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HEAVY METALS ADSORPTION BY OXYTETRACYCLINE HYDROCHLORIDE TETRACYCLINE ANTIBIOTIC WASTEWATER EXCESS ACTIVE SLUDGE

Songyan Qin[1], Wanpeng Kuang[1], Xintong Wang[1], Yi Luo[2] and Lixin Zhao[1*]

[1.] School of Environmental Science and Safety Engineering, Tianjin University of Technology, China.
[2.] College of Environmental Science and Engineering, Nankai University, China.

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Abstract: Tetracycline wastewater excess active sludge TEAS was studied for the possibility of heavy metal ions adsorption and barrier materials in the landfill. TEAS was characterized by SEM, element analysis, TGA and FT-IR techniques. The characterization of TEAS demonstrated mounts of remaining hypha residues existed in sludge. High-temperature drying of sludge reduced the potential risk of remaining Tetracycline bleaching. The Adsorption thermodynamics study of TEAS to the Cu2+, Ni2+ , and Cd2+ indicated a spontaneous and endothermic nature of the adsorption process. The best equilibrium data was given by Langmuir isotherm, and the maximum adsorption capacities were 18.484, 14.837 and 9.116 mg/g for Cu2+, Ni2+ and Cd2+, respectively. The kinetic data of adsorption were described by a pseudo-second-order equation, indicating their chemical adsorption. The main mechanism of metal biosorption was cation exchanged is expected that TEAS could be used as a promising co-disposal and attenuation material in the landfill to hinder the heavy metal solution into Landfill leachate.

Keywords: Tetracycline hydrochloride antibiotic; excess active sludge; heavy metal; adsorption; ion Exchange

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[*] Correspondence to: Lixin Zhao, Tel.: +022 6021 4749 E-mail: collition@sohu.com

INTRODUCTION

Heavy metal is one of the most hazard component of the landfill leachate (Al Raisi *et al*., 2014). Recently, in situ heavy metal attenuation and capture techniques in landfills are developed. One of the important waste management strategies is co-disposal, which is a technique for the controlled disposal of industrial wastes together with municipal solid wastes (Erses *et al*., 2003). Sewage sludge is an ideal co-disposal material due to its unique biochemical composition sequesters metal ions and metal complexes (Ahluwalia & Goyal, 2007). Non-living microbial biomass offers active sites such as carbonyl, carboxyl, hydroxyl, amino, sulfate and hydroxyl groups for binding of metal cations, meanwhile ion exchange is also involved for heavy metal capturing (Yunqcu *et al*., 2006a; Choi & Yun, 2006b; Hammaini *et al*., 2007c). Xue *et al.* (2011) found that the ion exchange of Ca^{2+} and Mg^{2+} are supposed to be responsible for Cu^{2+} bio-sorption on dried plant waste (Xue *et al*., 2011). Considering its abundant carbon content, biomass and surface area, Sewage sludge could be a potential candidate material for the heavy metal barrier from leachate in the landfill (Bilardi *et al*., 2018).

Ferment antibiotics such as tetracyclines are widely used as human medicine to treat or prevent microbial infections (Halling-Sorensen *et al.,* 1998). By 2012, the estimated usage of tetracyclines was 5954.36 and 113.2 tons in the United States and the European Commonwealth, respectively (Granados-Chinchilla & Rodríguez, 2017). Huge market requirements promote tetracyclines production, correspondingly large amounts of wastewater was discharged from the tetracyclines producing process, containing spent organic fermented substance and remaining hyphae residue. Tetracyclines producing wastewater in China are mainly treated through activated sludge process. High content nutrient stimulated sludge growth and the hyphae residue transferred to the sludge. Extra amount of excess active sludge (TEAS) discharged from Tetracyclines treatment process need to be disposed. Now the disposal way of TEAS is landfilled as general waste. The biomass contained in the TEAS such as remaining hyphae residues, EPS of bacteria, and large amount of hardness minerals could possibly have the adsorption ability to heavy metal. It could be considered to mix TEAS with heavy metal-containing waste to attenuate and capture heavy metal. However, the adsorption capability of TEAS for the heavy metals and the adsorption mechanism still remain unclear. Besides, the remaining tetracyclines release from TEAS needs to be investigated.

In this paper, we studied firstly the character of TEAS through element analysis, SEM, TGA and FTIR methods. Then the Adsorption capacity and kinetics of TEAS adsorption for the Cu^{2+}, Ni^{2+}, and Cd^{2+} from aqueous solution was investigated. The adsorption mechanisms were discussed. This study is expected to present parameters for TEAS co-disposal and help to alleviate heavy metal dissolution into the leachate

MATERIALS AND METHODS

The source of TEAS and samples preparation

TEAS was obtained from the wastewater treatment plant of a tetracycline manufactory. The treatment processes are mainly composed of air floatation, SBR, contact aeration and sedimentation units (**Fig. 1**). The excess active sludge comes from the above units. Sludge samples were prepared as follows: firstly, milled and sieved through 1mm mesh, then dried at 250°C for 2h.

Adsorbent characterization

The Surface morphology of TEAS was characterized by a scanning electron microscope (JSM-6700F, acceleration voltage: 10kV) and stereomicroscope (C-DSLS, Nikon). Elemental composition was analyzed using a Varro-ELIII elemental analyzer. Group variation during the adsorption process was recorded by FT-IR (TENSOR 37). The Surface area was measured with a surface area analyzer (Autosorb-iQ, Quantachrome) Thermo weight loss was performed using a TGA Q50 thermogravimetric analyzer (Waters TA). The concentration of metal ions was determined by flame atomic absorption spectrometer (FAAS, TAS990) and ICP-OES (VISTA-MPX).

