

Development of Eco-adsorbent Based on Solid Waste of Paper Industry to Adsorb Cadmium Ion in Water

Eko Siswoyo and Shunitz Tanaka

Abstract—Eco-adsorbent prepared from paper sludge, a solid waste of paper industry, was studied to adsorb cadmium ion in water. Some parameters such as mass of the adsorbent, pH of solution, and shaking time were investigated in order to know the adsorption ability of the adsorbent. The presence of carboxyl and phenolic hydroxyl functional groups in this adsorbent were important in the process of adsorption. It was found that pH 6 to 8 of solution and 60 minutes of shaking time was a suitable condition for this adsorbent in adsorbing cadmium ion. Langmuir isotherm adsorption model was fit for this adsorbent and the adsorption capacity for Cd(II) was 5.21 mg/g.

Index Terms—Cadmium, Eco-adsorbent, Langmuir, paper sludge carbon.

I. INTRODUCTION

The pollutions with heavy metal have become public concerns because of its potential damage to human health and environments. The high concentration of cadmium, one of most toxic metals, is very dangerous for human being and ecosystem. It can be released to the environment from many kinds of industrial activities such as ceramics, metal plating, textile, etc [1].

Itai-itai disease was one of the most severe environmental problems in Jinzu river area of Toyama prefecture, Japan. It is a disease caused by cadmium poisoning which brings softening of the bone and kidney failure. The rate of death among the patients was 72.6% and it was considered that itai-itai disease had a long-lasting negative effect on the patient's life span [2]. The concentration of cadmium in contaminated rice in the Jinzu area, one of most contaminated area in the past, was in the range between 0.02 – 1.06 ppm [3]. In the Watarase river water near Ashio mine, the concentration of cadmium was 0.02-0.34 $\mu\text{g/l}$ [4]. Based on the standard of Japan minister of environment, the concentration of cadmium ion in water in public area should be less than 0.01 mg/l. It is well known that heavy metals such as cadmium are accumulated in the livings and human body and its influence might be found out after several years. Therefore, even the low concentration of cadmium in water is still potential for kidney damage, bone damage, cancer, disturbing the respiratory and reproduction system due to the accumulation effect [5]. Generally, the concentration of

cadmium in aquatic environment of Japan is much lower in comparison with that of developing country such as Indonesia. The concentration of cadmium ion in the water area of Jakarta, the capital of Indonesia, was sometimes until 0.47 mg/l, higher than the standard of Indonesian government (0.03 mg/l) [6].

Many technologies have been developed to solve the pollution problem of heavy metals, that is, membrane technology, ion exchange, phytoremediation, adsorption, etc. Activated carbon is a common adsorbent widely used in many countries. However, this material is expensive, therefore alternative materials are needed as a raw material of adsorbent for heavy metal ions.

Recently, around 5 million tons of paper sludge is discharged annually as solid waste from paper industry in Japan [7]. The disposal of paper sludge to the landfill or the treatment by incineration is high cost and may cause other environmental problem. Application of the paper sludge as a raw material of adsorbent has multi advantages, reducing amount of solid waste and cost for treatment and also providing a low cost adsorbent for removal of heavy metals. Paper sludge and other organic waste materials from paper industry could be considered as material of adsorbent due to their high carbon content and cellulose fibres proportion [8]. The adsorbent from paper sludge has the ability as an adsorbent for the removal of various kinds of heavy metal ions in water [9]. However, the application of paper sludge as adsorbent for adsorption of heavy metal ions is still limited.

The purpose of this study was to investigate the ability of paper sludge as raw material of adsorbent to adsorb cadmium ion in water.

II. MATERIALS AND METHODS

A. Preparation of Adsorbent

The Eco-adsorbent used in this study was prepared using paper sludge, a solid waste of a paper industry. The paper sludge carbon was provided from Doh-Ei Paper Mfg. Co., Ltd. in Sapporo city, Japan, where paper is produced from the used paper as main raw material. The paper sludge was produced during the paper production process. After dehydration and dryness of the paper sludge, it was treated at 950°C to form paper sludge carbon. The paper sludge carbon was washed with distilled water and dried at 100°C for 24 hours. After cooling it at room temperature, the paper sludge carbon were crushed into powder form and then sifted with a 1 mm sieve. The powdery paper sludge carbon is used as the adsorbent to adsorb cadmium ion from the water. The stock solution of cadmium ion (Cd^{2+}) was prepared with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ of WAKO Pure Chemical Co (Osaka, Japan).

