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Characterization of Waste Activated Sludge of Crumb Rubber Industry (CRI-WAS) as Adsorbent of Cd(II)

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ABSTRACT

Characterization of waste activated sludge of crumb rubber industry (CRI-WAS) as adsorbent of Cd(II) from aqueous solution had been done. The sludge is discarded as waste from wastewater treatment processing, and expected to be an economical adsorbent for metal ion remediation from water and wastewater. The FTIR, XRF and SEM-EDX analysis were conducted to characterize the CRI-WAS. Batch adsorption experiments were carried out to investigate the effects of pH solution, dosage of adsorbent, and contact time. The results showed that Adsorbent developed from waste activated sludge of crumb rubber industry (CRI-WAS) containing high silica and alumina and also has an abundant functional groups. The optimum adsorption of Cd(II) was found at pH 5, dose 0.5 g, and contact time 210 minute with the maximum adsorption capacity was 30.38 mg/g.

Keywords: crumb rubber industry, waste activated sludge, CRI-WAS adsorbent, adsorption, Cd(II)

INTRODUCTION

Rapid industrialization has led to increased disposal of heavy metals into the environment. Industrial heavy metal pollution has become a serious environmental and sanitary problem all over the world in recent years. Heavy metals can not only have toxic and harmful effects on organisms living in water but also accumulate throughout the food chain and may also affect human beings [1]. Contamination by cadmium, one of the most toxic metal ions, is a worldwide environmental concern since it is a toxic heavy metal with no known useful function for higher organisms [2]. The presence of cadmium in the environment sometimes causes a serious problem for human beings and the ecosystem. Cadmium can be released to the environments by many kinds of industrial activities such as ceramics, alloy preparation, mining, metal plating and textile [3,4,5]. It adversely affects several important enzymes to cause bone disease and kidney damage. A variety of syndromes, renal function hypertension, hepatic injury, lung damage and teratogenic effects may result from cadmium toxicity [6]. Itai-Itai disease, which was caused by cadmium poisoning and which resulted in the softening of the bone and in kidney failure of the residents in the Jinzu river area of the Toyama prefecture, was one of the most severe environmental problems in Japan. The rate of death among the patients was 72.6% and it was considered that Itai-Itai disease has a long-lasting negative effect on the patient's life span. Many methods have been developed to minimize the weight of the metal ions in water such as chemical precipitation, adsorption, electrolysis, ion exchange and reverse osmosis, but it is often not effective or economical [7]. Adsorption is one of the common methods that have been widely applied for water and wastewater treatment. Activated carbon is a common adsorbent that is in use in many countries, however, it was quite expensive. The high costs of activated carbon have inspired many researchers to look for alternative development suitable and low-cost adsorbent.

As a result, recent research has focused on the development of alternative adsorbent effective and low cost by using a variety of natural resources and industrial waste. Several adsorbents were made from agricultural and industrial waste that showed a high ability to minimize metal ions Cd(II). There were by using Garcinia mangostana L. fruit shell [8], palm fruit (Arenga pinnata Merr) shell and Fruit [9,10], Ficus carcia leaves[11], the coconut shell [12], maize tassel [13], banana peel [14], Bamboo [15] and some research using sewage sludge such as from clarified sludge of the steel industry [16], the electroplating industry [17], municipal wastewater treatment sewage sludge [18-21], textile mills sewage sludge [22-23], cosmetic factory sewage sludge [24], Sea food processing sludge [25], paper industry sludge [26], palm oil sewage sludge [27-28], and a dairy factory [29,30].

Utilization of sewage sludge wastewater treatment plan of crumb rubber industry as adsorbent has not many reported yet. The latest has been reported for metal ion Cr(VI) adsorption with NaOH and H3PO4 activator [31,32]. The present study is aim to characterize a Crumb Rubber Industrial Waste Activated Sludge (CRI-WAS) PT Kilang 5 Gunung as low cost and readily available adsorbent for removal of Cd(II) from aqueous solutions that deals with a series of batch adsorption experiments to investigate and explore the feasibility of an adsorbent. Effect of different parameters such as initial pH, adsorbent dosage, and contact time on the adsorption of Cd(II) have been investigated. Experimental data were fitted to various isotherm equations to determine the best isotherm to correlate the experimental data.

