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Original Research

Adsorption of Zinc and Copper Heavy Metal Ions from Smelting Wastewater Using Modified Lava Particles

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Abstract

This paper investigated the ability of modified lava particles (MLP), a kind of modified surface media from volcanic eruption, to remove Cu(II) and Zn(II) from simulated smelting wastewater. The equilibrium adsorptive quantity was determined as a function of the initial pH, temperature, MLP dosage, and contact time in a batch test. The results showed that the metal ions uptake by MLP was rapid, and the equilibrium time was 8 h at 25ºC and pH 6, especially within 5-60 min, 80% equilibrium quantity was obtained. With the increase of initial pH value (from 3 to 6), the removal efficiency of Cu(II) and Zn(II) was also increase to 85.31% and 58.21%, respectively, but when pH was more than 6, sedimentation was found. Temperature and thermodynamic studies for the present adsorption process were performed at 15, 20, 25, 30, and 35ºC by determining the values of ΔGº and ΔHº, and it was confirmed that the adsorption process is endothermic and spontaneous. And the optimal MLP dosage of 10 g/L and 6 g/L were obtained for Cu(II) and Zn(II) removal, respectively. The mechanism of these two metal ions sorped by MLP was inferred that the hydroxide micro-precipitation and surface hydroxyl complex were predominant.

Keywords: adsorption, modified lava particles, heavy metals, smelting wastewater

Introduction

Wastewater pollution caused by heavy metal ions from various industrial effluents is a global problem that has received worldwide attention [1]. The effluent water of many industries, such as mining [2], metal smelting [3], tanneries [4], batteries [5], and so on, contains toxic heavy metal ions in which the non-ferrous metal smelting industry as one of the high pollution industries has attracted wide attention because of frequent heavy metal contamination accidents in China. Discharge of such toxic heavy metal can seriously impact the environment because they cannot be degraded, but accumulation through the food chain leads to critical ecological issues and health problems [6]. Thus, various technologies, such as chemical sedimentation, ion exchange, electrochemical technology, redox process and so on [7-9], have been developed to prevent the discharge of toxic metals in water. Nowadays, one of the most important priorities about technology development is simple operation and economical management. In general, some technologies are commercially impractical due to expensive cost and lack of versatility. Therefore, based on some limitations and the pros and cons of the available technologies, alternative methods for heavy metal ion removal have become necessary.

In recent years, different adsorption processes, such as biosorption [10-12], modified media adsorption [13], industrial wastes adsorption [14], and so on, have emerged as potential alternative methods in which, due to low cost

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Table 1. Smelting wastewater quality from wastewater plant of the smelting industry in China.

Items	Cu	Pb	Zn	Cd	Total As	pH
Meal value	11.9	1.67	10.58	1.21	1.91	6.5

and easy-to-get nature, the industrial wastes as absorbents have been used for the removal of toxic pollutants from wastewater [15-23], especially for dyes. Meanwhile, some naturally available adsorbents like hen feathers [24], and wheat husk [25] were also used for the removal of hazardous dye. However, it was seldom that the above absorbents were used for adsorption of heavy metal ions.

Therefore, in this study a kind of modified lava particle from the wastes of volcanic eruption, due to large surface, high porosity, and lower cost have been used for iron and manganese removal from coal mine drainage based on our research group results [26]. And it was prepared and its adsorption conditions were investigated by varying the initial pH, temperature, adsorbent dosage, and contact time for copper and zinc ion removal from smelting wastewater. Meanwhile, the mechanism of the adsorption also was confirmed by a series of experiments.

Materials and Methods

Preparation of Modified Lava Particles

Non-modified lava particles were provided from the Environmental Protection Company in Beijing, and its size was diameter of 0.45-0.90 mm with elements composed of O (62.8%), Na (3.63%), Mg (1.97%), Al (6.68%), Si (17.07%), K (0.70%), Ca (2.71%), Ti (0.64%), and Fe (4.11%) [26].

Preparation of modified lava particles (Fig. 1): lava particles were sun dried and washed with tap water several times to remove mud and dirt and then dried. Further, the particles were soaked in 0.8 M $MnCl_2 \cdot 4H_2O$ for 30 min (100 g of lava particles per liter), and then were soaked in 1.25% (mass/volume) $KMnO_4$ for 30 min. The absorbents were filtered and washed with distilled water to remove residual solution. Finally, the above steps were repeated 4 times and dried at room temperature.