Determined of TC

The quantity of TC released from TEAS aqueous solution was determined by UPLC-MS/MS. UPLC conditions as followed: (a) Column temperature: 50 °C; (b) Injection volume: 5 µL; (c) Velocity:0.45ml/min; (d) Mobile phase A: formic acid aqueous solution (0.1%); (e) Mobile phase B: acetonitrile. MS conditions as followed: (a) Ion source: ESI+ (electrospray ionization); (b) Capillary: 3.5 kv; (c) Source Temperature: 150 °C; (d) Desolvation temperature: 350°C.

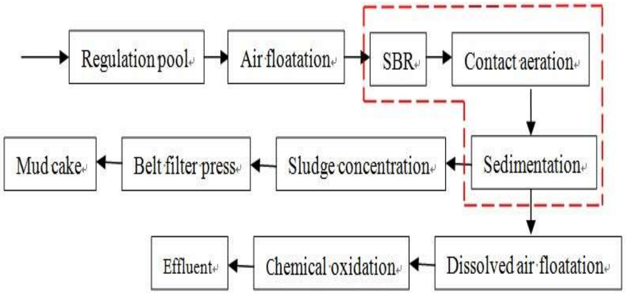

Fig. 1 The wastewater treatment process of TC manufactory.

Adsorption experiments of TEAS

TEAS were used as an adsorbent for the removal of heavy metal ions i.e. Cd^{2+}, Ni^{2+} and Cu^{2+} from aqueous system. Stock solutions (1000mg/L) of all the three ions were prepared by dissolving the exact amount of copper, nickel and cadmium sulfate in de-ionized water. The sludge was added to 50 ml of solution (100 mg/L). We have studied the effect of the mass of adsorbent from 0.1 to 2.3 g and pH from 2.0 to 8.0 at 30 °C for 90min. The adsorption isotherm and kinetic experiments were carried out by varying the initial concentration of metal solutions from 100 to 450 mg/L and temperature from 10 to 30℃ respect. Adsorption isotherm data obtained in this experimental study was evaluated with Freundlich and Langmuir isotherms models. The kinetic data were fitted to first-second-order and pseudo-second-order. △G°, △H°, and △S° were adopted to investigate adsorption thermodynamic study in the temperatures from 10 to 30℃。

The mechanism of adsorption

The amount of 1.0, 1.7 and 2.0g TEAS were added to 50 mL of Cu^{2+}, Ni^{2+}, and Cd^{2+} solution, respectively. The initial concentration of metals varied from 100 to 500mg/L. The desorption of Ca^{2+} and Mg^{2+} from sludge was measured by ICP. The quantity (mol) of desorbed cations released into solution and the adsorbed heavy metals were calculated as follows:

$$n = \frac{(C_0 - C_e) \times V}{M \times W} \qquad (1)$$

where C_o (mg/L) and Ce (mg/L) is the initial and the equilibrium liquid-phase concentration of cations, respectively. V (L) is the volume of the solution and W (g) is the weight of the corresponding adsorbent OWEAS. *M* is the relative atomic mass. The ratio of desorbed cations and adsorbed heavy metal ions demonstrated the role of ion exchange during OWEAS adsorption process.

RESULT AND DISCUSSION

Characterization of adsorbent

Morphology of TEAS

The fresh TEAS sample existed as large blocks before meshed. The sample was sieved through 1mm mesh and then dried at 105 °C for 2 h. Moisture content was 11.45% at 105℃ for 2h. The sample scattered as black uniform granular with loose structure, no peculiar smell (**Fig. 2**).

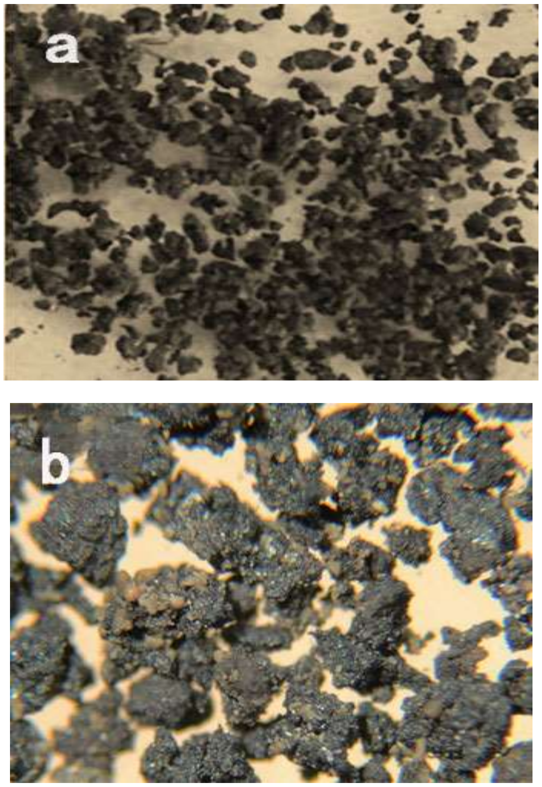

Fig. 2 OWEAS, (a) an overview image, (b) stereo microscope image (×50).

The SEM micrographs of TEAS exhibited that the sludge was comprised of 5-60um amorphous agglomerates (**Figs. 3a–3b**) consisting of remaining hypha residues of ca.0.5×2μm (**Fig. 3c**) in size. As a result of the aggregation of these remaining hypha residues in **Fig. 3(d)**, the disordered wormhole-like microspores were formed in the sludge and high porosity was beneficial for the diffusion of metal ions.

