The Removal of Metal Ions (Cu^{2+} and Zn^{2+}) using Waste-reclaimed Adsorbent for Plating Wastewater Treatment Process

Young-Hoon Jo, Si-Hyun Do, Yoon-Seok Jang, and Sung-Ho Kong

Abstract- **Heavy metals in plating wastewater are considered as one of the must-treated contaminants and the adsorption using low-cost materials has been studied as the cost-effective alternative. Based on the parameter (Q_o) calculated from Langmuir isotherm, Cu (1.68 mg/g) had a higher affinity to waste-reclaimed adsorbent than Zn (0.06 mg/g). The removal efficiency of metal ions (i.e. Cu and Zn) at various pHs was tested, and it was revealed that the removal of metal ions was interpreted by both adsorption and precipitation. The optimum pH for the removal (i.e. both adsorption and precipitation) of both Cu and Zn was 9, and the highest adsorption of Cu and Zn was observed at the pH of 5 for the artificial solution and at the pH of 7 for plating wastewater. Moreover, unlike the adsorption of Cu and Zn in the artificial solution, Cu and Zn in plating wastewater was adsorbed even at the pH of 12. To examine adsorption phenomenon, the relationship of the surface charge of adsorbent and the pH of solution was evaluated by measuring pzc (point of zero charge) of waste-reclaimed adsorbent. The pzc value of waste-reclaimed adsorbent was 6.27. Therefore, the optimum pH for adsorption should be over 6.27, which indicated the negative surface charge. However, it seemed unclear to be explained by surface charge, and other surface characteristics like ion exchange ability needed to be considered and evaluated.**

Key words: copper, zinc, waste-reclaimed adsorbent, adsorption, precipitation, plating wastewater

I. INTRODUCTION

Heavy metals in plating wastewater are considered as one of the must-treated contaminants and the adsorption using low-cost materials has been studied as the cost-effective alternative. This variety and complexity of effluents makes the removal process of heavy metals more difficult. Currently, the chemical flocculation followed by precipitation is the most widely used technique for heavy metals, but the efforts to find alternatives have been continued. The alternatives to remove heavy metals are adsorption, ion exchange, phytoextraction, ultra filtration, reverse osmosis, and electro dialysis. Among these, adsorption using low-cost adsorbents such as chitosan, zeolies, waste slurry, and lignin were tested to remove various types of heavy metals and this could be a cost-effective process with well performance [1].

Adsorption of various materials (i.e. metal ions, inorganic and organic compounds) depends on both surface chemistry and pore distribution of adsorbent, and the phenomena of adsorption of metal ions could be explained by surface characteristic, including ion exchange ability, surface charge, etc. The importance of ion exchange ability was appeared in several publications [2-4]. Synthetic zeolite, which had the ability of the hydronium ion exchanges, can be assigned to the higher metal ions removal [3]. Moreover, in ion exchange process, one suggested that the diffusion of exchangeable ions through the channel/void of adsorbent is the rate determining step [2], while Blanchard et al. reported that the surface reaction is the rate determining step and the exchange rate kinetic order is two [4]. In addition to ion exchange ability, the surface charge of adsorbent could be also considered as one of parameters to affect the adsorption process. The point of zero charge (pzc) is defined by the zero charge of surface, which the sum of positive equals the sum of negative. Depending on the pH value of the aqueous phase, the surface charge of adsorbent could be developed as either positive or negative. If pH (solution) < pzc, the surface is positively charged, and if pH (solution) > pzc, then the surface is negatively charged [5].

Zeolite, which is known for a popular adsorbent, has been studied to remove metal ions and its adsorption capacity for Zn and Cu were ranged as 0.04-5.5 mg/g and 0.37-5.1 mg/g, respectively [1]. Moreover, the selectivity of zeolite for metal ions has been reported as $Pb^{2+} > NH^{4+} > Ba^{2+} > Cu^{2+}, Zn^{2+} > Cd^{2+}, Sr^{2+} > Co^{2+}$ by Blanchard et al. [4], while that was as $Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ by Zamzow et al. [6]. Recently, fly ash was evaluated for adsorption of Cu, and it was reported that the adsorption capacity of 1.39 mg of Cu^{2+}/g was earned at the pH of 8.0 [7]. It was also found that adsorption capacity increased with an

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increase of CaO in fly ash.

In this study, we conducted a study on removal of heavy metals (Cu and Zn) by using a waste-reclaimed adsorbent. Samples of the plating wastewater have been taken from the industrial zone located at Ansan, Korea, and the adsorption of Cu and Zn has been carried out at batch reactor. At present, the adsorption phenomenon of metal ions on waste-reclaimed adsorbent was evaluated on basis of the relationship of the surface charge of adsorbent and the pH of solution, and later, other explanations like ion exchange ability will be adapted.underline.