MATERIALS AND METHODS

CRI-WAS Adsorbent Material

Crumb rubber industry waste activated sludge (CRI-WAS) was obtained from Kilang Lima Gunung Limited liability company of crumb rubber Industry in Padang city. The CRI-WAS was taken from the final clarifier in activated sludge processes.

Preparation of the CRI-WAS Adsorbent Material

The raw sludge samples were firstly sun-dried for three days and then dried in an oven (Memmert UNB 300) at 70^{o}C for approximately 5h. Then, grinded and passed it through 40–60 mesh sieves by using test siever merk Retsch 5657 Haun W. Germany.

Chemicals

All the necessary chemicals used in the study were of analytical grade. Cd(II) solutions were prepared by diluting a stock solution with double distilled water. The pH of each solution was adjusted to the desired value by adding diluted H_2SO_4 or NaOH, with the aid of a pH meter (Hanna HI 2213).

Experimental

The necessary amount of CRI-WAS adsorbent was taken in a 100 mL stopper conical flask containing 20 mL of desired concentration of the test solution. Then were shaken for the desired contact time in an electrically Adjustable Reciprocating Orbital Shaker (AROS)-160TM at 180 rpm. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time until equilibrium was reached. The samples were withdrawn from the flasks through Waltman 42 filter paper and the filtrate was analyzed for remaining metal concentration in the sample using Atomic Absorption Spectrophotometer GBC 932 AA. The amount of Cd(II) adsorbed per unit mass of the adsorbent was evaluated by using the same following equation:

$$qe = \frac{(C0 - Ce)\,V}{m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where qe is the amount of Cd(II) ions adsorbed per unit mass of the adsorbent (mg/g), V is the volume of the solution (L), m is the mass of the adsorbent (g); C_0 and C_e are the concentration of Cd(II) ions in the initial solution and in aqueous solution after adsorption for minute in mg/L, respectively.

Characterization of CRI WAS adsorbent
CRI-WAS adsorbent characterization performed on samples before and after the adsorption process. Elemental composition was determined by XRF (X-ray fluorescence spectrometer) merk PANalytical Epsilon3. Available surface functional groups were qualitatively determined by Fourier Transform Infrared (FTIR) spectroscopy (SpectrumTM One Spectrometer, Perkin Elmer). Surface morphology of adsorbents was obtained by scanning electron microscopy coupled with EDX (SEM-EDX, Hitachi model S-3400N).

RESULTS AND DISCUSSION

Characteristics of A CRI-WAS Adsorbent
The sludge is a heterogeneous material, one of the primary objectives is to analyze the chemical constituents of the sludge which can influence its adsorptive capacity [25]. The results of elemental analysis of the CRI-WAS adsorbent by XRF method is presented in Table 1. The analyses indicate that the sludge primarily consists of a Silica oxide, with an aluminum oxide and Calcium Oxide as another most abundant materials. These results are expected since the sludge consists of Crumb rubber processing waste with added alumina for precipitation and lime for pH control.

Tabel 1. Content of the Waste Activated Sludge of Crumb Rubber Industry (CRI-WAS)

Parameter	Concentration (%)	Oxide	Concentration (%)
Si	55.786	SiO_2	63.203
Al	13.628	Al_2O_3	16.076
Ca	11.93	CaO	6.656
Fe	6.223	Fe_2O_3	3.168
S	4.582	SO_3	4.919
P	3.865	P_2O_5	3.896
Cu	0.028	CuO	0.012
Mn	0.229	MnO	0.106
Cr	0.013	Cr_2O_3	0.007
Zn	0.114	ZnO	0.048
Pb	0.04	PbO	0.001
Cd	0	CdO	0
Ni	0	NiO	0

Table 1 shows the contents of minerals and metals from CRI-WAS. Silica and alumina are the highest mineral content which allegedly acted as the active side of the adsorbents to absorb metal ions Cd(II). Toxic metals like copper, chromium, and lead are released at a relatively lower concentration, Likewise [28,33] reported the leaching of chromium, nickel, copper, zinc, lead and cadmium from POM sludge and sewage sludge. The characteristics of higher silica and alumina content in CRI-WAS adsorbent also supported by SEM-EDX method characterization (Figure 1 (B1) and (B2)). From Figure 1 (B1) showed that Si and Al were a dominant elemental in CRI WAS adsorbent before Cd(II) loaded. On the other hand, after Cd(II) loaded (B1), Cd(II) appeared in CRI-WAS adsorbent.