N_2 adsorption-desorption isotherm was used to investigate the surface area of TEAS. The BET surface area of TEAS was 11.916 m^2/g, much higher than that of the urban sewage, 6.31 m^2/g (Phuengprasopa et al., 2011). The remaining hypha residues stacked and arrayed irregularly to form pores, which developed high porosity and lead to the large surface area.

Composition and TGA of TEAS

Thermal behavior of the TEAS was studied by TGA analysis in air up to 900℃. **Fig. 4** represents the TGA curve of pharmaceutical wastewater excess sludge，TGA graph shows three major weight loss regions, at three different temperature ranges. The initial weight loss region between 50 and 100℃ can be ascribed to the desorption of the physically absorbed water from the sample. The second weight loss between 250℃ and

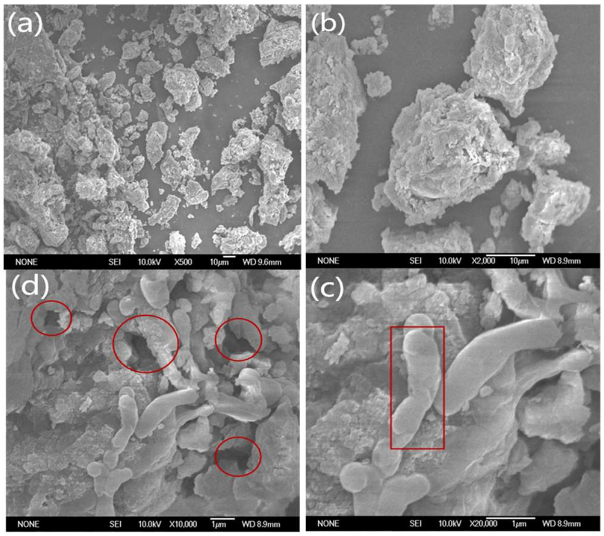

Fig. 3 SEM micrograph of the surface of TEAS.

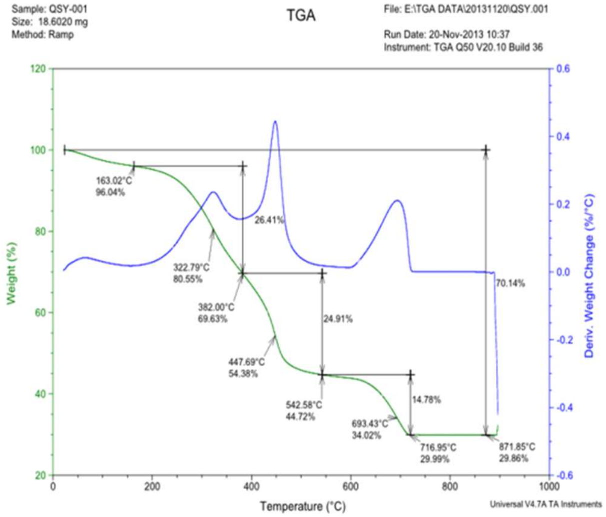

Fig. 4 TGA profile of TEAS.

400℃ can be regarded as thermal decomposition of volatile organic carbon, it was 55.28% of the whole part, also relatively correspond to the value of VSS (50.24%). To protect the organic group and violate the pore water, we chose 250℃ to dry sludge.

Release of TC

There was 39.32μg/g TC in the wastewater excess active sludge and it released 1.12μg/g OTC after 2 hours leaching, then increased to 1.96μg/g after 24 hours. After drying at 250 ℃ the TC decreased to 0. 269μg/g after 2 hours, this value is lower than the average level of sewage plant (0.295μg/g) (Li, 2014). TC is decreased because the temperature reached the melting point (183℃), which made it volatilized. The TEAS after heating still contains a small amount of TC probably due to form the complexes with divalent calcium ions (Lunestad & Goksøyr, 1990), divalent calcium ions existed largely in TEAS which mentioned in next part. TC can be degraded under natural illumination condition, Li studied that the removal rate of TC by direct illumination 60 min reached to 45% and 90% under pH 7 and 9, respectively (Li, 2012). There was 0.731μg/g TC in the TEAS after 24 hours leaching (**Fig. 5**). Considering the remaining TC leaching, High - temperature drying is suggested for the TEAS dewatering treatment process.

Adsorption studies

Effect of adsorbent mass

The quantity of adsorbent is an important parameter for adsorption of metal ions from aqueous solutions. **Figure 6** shows that adsorption efficiency rose gradually as adsorbed dose increased until up to a certain value because the adsorption sites were saturated gradually, Optimal dosing of adsorbents was determined to be 1.0, 1.7 and 2.0g for Cu^{2+}, Ni^{2+}, and Cd^{2+}, respectively. Consequently, the rest of the adsorption experiments were performed at this mass of those metal solutions. After this maximum equilibrium value, the removal efficiency did not rise with increasing adsorbent mass. These results suggest that the relationship between adsorbent dosage and removal efficiency was related to increases in the number of adsorption sites and that increasing this number had no effect after equilibrium was reached(Argun et al.,2007).The mechanism through which the metal ions adsorbed on TEAS may be attributed to the complex formation of different metal ions.