II. MATERIALS AND METHODS

2.1. Characteristics of waste-reclaimed adsorbent

Waste-reclaimed adsorbent was taken from department of material engineering, Kyonggi University. It passed through 3-6 mesh (sieve size), washed with distilled water, dried in an oven at 105 ^{o}C for 3 h, and stored in desiccators. Chemical compositions of waste-reclaimed adsorbent were shown in Table 1.

Table 1. Chemical compositions of waste-reclaimed adsorbent

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	C	ZrO_2	Ig.loss	Total
45.58	18.60	8.08	2.17	0.78	0.18	0.51	1.33	0.24	0.05	18.07	0.33	4.07	100.00

2.2. Batch experiment

The removal of metal ions using waste-reclaimed adsorbent at various pHs was carried out using the single batch system, which was a 40 mL glass vial with caps. Batch experiments were conducted using 10g of waste-reclaimed adsorbent with 20mL of solution at different pH (i.e. 3, 5, 7, 9, and 12). The pH of solution was adjusted by adding 0.1 N HNO_3 and 0.1 N NaOH (KANTO). The concentration of Cu and Zn was 20 mg/L, respectively. These prepared batch reactors were mounted on orbital shaker at 200 rpm for 24 h. Controls, which were without adsorbent, were also prepared to check the portion of precipitation. The experiment of adsorption isotherm was conducted with the same condition except the concentration of Cu and Zn, which were ranged from 5 to 50 mg/L, respectively. After 24 h of reaction time, the reactor was retrieved from shaker, and 2 mL of supernatant was filtered through 0.45-um Teflon filter. The diluted sample dilute with pH 3 was stored at refrigerator until the analytical procedure was preceded. The mass distribution of metal ions can be expressed as following equations.

Total mass of metal ions = metal ions remaining in the aqueous phase + metal ions removed (1)

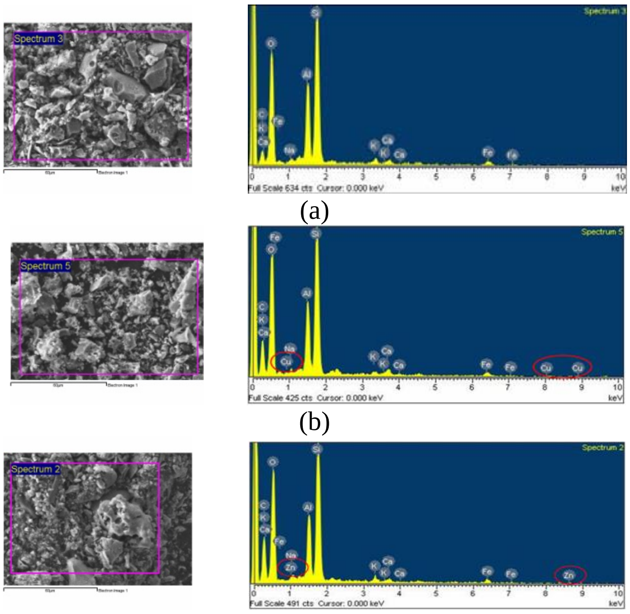
Metal ions removed = metal ions adsorbed on adsorbent + metal ions precipitated by pH of solution (2)

2.3. Analytical procedures

Concentrations of metal ions were determined by ICP (1000 IV Inductively Coupled Plasma). The micrographs of waste-reclaimed adsorbent were obtained using a JSM-700F scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Point of zero charge (pzc) of waste-reclaimed adsorbent was determined by the mass titration method [5].

III. RESULTS AND DISCUSSIONS

3.1. The surface of waste-reclaimed adsorbent



(a)

(b)

(c)

Fig.1. Energy Dispersive Spectroscopy (EDS) spectra collected onto the rectangular zones of Scanning Electron Microscopy (SEM): (a) raw material, (b) after adsorption of Cu (c) after adsorption of Zn [experimental condition: T = 25 ^{o}C, reaction time = 24 h, waste-reclaimed adsorbent dosage = 10 g, volume of solution = 20 mL, initial concentration of Cu = 20 mg/L, the pH of batch reactor: 5.0].

SEM-EDS analysis (Fig. 1.) revealed the existence of Cu and Zn on waste-reclaimed adsorbent. This technique was used to provide information on the association of Cu and Zn in absorbent. Furthermore, EDS analysis was indicated to analyze the elemental constitution of Cu-impregnated and Zn-impregnated in absorbent.