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Some physical and chemical characteristics such as surface area, pore size distribution, porosity, density, and main elements of the paper sludge carbon were determined using BELSORP-mini (BEL Japan INC, Osaka, Japan), FT/IR-4100 FT-IR Spectrometer (JASCO, Japan), and Element analyzer (MICRO CORDER JM10, Yanaco, Japan).

B. Process of Adsorptions

Adsorption process in this study was conducted by the batch system. Parameters such as mass of adsorbent, pH of the solution, shaking time and the concentration of cadmium ion in the solution were investigated to know the ability and the optimum condition for adsorption using this adsorbent. In order to estimate the effect of mass of the adsorbent, 0.1 to 2.0 g of adsorbent was added to 50 ml of cadmium solution and agitated at 1000 rpm for 24 hours using a shaker (EYELA CUTE MIXER CM-1000). The influence of pH on the adsorption of cadmium ion was investigated by using the solution of pH 2 to 10. Acetic acid, HNO₃ and NaOH were utilized to adjust the desired pHs of solution. Various shaking time from 15 to 1440 minutes was applied to know the influence of shaking time on the adsorption of cadmium ion. After equilibrium, the solution was centrifuged at 4000 rpm for 5 minutes using a centrifuge (IEC61010-2-020, KUBOTA, Japan) and then the concentration of cadmium ion in supernatant solution was determined using Flame Atomic Absorption Spectrophotometer (FAAS) (HITACHI A-2000, Japan).

The efficiency of adsorption is calculated by using the following equation:

$$\text{Efficiency of adsorption(\%)} = \frac{C_{\text{initial}} - C_{\text{equilibrium}}}{C_{\text{initial}}} \times 100\% \quad (1)$$

III. RESULTS AND DISCUSSION

A. Characteristic of Adsorbent

Based on the elemental analysis, the composition of main elements of paper sludge carbon were 19.4, 0.1, 16.3, 0.0, 0.0, and 64.2% for C, H, O, N, S, and ash, respectively. The IR spectra of the paper sludge carbon suggested the presence of some functional groups such as carboxyl and phenolic hydroxyl group. These functional groups might participate in the adsorption of cadmium ion.

TABLE I: CHARACTERISTIC OF THE PAPER SLUDGE

Parameter	Value
pH	10
Alkalinity	0.17
Surface area	75.53 m ² /g
Porosity	0.85
Diameter	3.8 nm
Pore capacity	0.14 cm ³ /g
Water adsorbed	1.3 g/g
Density	400 kg/m ³

Physicals and chemicals properties of the paper sludge carbon are shown in the Table I. According to the report from the paper company, silicate, calcium oxide and carbon were main elements of the paper sludge carbon and with 75.53

m²/g of surface area, this adsorbent may have a good performance in adsorbing cadmium ion in water. Fig.1 shows the surface texture and porosity of this adsorbent captured using Analytical Scanning Electron Microscope (SEM) (JEOL JSM-6360 LA, Japan). These high porosity and large surface are essential for the high efficiency of adsorbent.

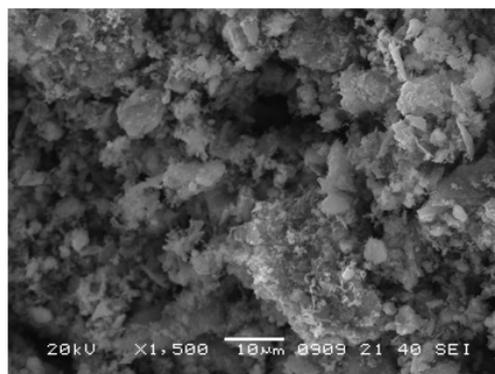


Fig. 1. SEM photograph of adsorbent

B. Effect of Mass of Adsorbent

Fig. 2 shows the removal efficiency of cadmium ion as a function of the mass of adsorbent. Increasing the mass of adsorbent led to the enhancement of the adsorption efficiency of cadmium ion in the water. The adsorption efficiency for cadmium ion increased increasing the mass of the adsorbent and became almost constant over 0.5 g. For 50 ml of cadmium solution, the favorable mass of adsorbent was 0.5 g, where the adsorption efficiency was 95.35%. The increase of the adsorption efficiency of cadmium ion is due to the greater availability of the binding sites or surface area [10].