The microstructure of the sludge surface was studied by using a scanning electron microscope (SEM) and energy-dispersive X-ray spectra (EDX). The SEM was used to observe the surface morphology structure of CRI-WAS adsorbent used, and the surface components of CRI-WAS adsorbent were examined using EDX and photo SEM with magnified 500 times. Clearly depicted are the surface morphology and internal structure of CRI-WAS adsorbent before and after Cd(II) is loaded (figures 1 A1 and A2). The surface was a rough, wrinkled and porous structure, making it possible for the adsorption of metal ions. As can be seen in Figures 1 (A1) and (A2), the possible mechanism of adsorption of metal ions on CRI-WAS adsorbent may be due to physical and chemical adsorption on the surface sites.

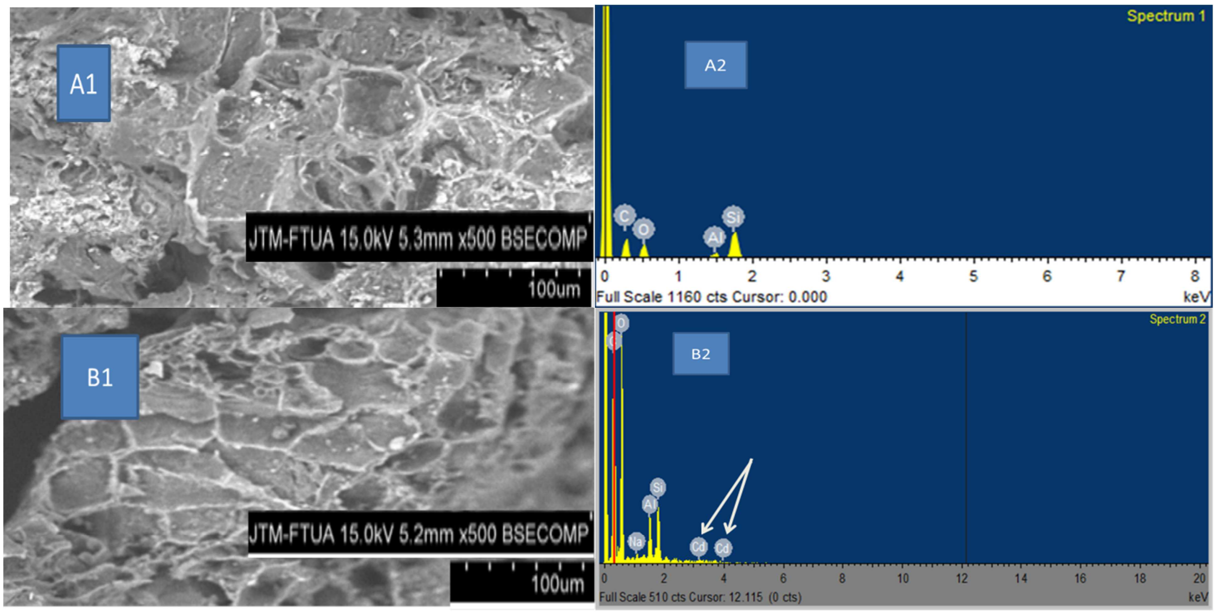

Figure 1. SEM images and EDX spectra of CRI-WAS adsorbents (A1) and (A2) before, (B1) and (B2) after Cd(II) is loaded