3.2. Point of zero charge of waste-reclaimed adsorbent

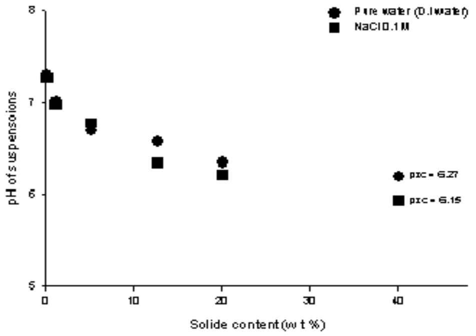
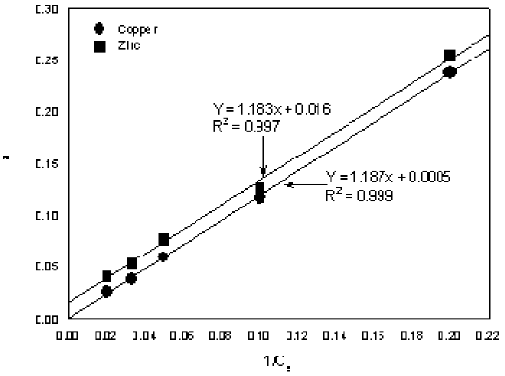


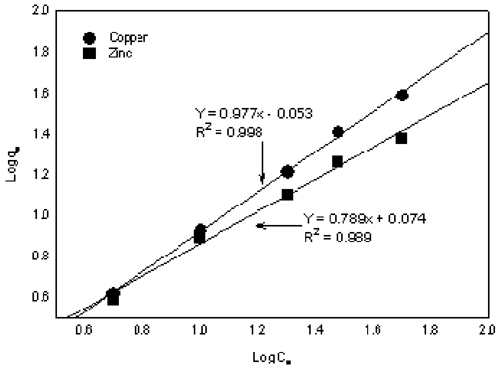
Fig. 2. Point of zero charge of waste-reclaimed adsorbent.

The measured point of zero charge of waste-reclaimed adsorbent was 6.15 with 0.1 M NaCl and 6.27 with pure water. Because of the negligible difference of pzc between NaCl and pure water, the measured pzc was determined as 6.27.

3.3. Adsorption isotherms



(a)



(b)

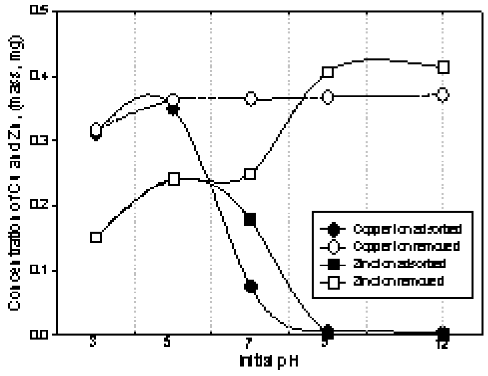
Fig. 3. (a) Langmuir and (b) Freundlich isotherms for adsorption of copper and zinc on waste-reclaimed adsorbent [experimental condition: T = 25 ^oC, t = 24 h, adsorbent dosage = 10 g, volume of solution = 20 mL, and the pH of solution: 5.0]

These results showed that both Langmuir and Freundlich isotherm could demonstrate the behavior of Cu and Zn adsorption on waste-reclaimed adsorbent. Values of coefficients were shown in Table 2. Based on the parameter (Q_o) calculated from Langmuir isotherm, Cu had a higher affinity to waste-reclaimed adsorbent than Zn. Moreover, the adsorption capacity of waste-reclaimed adsorbent for both Cu and Zn was similar to that of zeolite, which was reported as 0.37 - 5.1 mg/g for Cu and 0.04 - 5.5 mg/g for Zn, respectively [1].

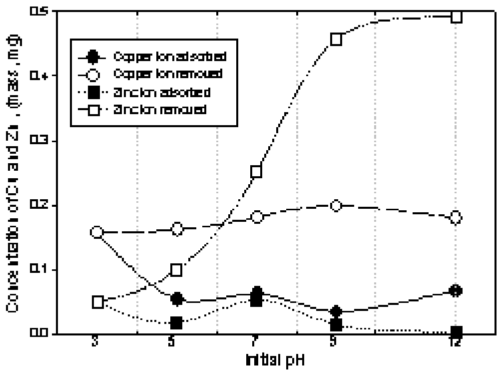
Table 2. Coefficients for Langmuir and Freundlich isotherms