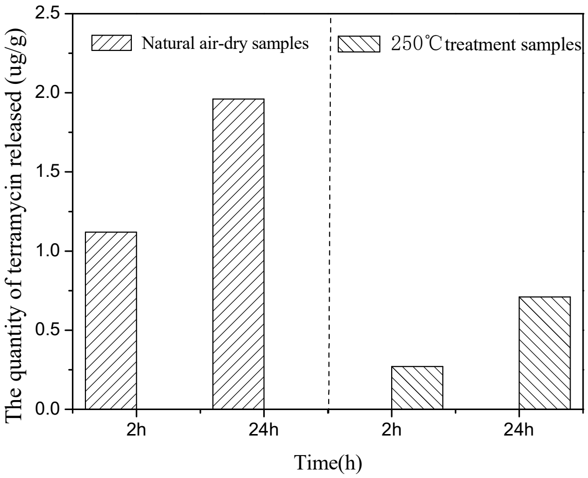

Fig. 5 The release of TC

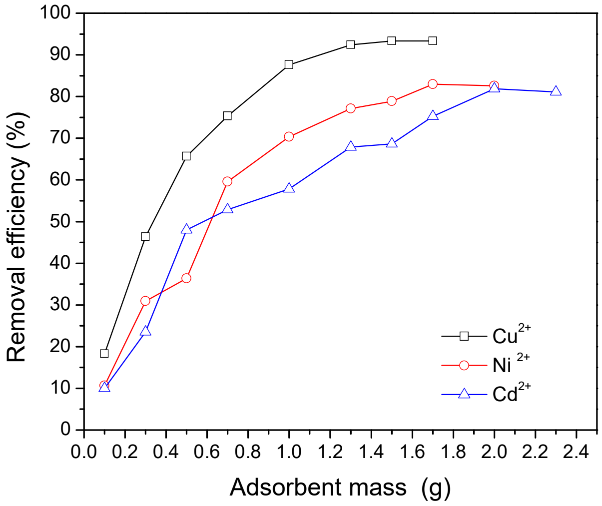

Fig. 6 Effect of quality of TEAS

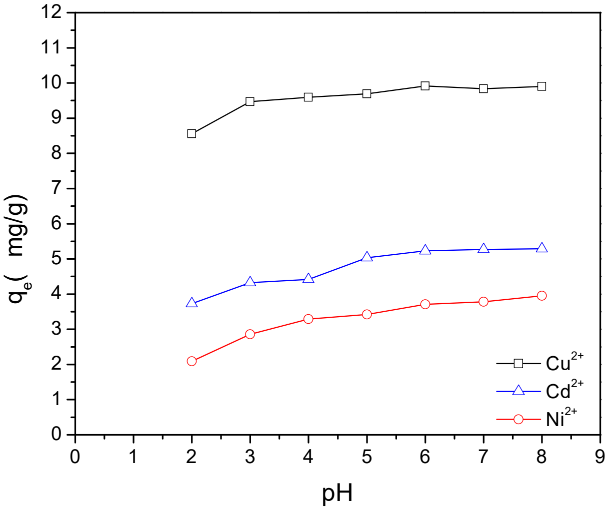

Fig. 7 Effect of Ph

Effect of solution pH

pH affects the solubility of the metal ions, concentration of the counterions on the adsorbent and the degree of ionization of the adsorbate during reaction (Shin et al.,2011). To study the pH effect on the metals sorption by TEAS, the initial pH of the solution was adjusted within the range of 2 to 8, this range was chosen to avoid metal solid hydroxide precipitation and sludge surface dissociation. Although the maximum adsorption of Cu^{2+} was observed at pH 6 and that of Ni^{2+} and Cd^{2+} at pH 7, the adsorption amount was basically maintained at the optimum level with the pH range of 6-8(**Fig. 7**). Consequently, the rest of adsorption experiments were carried out at neutral pH of those metal solutions. At low values of pH 2 to 5, the decrease in the removal efficiency could be referred to the fact that the mobility of the hydrogen ions is higher than that of the metal ions and it reacts with active sites before adsorbing the metal ions.

Adsorption isotherm study

Heavy metal removal performance of the TEAS was evaluated as a function of the initial ions concentration ranged from 100 to 450mg/L with a corresponding fixed adsorbent mass（determined in 3.2.1）at pH 7. In this study, the sorption time was fixed at 90 min because the adsorption of Cu^{2+}, Ni^{2+}, and Cd^{2+} ions onto the TEAS sufficiently reached an equilibrium state for 90 min based on the following contact time dependency test (**Fig. 8**). The obtained experimental data for heavy metal ions adsorption onto the TEAS were analyzed using Langmuir and Freundlich isotherm models, expressed by Eqs. (2) and (3), respectively.

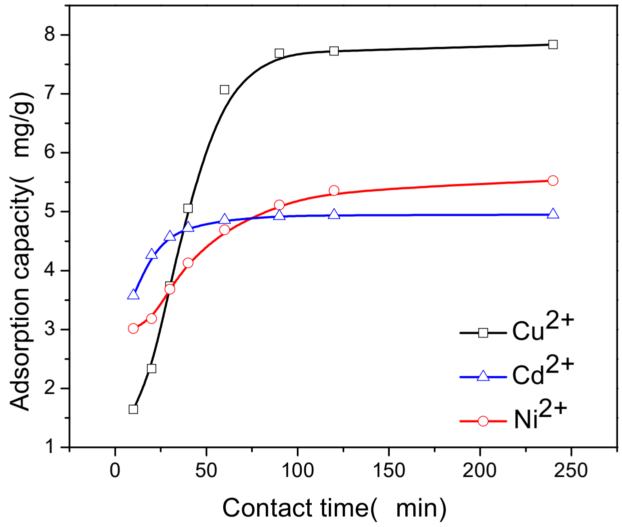

Fig. 8 Effect of shacking time on heavy metal ion Langmuir Isotherm applies to adsorption on completely homogeneous surfaces with negligible interaction between adsorbed molecules.

It is represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{2}$$

where q_e is the equilibrium adsorption capacity of ions on the adsorbent (mg/g), C_e is the equilibrium ions concentration in solution (mg/L), q_m is the maximum capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant (L/mg).