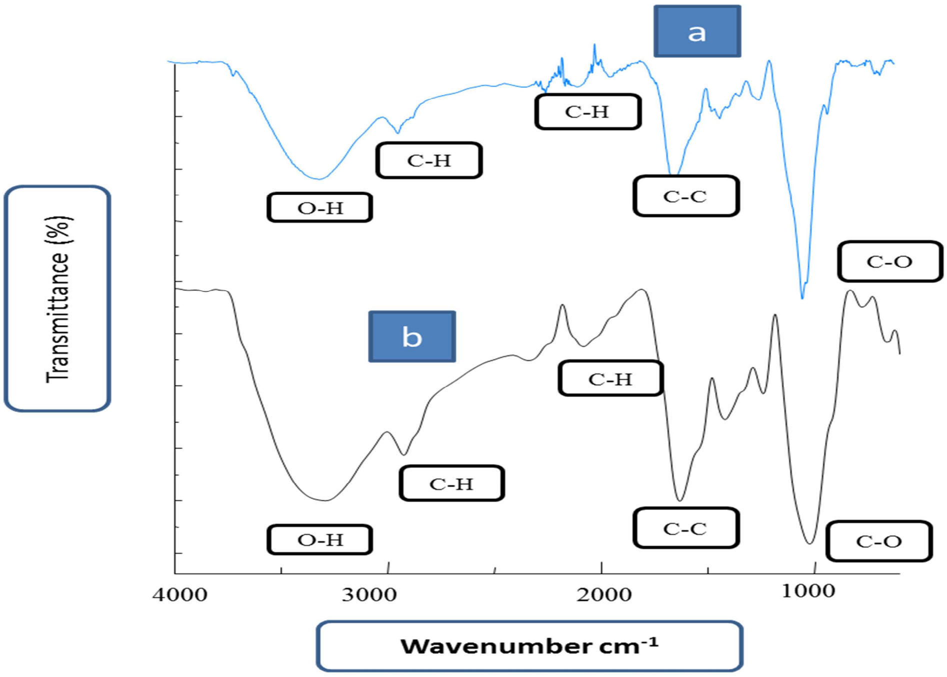

Figure 2. FTIR Spectra of CRI-WAS adsorbents (a) before, (b) after Cd(II) is loaded

Major functional groups of CRI-WAS adsorbents that involve in adsorption process were analyzed with FTIR. The results are shown in Figure 2. FTIR spectra of before and after sorption of Cd(II) were recorded in the wave number range 4,000–600 cm^{-1}. Both of The CRI-WAS adsorbents show a broad peak centered in 3291 cm^{-1} which indicates the presence of –OH stretching in bonded and non-bonded hydroxyl groups, and water molecules [23,26], Narrow band ranging in 2800 cm^{-1} which indicate the presence of alkanes functional groups [27]. C-H stretching was shown at 2083 cm^{-1}. Cyclohexane ring vibrations also are shown at a band range of 1016–911 cm^{-1}. A second broad peak is at 1634, indicating the presence of C–C stretching of carboxylate ion groups [7,8]. The third broad peak centered at 1095 cm^{-1}, that implies the presence of C-O and carboxylic acid functional groups [7,28]. It is supported by small intensity peaks varying from 796–694 cm^{-1}, whereas –Si–C– at 721.03 cm^{-1} and –CH CH– at 694.16 cm^{-1}. There was a change in intensity and shift in the position of the peaks that could be observed in FTIR spectra after Cd(II) adsorption. The enhancement of the intensity at all the peaks indicates the involvement of O-H, C-H and C-O groups in the adsorption process. From the results shown in Figure 2, it is clear that these functional groups acquire a positive charge when protonated and may interact with the negatively charged metal complex [8].