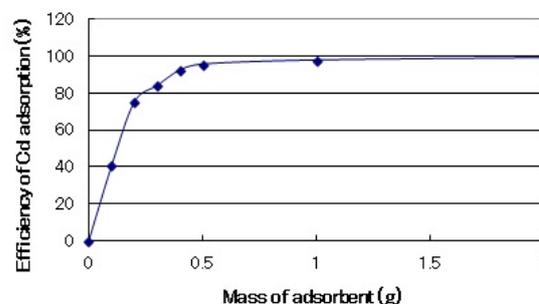


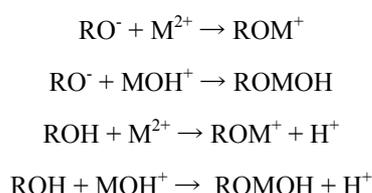
Fig. 2. Effect of mass of adsorbent on adsorption of cadmium ion (the pH of solution was 6.0, shaking time 24 hours for 50 ml of 10 mg/l Cd(II)).

C. Effect of pH of Solution

The binding of Cd(II) with surface functional groups strongly depended on the pH of solution. The effect of pH on the adsorption of 10 mg/l cadmium ion is shown in the Fig.3. The percent removal of cadmium ion increased with pH of the solution because cadmium ion forms complex with some functional groups in the adsorbent. The removal of metal cation at any pH was much greater than that by hydroxide precipitation. Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and the distribution of metal species which distribution also depends on the pH of the solution. The removal efficiency of cadmium decreased with the decrease of pH, because protons compete with metal ion for the adsorption sites on the adsorbent surface as well as the ion existing decrease of negative charge by association of the functional group with proton. The increase in metal ion removal as pH increase can be

explained on the basis of the decrease in H^+ on the surface, which results in less repulsion with adsorbing metal ions [11] and [12]. Rao M. M, (2006) reported that the point of zero charge of adsorbent was 5.7, where under 5.7 of pH, the surface of adsorbent was positively charged and adsorption of metal ion was low due to the electrostatic repulsion. Another researcher mentioned that in the highly acidic medium, the dissolution of the adsorbent occurs to a consequent decrease in the active sites. In this condition, the adsorbent surface is highly protonated, which is not favorable for the uptake of cadmium ion because of the electrostatic repulsion [13] and [14].

The cadmium ion was precipitated when the pH of solution was 8.2 [15] and 9.0 [1] and [16]. In this study, it was confirmed that cadmium ions were precipitated at the higher pH than 8. The ideal pH for adsorption of 10 mg/l of cadmium solution was within the range of 6 to 8. The possible mechanisms of adsorption are shown as follows.



where RO^- denotes a negatively charged surface, ROH denotes a neutral surface and M denotes metal such as Cd.

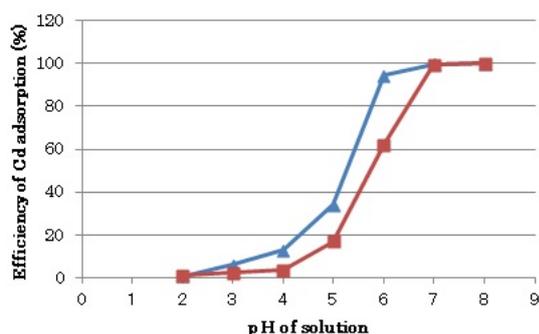


Fig. 3. Effect of pH of solution for Cd adsorption on the 0.01M (■) and 0.1M (▲) of buffer solution (adsorbent was 0.5g, shaking time 24hours for 50 ml of 10 mg/l Cd(II)).

D. Effect of Shaking Time

The effect of shaking time on the adsorption of cadmium ion is shown in Fig. 4. The equilibrium adsorption for 10 mg/l of cadmium was achieved after around 30 minute with 85% adsorption capacity and then became 95% after 24 hours of shaking. This result is important because the equilibrium time is one of the considerations for the application of economical wastewater treatment plant [10].