Wastewater and Reagents

The wastewater quality of real smelting wastewater, from the smelting industry in China, is seen in Table 1. Because of higher Cu(II) and Zn(II) concentrations and complex water quality, the simulated smelting wastewater was prepared by stock solutions and tap water with Cu(II) and Zn(II) concentrations of 10 mg/L, respectively. Stock solutions of metal ions (Zn(II), Cu(II), respectively), containing 1000 mg/L, were prepared by dissolving appropriate metal salts in DI water.

Equipment and Analysis Methods

The water sample was filtered by 0.45 μm filter and then the ICP-OES (Model ICAP6000, Thermo Electron, US) was used for determination of metal ion concentrations before and after absorption. Other parameters were analyzed based on "Water and Wastewater Monitoring Analysis Method" (4th edition) [27].

Batch Absorption Experiment

The absorption experiments were carried for a single component by batch technique by varying MLP dose from 2 to 12 mg/L, temperature from 15ºC to 35ºC and initial pH from 2 to 12 in 100 mL conical flasks. The kinetic studies were carried out by varying the time intervals from 5 min to 9 h. After equilibrium, the solutions were filtered and analyzed for residual metal concentration using ICP-OES. All the data presented in this manuscript are the average of three experimental runs.

Results and Discussion

Effect of pH

The effect of pH was studied by adjusting the pH by 5% HCl or 5% NaOH in the range of 2-12 for Zn(II) and Cu(II) (Fig. 2) at 25ºC. Such a study helps in designing the appropriate pH of the influent/wastewater for achieving maximum efficiency for the removal of metal ions by MLP. The sorption efficiency of Zn(II) and Cu(II) is very low at pH 2, which then increased to 85.31% for Cu(II) within the next four pH units and 58.21% for Zn(II) within the next five pH

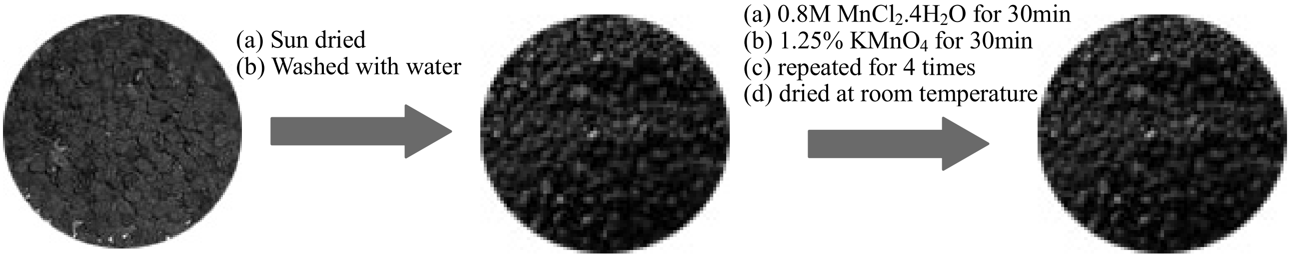

Fig. 1. Preparation of modified lava particles.

units. Increasing the pH from 7 to 12, the adsorption rate of Zn(II) and Cu(II) become slow and precipitation appeared, but the removal efficiency of both were more than 95%. Thus the following calculation was carried out.

(1) The critical pH of Cu(II) precipitation

$$Cu^{2+} + 2OH^{-} \Leftrightarrow Cu(OH)_2$$

$$K_{sp}\left(Cu(OH)_2\right) = \left\{c(Cu^{2+})\right\}\left\{c(OH^{-})\right\}^2$$

$$c(OH^{-}) = \sqrt{K_{sp} / c(Cu^{2+})} \tag{1}$$

$$pH = -\lg c(H^{+}) = -\lg\left(K_w / c(OH^{-})\right) \tag{2}$$

When the initial Cu(II) concentration of $c(Cu^{2+})$=10 mg/L = 0.1563 mmol/L and the solubility product constant of $Cu(OH)_2$, $K_{sp} = 2.2\times10^{-20}$ at 25ºC, based on equation (1), the OH^- concentration with precipitation produced should be:

$$c(OH^{-}) = \sqrt{K_{sp} / c(Cu^{2+})} =$$

$$\sqrt{2.2\times10^{-20} / 0.1563\times10^{-3}} = 1.1866\times10^{-8}$$

Also, the water ion product, Kw, is 1×10^{-14}, then the pH is:

$$pH = -\lg c(H^{+}) = -\lg\left(K_w / c(OH^{-})\right) =$$

$$-\lg(10^{-14} / 1.1866\times10^{-8}) \approx 6.08$$

(2) The critical pH of Zn(II) precipitation

$$Zn^{2+} + 2OH^{-} \Leftrightarrow Zn(OH)_2$$

$$K_{sp}\left(Zn(OH)_2\right) = \left\{c(Zn^{2+})\right\}\left\{c(OH^{-})\right\}^2$$

$$c(OH^{-}) = \sqrt{K_{sp} / c(Zn^{2+})} \tag{3}$$

When the initial Zn(II) concentration of $c(Zn^{2+})$=10 mg/L = 0.1539 mmol/L and the solubility product constant of $Zn(OH)_2$, $K_{sp} = 6.8\times10^{-17}$ at 25ºC, based on equation (3), the OH^- concentration with precipitation produced should be:

$$c(OH^{-}) = \sqrt{K_{sp} / c(Zn^{2+})} =$$

$$\sqrt{6.8\times10^{-17} / 0.1539\times10^{-3}} = 6.648\times10^{-7}$$

Also, the water ion product, K_w, is 1×10^{-14}, then the pH is:

$$pH = -\lg c(H^{+}) = -\lg\left(K_w / c(OH^{-})\right) =$$

$$-\lg(10^{-14} / 6.648\times10^{-7}) \approx 7.82$$

Based on the above calculation, it can be found that the critical pH value of zinc and copper ions is 6.08 and 7.82, respectively, in initial concentration of 10 mg/L. When the solution pH value is less than the above critical pH value, the heavy metal ion will be removed by adsorption, and in such a system, H^+ competes adsorption active sites with metal zinc and copper ions, resulting in pH value increases (namely H^+ concentration decrease), the removal of zinc and copper ions gradually increases. In contrast, when the solution pH value is higher than critical pH value, the removal of zinc and copper ions also increases gradually, accompanied by the precipitation of metal hydroxide, namely $Cu(OH)_2$ and $Zn(OH)_2$. Therefore, the solution pH value should be lower than critical pH to prevent the precipitation of metal hydroxide interfering the adsorption of Cu(II) and Zn(II).

Effect of Temperature

At the initial pH of 6 and the concentration of Cu(II) and Zn(II) of 10 mg/L respectively, the effect of another important parameter, temperature, was investigated at 15, 20, 25, 30, and 35ºC, respectively.

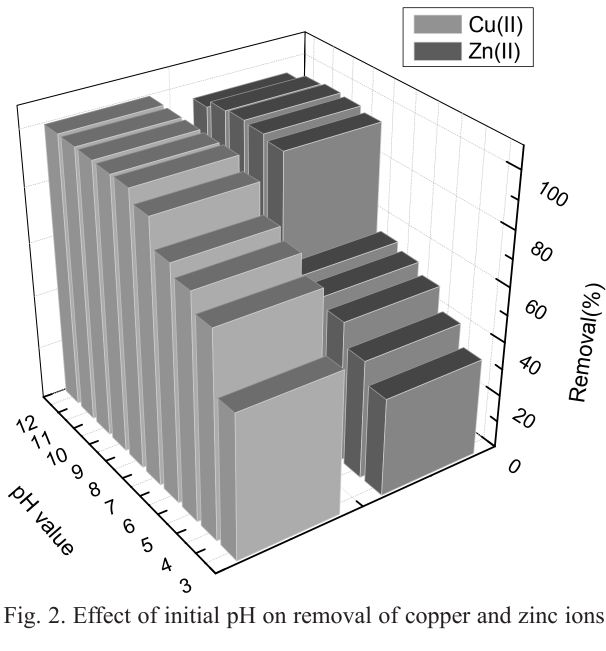

Fig. 2. Effect of initial pH on removal of copper and zinc ions.

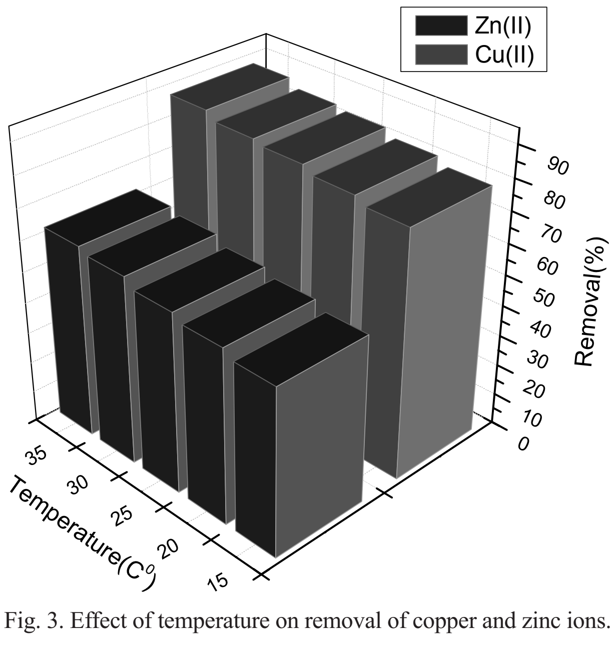

Fig. 3. Effect of temperature on removal of copper and zinc ions.