Freundlich isotherm can be applied for heterogeneous surfaces and multilayer sorption. It is expressed as:

$$q_e = K_F Ce^{1/n} \tag{3}$$

Table 1. Langmuir and Freundlich parameters for adsorption of OWEAS

Cations	Langmuir			Freundlich		
	q_m（mg/g）	b（L/g）	R^2	K_F（mg/g）	N（L/g）	R^2
Cu^{2+}	16.860	0.054 6	0.977 6	3.070	2.999	0.967 4
Ni^{2+}	14.837	0.034 3	0.982 3	1.893	2.594	0.879 7
Cd^{2+}	9.115 8	0.271 1	0.988 2	7.932	5.537	0.974 7

$$log\, q_e = log\, K_F + \frac{1}{n} logC_e \quad (4)$$

where equilibrium capacity q_e and C_e are defined as above, K_F is the Freundlich constant (L/mg) and n is the heterogeneity factor.

The regression parameters and correlation coefficients (R^2) presented in **Table 1**. In fact, the adsorption isotherm data for the metal ions were consistently better with Langmuir isotherm as compared to Freundlich isotherms, which were determined by the correlation coefficients (R^2). Accordingly, it is considered that the OWEAS has a homogenous surface for adsorption.

In particular, the Langmuir isotherm can be represented in terms of a dimensionless constant separation factor (R_L) (Shin et al., 2011a; Rafatullaha et al.,2009b; Corami et al.,2007c). The R_L is equal to the ratio of the unused adsorbent capacity to the maximum adsorbent capacity and thus it can be a measurement of the adsorbent capacity and the affinity between the adsorbate and adsorbent. R_L value was calculated by the following Eq. 5:

$$R_L = \frac{1}{1+bC_0} \quad (5)$$

where b and C_0 are the Langmuir constant and initial concentration of heavy metal ions. In general, R_L classified as $R_L＞1$, $R_L=1$,$0＜R_L＜1$ and $R_L=0$ indicates that the type of adsorption isotherm is unfavorable, linear, favorable and irreversible, respectively(Shin et al.,2011). Our R_L value was $0＜R_L＜1$ suggesting the favorable adsorption isotherm of Cu^{2+},Ni^{2+}, and Cd^{2+} on TEAS.

The maximum adsorption capacity (q_m) calculated by Langmuir isotherm has been shown in **Table 1** for Cu^{2+}, Ni^{2+} and Cd^{2+} were 16.860,14.837 and 9.115 8 mg/g, respectively. The removal percentage was in the order of $Cu^{2+} > Ni^{2+} > Cd^{2+}$. Similarly, the high tendency of Cu^{2+} ions for bio-sorption among the heavy metal ions was studied in literature (Al-Qodah,2006) that the maximum loading capacity of the NaOH treated slugged was $Cu^{2+} > Cd^{2+}$. One of the possible reasons for this tendency is that the disparity in metal ion radius and oxidation states of the heavy metal ions could also affect the different adsorption capability (Song et al., 2011). The radius of Cd^{2+} is greater than the Cu^{2+} induces the lower adsorption capacity than Cu^{2+}, in consequence of the negative correlation between ion radius and adsorption capacity. Nickel was found to be associated predominantly with the soluble polymers than for biomass, which can explain the lower binding capacity of OWEAS for Ni^{2+}, and indicates these soluble complexes may be unavailable for the uptake by the biomass (Yuncu et al., 2006).

Adsorption kinetic study

Kinetic analysis of the adsorption process is very important because the kinetics provide essential information on the adsorption mechanism and the metal ion uptake rate. **Figure 8** displays the time dependence of heavy metal ion adsorption capacity onto the OWEAS. The pseudo-first-order and pseudo-second-order kinetic models were employed to interpret the experimental data. The adsorption amount increased with contact time and reached equilibrium at 90 min, however, the reaction time was continued for 240min to keep the sufficient condition for the stability of the adsorption equilibrium state.

The pseudo-first-order (6) and pseudo-second-order (7) kinetic model are respectively represented as:

$$log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (7)$$

where k_1 and k_2 are pseudo-first-order rate constant (min^{-1}), pseudo-second-order rate constant (g $mg^{-1}min^{-1}$) of adsorption, respectively. q_e and q_t are the adsorption capacity (mg/g) at equilibrium time and at time t (min), respectively. The kinetic parameters for the adsorption of TEAS were given in **Table 2** and **Fig. 9**.

Based on the correlation coefficient (R^2) of each kinetic model, the pseudo-second-order model obviously fitted for the experimental kinetic data. Simultaneously, the experimental q_e value is more

Table 2. the kinetic adsorption parameters obtained using pseudo-first-order and pseudo-second-order at 30°C for the adsorption of heavy metal ion.

Cations	Pseudo-first-order				Pseudo-second-order		
	k_1 (min^{-1})	q_e (mg/g)	q_{e1} (mg/g)	R^2	q_{e2}(mg/g)	k_2	R^2
Cu^{2+}	0.007 9	7.835	11.537	0.959 6	13.004	0.001 1	0.963 8
Ni^{2+}	0.009 5	5.526	3.704	0.910 8	5.144	0.043 9	0.821 2
Cd^{2+}	0.004 7	4.948	1.895 4	0.933 3	5.203	0.008 5	0.995 4