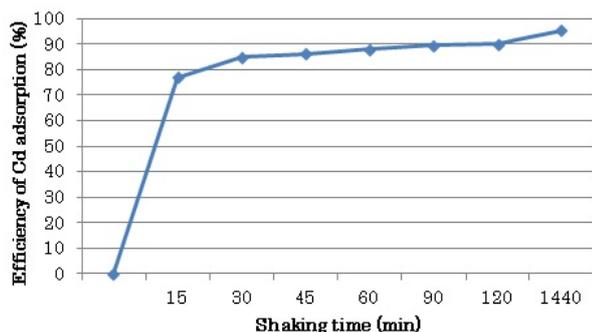


Fig. 4. Effect of shaking time on the adsorption of Cd (0.5g adsorbent was used for 50 ml of 10 mg/l Cd(II) at pH 6.0)

E. Isotherm of Adsorption

The adsorption isotherm is shown in the Fig. 5. The Langmuir isotherm model was applied to the equilibrium constant of adsorption by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (2)$$

where C_e is the equilibrium concentration (mg/l), q_e is the adsorbed amount of cadmium at equilibrium (mg/g), q_m and K_L are the constants of Langmuir related to the adsorption capacity and energy of adsorption, respectively. From the equation above, a plot of C_e/q_e versus C_e will be used to determine the values of q_m and K_L as the tangent and intercept of the curve. The value of q_m , K_L , and R^2 determined from the above equation were 5.2 mg/g, 0.24, and 0.9995, respectively.

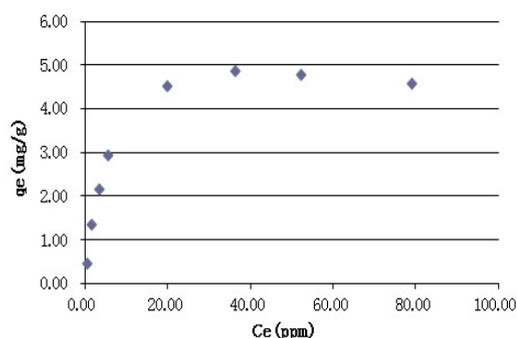


Fig. 5. Langmuir isotherm for adsorption of Cd(II) (0.5 g adsorbent was used for 50 ml Cd(II) solution of pH 6.0, and for 24 hours shaking time)

TABLE II: COMPARISON OF ADSORPTION CAPACITY WITH OTHERS MATERIALS

Adsorbent	q_m (mg/g)	Reference
Hematite	0.244	[13]
Fly ash pellets	4.88	[14]
Waste slurry	15.73	[15]
Perlite	0.64	[18]
Cushew nut shells	14.29	[19]
Olive stones	0.83	[20]
Dried activated sludge	1.28	[21]
Bagasse fly ash	1.20	[22]
Activated carbon from coconut coirpith	93.4	[23]
Paper sludge	5.21	This study

The essential characteristics of the Langmuir isotherm can be expressed due to a dimensionless constant of the separation factor or equilibrium parameter, R_L , which is defined as:

$$R_L = 1 / (1 + K_L C_0) \quad (3)$$

where K_L is the Langmuir constant and C_0 is the initial concentration of cadmium ion in the solution. The R_L value indicates the shape of the isotherm as follows:

- $R_L > 1$ Unfavorable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favorable
- $R_L = 0$ Irreversible

The R_L value between 0 and 1 is favorable adsorption [17]. The R_L values for the concentrations of 10 and 150 mg/l Cd^{2+} were 0.296 to 0.027, respectively. It means that the adsorbent was favorable adsorption for cadmium ion. The comparison of this adsorbent with some materials can be seen in Table II. Compared to the other materials, this adsorbent is quite good and could be considered as a low cost adsorbent.

IV. CONCLUSION

The ability of paper sludge carbon as a material of adsorbent for cadmium (II) is not so high, however, the application of this material will give some advantages such as reducing amount of solid waste in the landfill and decreasing cost for its treatment. Another benefit is that the paper sludge carbon has a magnetization property, therefore the development of a magnetic adsorbent based on the paper sludge for some heavy metal ions will give more advantages in the future.

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