Table 2. The thermodynamic parameters of modified lava adsorption for copper and zinc ions.

Heavy metal ions	Temperature (K)	Equilibrium constant, K^0	Gibbs free energy, ΔG^0 (kJ/mol)	Enthalpy, ΔH^0 (kJ/mol)
Cu^{2+}	288.16	3.78	-3.19	–
	293.16	4.44	-3.63	22.45
	298.16	5.25	-4.11	23.32
	303.13	7.70	-5.15	34.47
	308.16	8.49	-5.48	29.85
Zn^{2+}	288.16	1.09	-0.20	–
	293.16	1.26	-0.57	20.82
	298.16	1.43	-0.88	19.38
	303.13	1.52	-1.07	16.44
	308.16	1.84	-1.56	19.34

Fig. 3 sees the removal of Cu(II) and Zn(II) all increased as the temperature increases, but this trend was not significant, and their thermodynamic parameters like Gibbs free energy(ΔG^o) and enthalpy (ΔH^o) were calculated as follows:

$$K^0 = C_s / C_e \quad [28] \tag{4}$$

$$\Delta G^0 = -RT \ln K^0 \tag{5}$$

$$\Delta H^0 = -RT_1T_2 / (T_2 - T_1) \ln(K_1{}^0 / K_2{}^0) \quad [29] \tag{6}$$

where:

R – molar gas constant, its value is 8.314×10^{-3} kJ/(mol·K)

T – thermodynamic temperature, K

K^0 – equilibrium constant, K_1 and K_2 is the equilibrium constant at T_1 and T_2

C_s – heavy metal concentration adsorbed, mg/L

C_e – heavy metal concentration at adsorption equilibrium, mg/L

ΔG^0 – Gibbs free energy, kJ/mol

ΔH^0 – enthalpy, kJ/mol

Based on the above equations, the ΔH^0 and ΔG^0 value of adsorption of Cu(II) and Zn(II) at 15, 20, 25, 30, and 35ºC are given in Table 2. The positive values of enthalpy change confirmed that the adsorption process is endothermic in nature, which indicates that an increase in temperature is tending to increase the adsorption capacity. Generally, the physical adsorption is exothermic and chemical adsorption is endothermic, so it was interfered that the chemisorption took part in this adsorption process. Meanwhile, the overall free energy changes during the adsorption process at 15, 20, 25, 30, and 35ºC are negative, corresponding to a spontaneous and thermodynamically favorable process of adsorption of Cu(II) and Zn(II). And as temperature increased, the absolute value of ΔG^0 was higher and higher, and the removal efficiency of heavy metal ions also was larger and larger, and similar results were obtained by Wang et al. [30].

Effect of MLP Dosage

To estimate the adsorption capacity of the MLP, it is important that the experimental solution be allowed enough time to attain equilibrium. The dependence of MLP loading on the adsorption of Cu(II) and Zn(II) ions was studied by varying the amount of MLP from 2 g/L to 12 g/L, while keeping all other variables (pH=6, Cu(II) and Zn(II) ions concentration = 10 mg/L, contact time = 8 h, and temperature = 25ºC) constant.

The effects of MLP dosage on the removal of Cu(II) and Zn(II) removal are shown in Fig. 4. The amount of MLP significantly influenced the extent of Cu(II) and Zn(II) adsorption, i.e., the adsorption of metal ions increased significantly with increasing dosage at the range of 2 g/L to 6 g/L, and the removal of Cu(II) and Zn(II) increased from 48.71% and 38.02% to 73.27% and 52.35%, respectively.