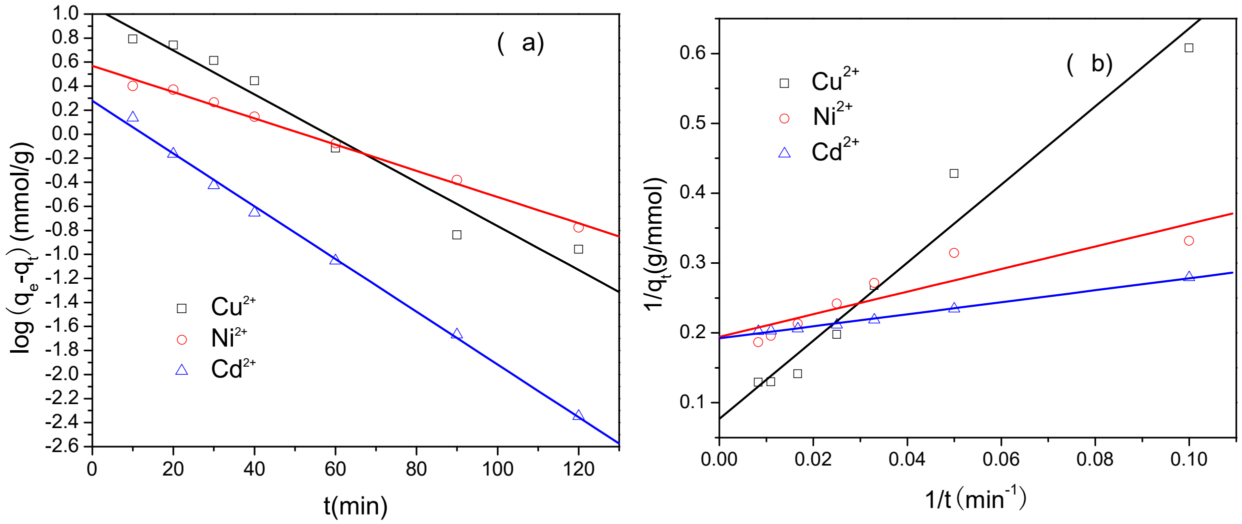

Fig. 9 Adsorption of heavy metal ions onto OWEAS by (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics model.

in agreement with the pseudo-second-order model than the kinetics pseudo-first-order for all three heavy metal ions. Because of pseudo-second-order model assumed that the determining rate step may be chemisorption promoted by covalent forces through the electrons sharing between sorbent and sorbate, suggestion that the adsorption of heavy metal ions on OWEAS is mainly the chemical reactive adsorption.

Adsorption thermodynamic study

The effect of temperature on adsorption of Cu^{2+}, Ni^{2+} and Cd^{2+} ions by OWEAS was studied by allowing 1.0,1.7 and 2.0 g TEAS to equilibrate with 50 mL of metal cation solutions (100 mg/L) at 283, 288, 293, 298, 303K. The results found that the adsorption capacity increased by rising temperature (**Fig. 10a**). This indicates that the adsorption process is endothermic in nature. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from the following equations:

$$K_c = \frac{C_{ad}}{C_e} \tag{8}$$

where C_{ad} is the concentration of solute adsorbed on OWEAS at equilibrium (mg/L) and C_e is the equilibrium concentration of metal ion in the solution (mg/L). To calculate the free energy of the adsorption (ΔG°), the following equation was employed:

$$\Delta G^\circ = -RTlnK_c \tag{9}$$

The Eq. (8) allows evaluating the standard enthalpy (ΔH°_{ads}) and entropy (ΔS°_{ads}) of the adsorption by plotting ln K_c versus 1/T.

$$lnK_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

where R (8.314 J/mol K) is the gas constant.

The values of the slope $-\Delta H^\circ/R$ and the intercept $\Delta S^\circ/R$ from **Fig. 10** (***b***) give ΔH° and ΔS° for the adsorption of Cu^{2+}, Ni^{2+} and Cd^{2+} ions on OWEAS. The calculated values of thermodynamic parameters in **Table 3** show that ΔG° for all ions at every temperature always kept negative values, and the ΔG° values increased as temperature rises, which indicated the spontaneous nature of the adsorption by OWEAS. The positive value of ΔH° and ΔS° of the processes further confirms the endothermic nature of the process.

Table 3. values of thermodynamic parameters for the adsorption of metal ions on OWEAS

T(K)	K_c			$-\Delta G^\circ$(kJ/mol)		
	Cu^{2+}	Ni^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}
283	9.90	7.74	11.67	5.3946	4.8176	5.781 9
288	11.13	7.857	13.492	5.7703	4.9360	6.230 7
293	15.58	14.89	30.05	6.6890	6.5802	8.289 9
299	20.32	12.90	36.17	7.4608	6.337	8.890 4
303	20.05	12.14	74.75	7.5524	6.2892	10.868
	ΔH°(kJ/mol)			ΔS° (J/mol K)		
	Cu^{2+}	Ni^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}
	28.761	20.102	66.836 6	120.602	88.378	255.547