Effect of pH Solution

In general, the adsorption capacity of heavy metal ions from aqueous solution will be influenced by solution pH. The acidity of the medium affects the competition of the hydrogen ions and metal ions for the active sites on the adsorbent surface [4]. adsorption capacity was analyzed over a pH range of 1 to 7. The effect pH of Cd(II) adsorption is presented in Figure 3. From Figure 3 shows that the adsorption capacity of Cd(II) increases with the increase in pH up to a maximum absorption at pH 5, and then decreased with increasing pH from pH 5 to pH 7. The pH optimum for the uptake of Cd(II) obtained at pH 5 and is used as a further treatment. At lower pH values Cd(II) removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as a consequence of the repulsive force [11]. As the pH increased, the active sites in CRI-WAS adsorbent would be exposed, increasing the negative charge density on the CRI-WAS adsorbent surface, increasing the attraction of metal ions with a positive charge, and allowing the sorption onto the CRI-WAS adsorbent surface. In this study, the adsorption of Cd(II) at pH 4.0 to 5.0 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent, as shown in Figure 3. The decrease in Cd(II) adsorption above pH 5.0 to 7.0 was probably due to the precipitation of Cd(II) ions as cadmium hydroxides, but not due to adsorption [7,16].

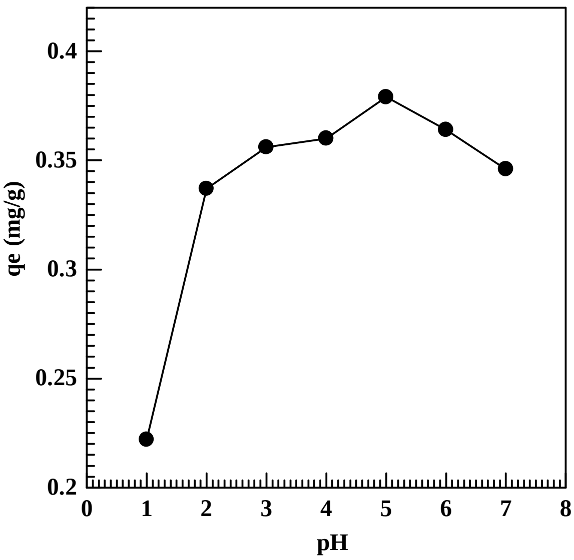

Figure 3. Effect of pH solution on adsorption capacity of Cd(II) by CRI-WAS adsorbent

Effect of Contact Time

The contact time affects of concentration of Cd(II). During the experiment, contact time was varied from 10 to 270 min. It is obvious that increase in contact time from 10 to 210 minute enhanced significantly the adsorption capacity of Cd(II). The adsorption capacity for 100 and 200 mg/l of Cd(II) presents a shape characterized by a strong increase of the amount of Cd(II) adsorbed during the first 30 minutes of contact solution-CRI-WAS adsorbents, follow-up of a slow increase until to reach a state of equilibrium at 210 minute of shaking and then the concentration of Cd(II) decreases when it reaches saturation point. It was clear from the result of this study in Figure. 4 that contact time required for maximum adsorption of Cd(II) by this adsorbent was dependent on the initial cadmium concentration. The adsorption capacity of cadmium ion for high initial cadmium ion concentration was higher than for low initial cadmium ion concentration of the solution at the same time. This result is important because the time required to reach equilibrium is one of the considerations for the application of economical wastewater treatment plant [7].

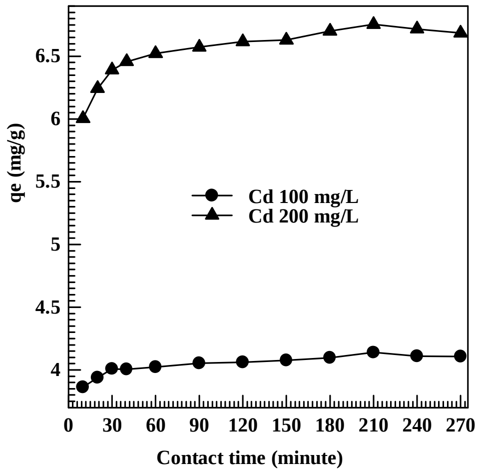

Figure 4. Effect of Contact time on adsorption capacity of Cd(II) by CRI-WAS adsorbent