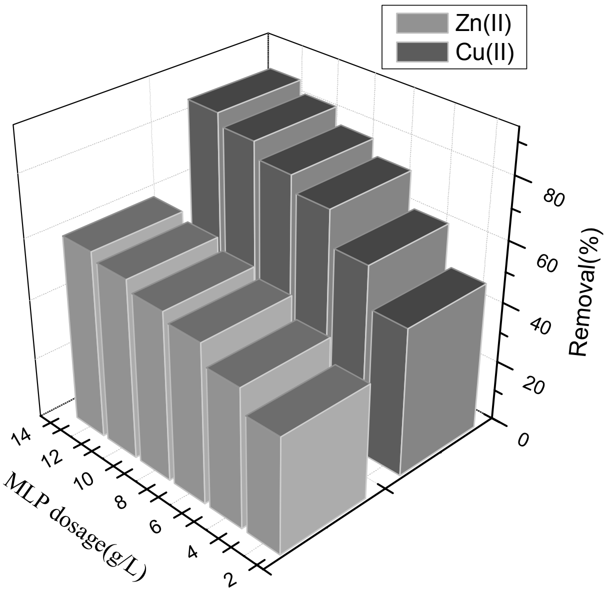

Fig. 4. Effect of absorbents dosage on removal of copper and zinc ions.

And at a higher dosage than 6 g/L, the removal of Cu(II) and Zn(II) increased insignificantly, namely the value was 87.43% and 61.41%, respectively, at dosage of 12 g/L. Therefore, the optimum dosage of MLP was selected 10 g/L for Cu(II) and 6 g/L for Zn(II) based on the consideration of economic cost and effluent metal ions concentrations.

Effect of Contact Time

It is essential to evaluate the effects of contact time to reach equilibrium for batch adsorption experiments. The removal of heavy metal ions as a function of time (5 min-9 h) at pH = 6, temperature = 25ºC, initial Cu(II) and Zn(II) concentration = 10 mg/L, has been studied (Fig. 5). The metal ions adsorption increased sharply at first one hour with 80% equilibrium quantity and slowed gradually as equilibrium was reached. The fast adsorption rate at the initial stage may be explained as the availability of a large number of vacant surface active sites initially. Thus the amount of metal ions accumulated on the adsorbent surface rapidly increased within the 5-60 min. In the later stage, sorption is likely an attachment controlled process due to less available sorption sites. Results indicate that the time to reach equilibrium is 8 h.

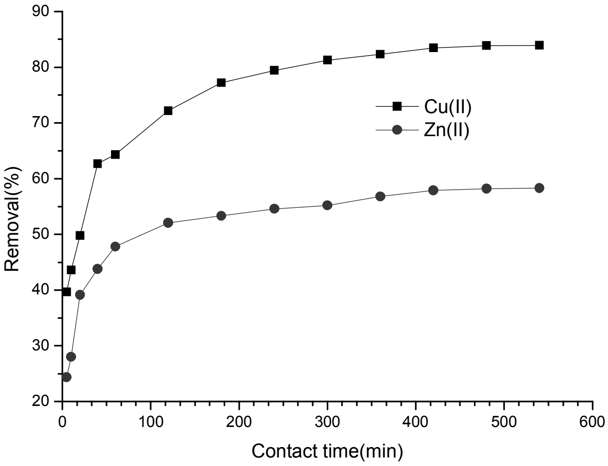

Fig. 5. Effect of contact time on removal of copper and zinc ions.

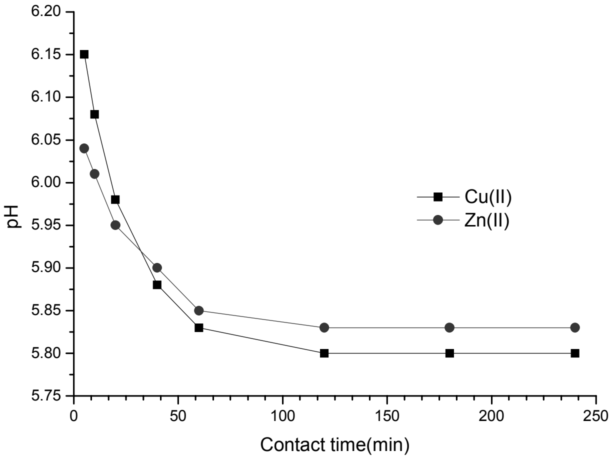

Fig. 6. The change of solution pH during copper and zinc ions adsorption.

Investigation of Adsorption Mechanism

Adsorption is a complex process, and it involves complex mechanisms such a complexation, ion exchange, and micro-precipitation, in which ion exchange adsorption is impossible based on the data of Table 2. To understand the mechanism, the pH variation during adsorption was investigated in order to confirm whether the OH^- take part in the adsorption process, and the following experiment was designed, namely 100 mL solution with 10 mg/L Cu(II) and Zn(II), respectively, and initial pH was kept at 6 (namely lower than critical pH), and modified lava dosage was 6 g/L.

