q_{max}	maximum capacity or “Langmuir” monolayer sorption capacity, mg/g
Q_o	amount of metal ion adsorbed, mg/g
t	time, min
v	volume of the solution, L

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