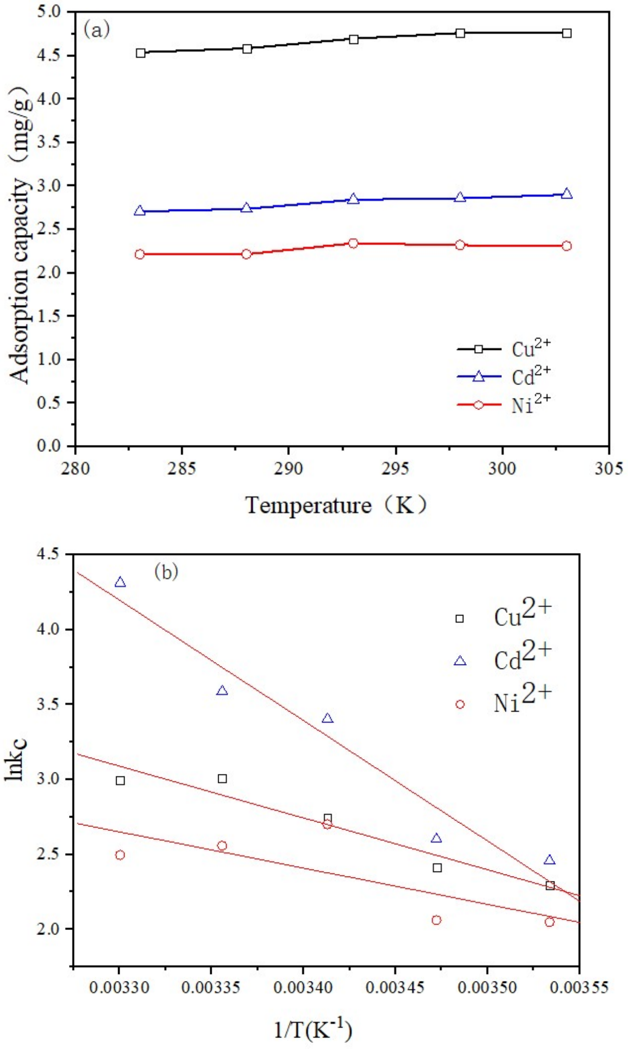

Fig. 10 Thermodynamic plots for Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on OWEAS.

Mechanism for heavy metal ions onto TEAS

Complexation with functional groups

The adsorption of Cu^{2+} is supported by FT-IR analysis. The spectra recorded in the 400-4000cm^{-1} range for OWEAS before and after adsorption are in **Fig. 11**. The strong and broadband centered around 3387cm^{-1} are associated with the O-H stretching vibrations of the hydroxyl groups in layers and interlayer water molecules. The peak around 2927 cm^{-1} related to $C{=}H_2$ group, and the peak at 2082 cm^{-1} N=N bonds. Those groups have the ability to bind metal cations and vibrated after heavy metal adsorption. However, in our study no obvious changes were observed.

Ion exchange

To study the possibility of cation exchange during adsorption, the desorbed cations (Ca^{2+} and $Mg^{2+)}$ from the sludge during adsorption tests were also analyzed. The amount of Ca^{2+} and Mg^{2+} ions in solution increased with the increasing quantity of adsorbed metal ions (**Fig. 12**). Meanwhile, Zn^{2+} was replaced only in the solution of Cu^{2+} describe the Cu^{2+} was more easily to reaction. The Mg^{2+} reached equilibrium which had little change in 300 to 500 mg/L initial concentration of Cu^{2+} maybe is one reason that leads to the Zn^{2+} substitution. The release of divalent cations during biosorption of heavy metals by OWEAS could be attributed to a cation exchange mechanism.