Effect of Adsorbent Dosage

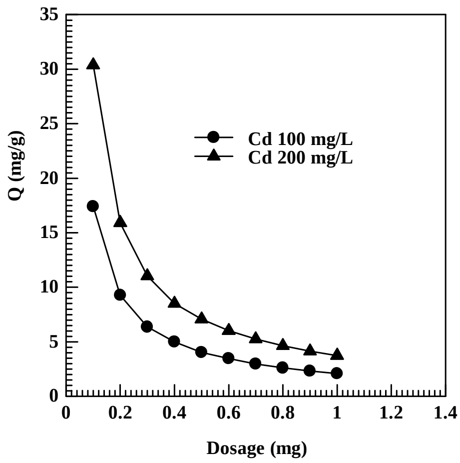

Figure 5. Effect of CRI-WAS adsorbent dosage on adsorption capacity of Cd(II)

The adsorbent dosage is another important parameter because it has direct relation to the uptake capacity of an adsorbent for a given initial concentration of Cd(II) at the operating conditions. [21,34]. Figure. 5 shows the adsorption capacity of Cd(II) on CRI-WAS adsorbent in water in the different adsorbent dose. Effect of adsorbent dose on adsorption behavior was studied by varying the CRI-WAS adsorbent in the range of 0.1 to 1.0 mg. According to [35] showed that the adsorption capacity decreased with increasing the amount of dosage. The optimum CRI-WAS adsorbent dosage for Cd(II) was found in 0.1 gram with adsorption capacity 17.41 mg/g and 30.38mg/L for initial concentration of Cd(II) 100 mg/L and 200 mg/L respectively.

Adsorption Isotherm Analysis

In order to gain a better understanding of sorption mechanisms and evaluate the sorption performance, the experimental data for Cd(II) adsorption onto CRI-WAS adsorbent was analyzed using the Langmuir and Freundlich adsorption isotherm models. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of Cd(II) per unit mass of adsorbent qe and the solute concentration of the solution at equilibrium Ce [16]. Figure 7 and 8 show a plot of linear Langmuir equation as 1/qe versus 1/Ce and linear Freundlich equation as ln qe versus ln Ce, respectively (17). The plots are linear with good correlation. The sorption isotherms fit to Langmuir model better than Freundlich model due to the larger correlation coefficient (R2) [36] which are 0.992 and 0.979 for Langmuir model and Freundlich model respectively. It is suggesting that Cd(II) sorption on CRI-WAS adsorbent is monolayer chemical sorption process.

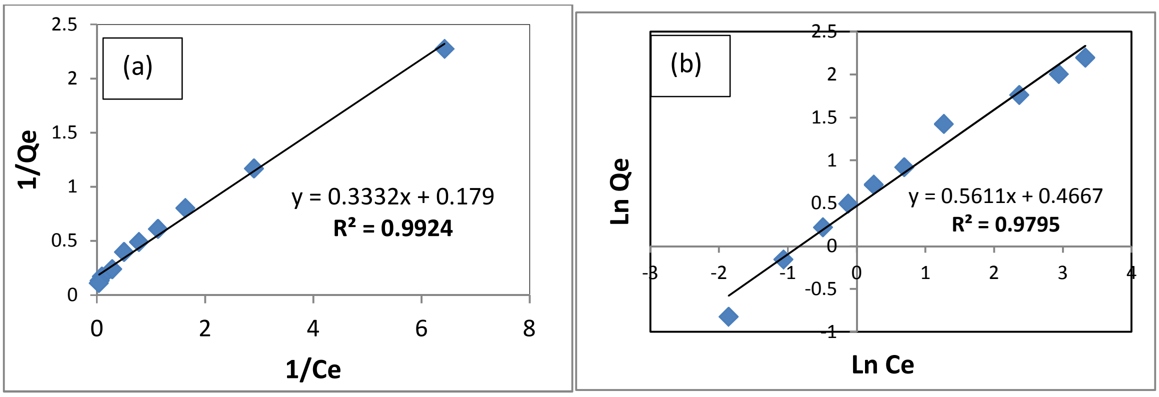

Figure 7. Isotherm Adsorption of Cd(II) on the CRI-WAS adsorbent (a) Langmuir and (b) Freundlich

CONCLUSION

Waste activated sludge of crumb rubber industry (CRI-WAS) containing high silica and alumina and also has an abundant functional groups. In the pH optimum at pH 5 can be used as adsorbent of Cd(II), which is expected to be an economical product for adsorbent of wastewater treatment.

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