	Langmuir			Freundlich		
	Q_o(mg/g)	b(L/g)	R^2	K_f(L/g)	1/n	R^2
Cu	1.68	0.0005	0.999	0.886	0.977	0.998
Zn	0.60	0.0132	0.997	1.187	0.789	0.988

3.4. The effect of pH



(a) Artificial solution



(b) Plating wastewater

Fig. 4. The effect of pH on the removal of metals ion using a adsorbent [experimental condition: T = 25 ℃, t = 24 h, adsorbent dosage = 10 g, volume of solution = 20 mL (a) initial Cu = 0.376 mg and Zn = 0.414 mg and (b) initial Cu = 0.227 mg and Zn = 0.492 mg]

In the artificial solution, over 95% of Cu was removed at the pH ranged from 5 to 12, and the Cu removal at pH 5 indicated that the most of Cu was removed by the adsorption of Cu on waste-reclaimed adsorbent. However, the removal of Cu above pH 7 showed that the precipitation was dominant. On the other hand, over 98% of Zn was removed above pH 9, and the most of Zn was removed by the precipitation. Even though the optimum pH for Cu and Zn removal was different, the highest adsorption of both Cu and Zn was observed at pH 5. According to pzc, the higher adsorption should be observed above the pH of 6.27. However, it was observed that the power of precipitation was dominant over that of adsorption. Therefore, the highest adsorption at pH 5 could be interpreted by other concepts like ion exchange.

The Cu and Zn distribution of surface of absorbent was studied by SEM-EDS analysis. As amount (mass, mg) of Cu and Zn was not able to determine, another analysis detected Cu and Zn with adsorbent in extraction. It was measured in 0.15 mg of Cu and 0.14 mg of Zn for desorption with 0.1N HNO_3.

In real plating wastewater, the behavior of Zn removal was similar to that in the artificial solution while the point of the highest Cu removal shifted to pH 9. Moreover, the behavior of adsorption in plating wastewater was different from that in artificial solution. The results showed that the optimum pH for adsorption was the pH of 7. Interestingly, the adsorption of Cu was observed, even at the pH of 12.

Overall, the optimum pH for the removal of both Cu and Zn was 9, and the highest adsorption of Cu and Zn was observed in the pH ranged 5 to 7. To explain those observations, other theories need to be evaluated.

Table 4. Removal of metal ions in the artificial solution [experimental condition T = 25℃, t = 24hr, adsorbent dosage = 10g and volume of solution = 20mL, initial Cu = 0.376 mg and Zn = 0.414 mg]

	Cu (mg)			Zn (mg)		
pH	Adsorption	Precipitation	Total removal	Adsorption	Precipitation	Total removal
3	0.311	0.006	0.317	0.151	N.D.(a)	0.151
5	0.350	0.013	0.363	0.240	0.002	0.242
7	0.076	0.289	0.365	0.179	0.070	0.249
9	0.007	0.361	0.368	0.003	0.404	0.407
12	0.004	0.367	0.371	0.002	0.412	0.414

(a): not detected

Table 5. Removal of metal ions in the plating wastewater [experimental condition T = 25℃, t = 24hr, adsorbent dosage = 10g and volume of solution = 20mL, initial Cu = 0.227 mg and Zn = 0.492 mg]

	Cu (mg)			Zn (mg)		
pH	Adsorption	Precipitation	Total removal	Adsorption	Precipitation	Total removal
3	0.158	N.D.(a)	0.158	0.050	N.D.(a)	0.050
5	0.054	0.108	0.162	0.018	0.082	0.100
7	0.063	0.118	0.181	0.054	0.197	0.251
9	0.035	0.164	0.199	0.015	0.442	0.457
12	0.068	0.112	0.180	0.004	0.448	0.492

(a): not detected

The increase in the Si^{+}, Ca^{+}, K^{+}, Mg^{+} and Na^{+} content in the total amount of the exchangeable cations released from Cu and Zn indicate effectiveness of the conditioning. However, this is also evident from the decrease in Na^{+} content of Zn solution when compared to Cu solution.

Table 6. Effect of conditioning on metal adsorption and each exchangeable cation to total release amount (mass, mg) [experimental condition: T = 25 ^{o}C, t = 24 h, adsorbent dosage = 10 g, volume of solution = 20 mL, and the pH of solution: 5.0]

Solution	Exchangeable cation (mg)				
	Si^{+}	Ca^{+}	K^{+}	Mg^{+}	Na^{+}
Water	0.13	0.31	0.17	0.09	0.44
Cu	0.15	0.34	0.22	0.13	0.71
Zn	0.16	0.35	0.20	0.12	0.55

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