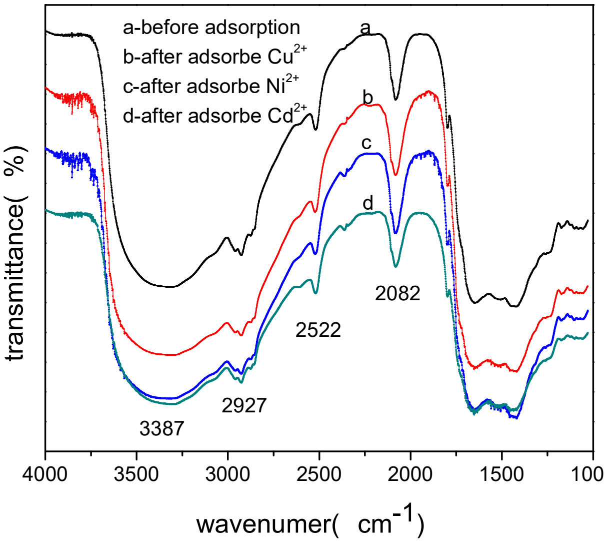

Fig. 11 FT-IR spectra of the OWEAS before and after adsorption

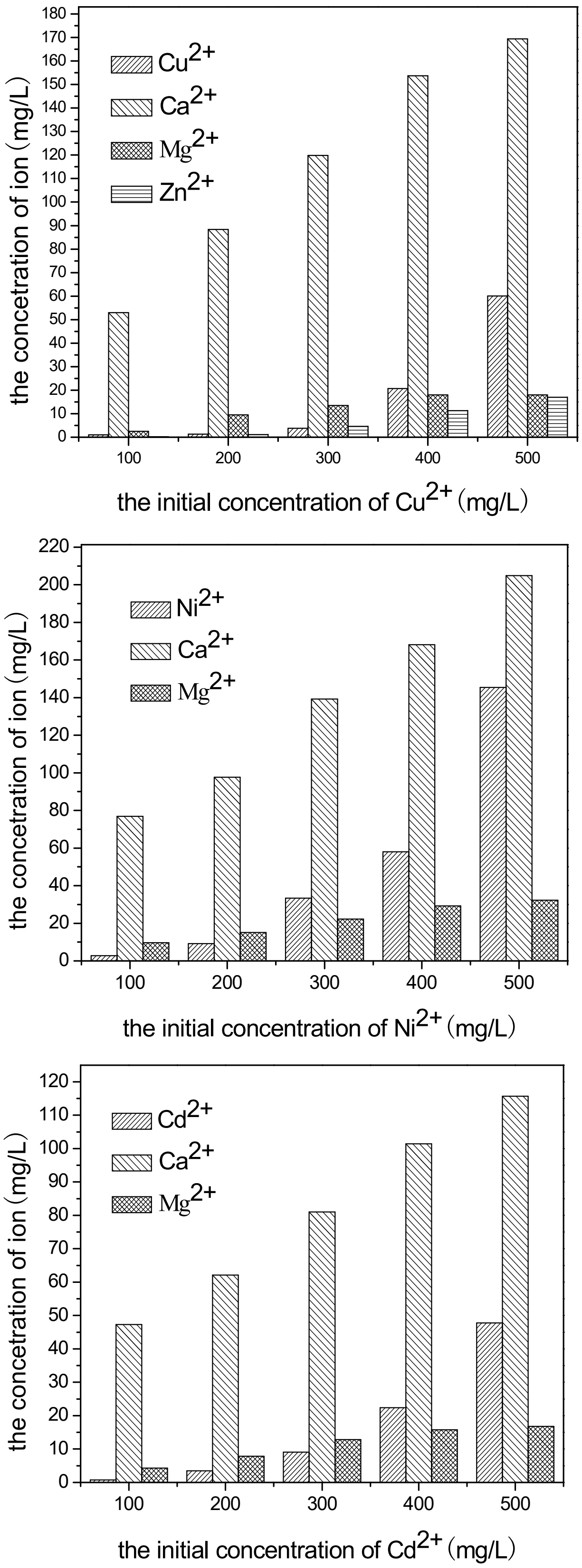

Fig. 12 The concentration of Ca^{2+} and Mg^{2+} decrease with biosorption for different initial concentration of Cu^{2+} (b), Ni^{2+}(c) and Cd^{2+}(d)

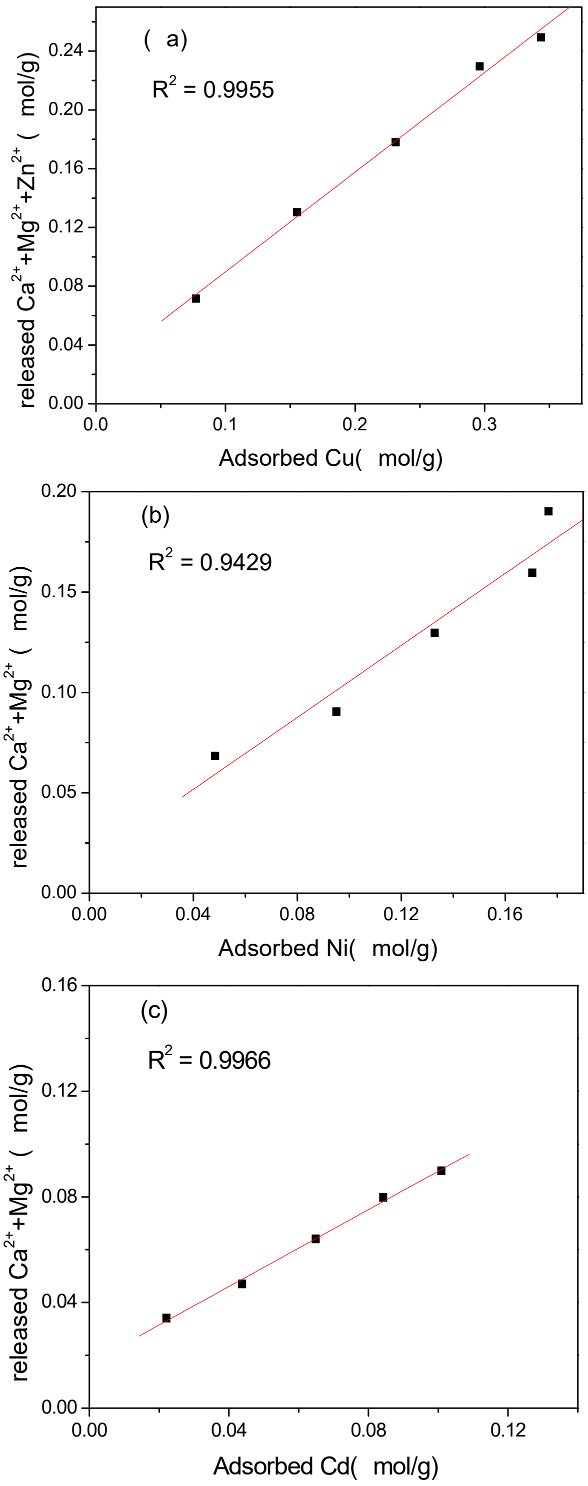

Fig. 13 Release of Ca^{2+} and Mg^{2+} during adsorption of Cu^{2+} (a), Ni^{2+}(b) and Cd^{2+}(c)

Figure 13 presents the quantity of Ca^{2+} and Mg^{2+} released into solution increased linearly with equilibrium metal concentration. The slope value of the regression line obtained can be expressed in mol of counter ions per g of adsorbed metal ion. Thus, it represents the cation release ratio: cations released (mol)/metal ions adsorbed OWEAS (g). These ratios were close nearly to 1 for both Cu^{2+}, Ni^{2+}, and Cd^{2+} indicates that the whole metal removal process can be mainly explained by ion exchange.

CONCLUSION

TEAS is a promising co-disposal material for alleviating heavy metal dissolution into leachate. Based on the metal-binding properties of the TEAS, it was verified that the uptake capacity of heavy metal ions increased as the solution pH increased. The best adsorption isotherm fit for Cu^{2+}, Ni^{2+}, and Cd^{2+} was obtained with Langmuir adsorption isotherm and the metal affinity to TEAS was found to be in the sequence of $Cu^{2+} > Ni^{2+} > Cd^{2+}$.In addition, the dynamic date fit the pseudo-second-order kinetic model, which suggests that the adsorption of metal ions onto OWEAS was mainly performed through a chemical binding process. The metal biosorption mechanisms proved this chemical binding process was cation exchange.

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