From Fig. 6, it was observed that pH value was slightly higher than initial pH of 6 within 5-20 min and then gradually dropped, which we analyzed as small amounts of OH^- was consumed during the adsorption process of Cu(II) and Zn(II) by MLP. Therefore, it was confirmed that the adsorption of both of them must involve OH^-, namely this process maybe was accompanied by production of heavy metal hydroxide or other hydroxyl complexes. So analysis on the solubility product of surface precipitate was carried out.

In solid-solution interface region, because the permittivity of the medium is much lower than the value of the solution, the formation conditions of metal hydroxide precipitation would be changed, thus solubility product also changes. Based on the James equation [31], namely,

$$\log(K_{sp} / K'_{sp}) = (G_M + G_{OH^-}) / KT \qquad (7)$$

...where, the solubility product of metal ion in solution and in solid-solution interface is determined as K_{sp} and K'_{sp}, respectively, and $(G_M+G_{OH^-})$ is solid-solution interface free energy.

The fact that the permittivity of the medium is much lower than the value of the solution, it was confirmed that $(G_M+G_{OH^-})$ is more than zero. Therefore, $\log(K_{sp}/K'_{sp})>0$, namely $K_{sp}>K'_{sp}$.

Based on the above theory, the precipitation of metal ions is much easier in solid-solution interface than in solution. Therefor it is inferred that there are two mechanisms for Cu(II) and Zn(II) removal in this system. One is that hydroxide micro-precipitation of Cu(II) and the Zn(II) is produced and then adsorbed by MLP, and the other is that hydroxyl complex is formed due to the complexation between Cu(II), Zn(II) and hydroxyl from MLP surface, which may be explained by the surface complexation model [32].

Based on the results from XRD for surface element of modified lava media, it can be confirmed that modified lava media is covered with hydrous manganese dioxide[26], which has high adsorption capacity to metal ion due to a quantity of surface hydroxyl groups [33, 34]. According to the surface complexation model (Fig. 7), the H from hydroxyl groups could form complexation with copper and zinc ions

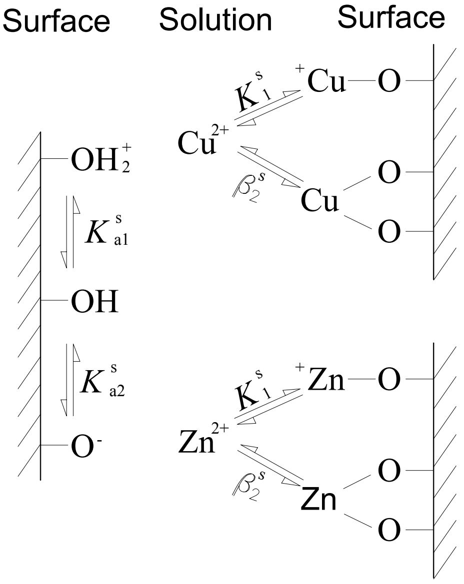

Fig. 7. Surface complexation model of Cu(II) and Zn(II) with modified lava particles.

from solution, finally they are adsorbed by surface hydroxyl and the H^+ are released (see equation (8) and (9)), which also may be confirmed by the phenomenon from Fig. 6.

For Cu^{2+} adsorption: $\text{-Mn-OH} + Cu^{2+} = \text{-Mn-O-}Cu^{+} + H^{+}$ (8)

For Zn^{2+} adsorption: $\text{-Mn-OH} + Zn^{2+} = \text{-Mn-O-}Zn^{+} + H^{+}$ (9)

Conclusions

In this paper, modified lava particles have been used as adsorbent for removal of copper and zinc metal ions from smelting wastewater. The adsorption performance was strongly affected by parameters such as initial pH of solution, temperature, modified media dose, and contact time. Thermodynamic parameters have been evaluated with change in temperature, which indicated a spontaneous and endothermic process. The results of adsorption mechanism indicate that there are two mechanisms for Cu(II) and Zn(II) removal in this system. One is micro-precipitation that hydroxide precipitation of Cu(II) and Zn(II) is produced and then adsorbed by MLP, and another is hydroxyl complex, which is due to the complexation between Cu(II), Zn(II) and hydroxyl group from MLP surface.

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