Transactions of the Materials Research Society of Japan 30[2] 429-432 (2005)

Processing and Recycle of Acid Drainage Water Contained of Cu(Ⅱ) Ion by Using Rice Bran

Kazuhiro HONDA and Takayuki YOSHIKAWA

Department of Applied Chemistry, Kanagawa Institute of Technology ;
Atsugi－shi 243-0292, Japan
Fax:81-46－242－8760,E－mail:Honda@chem..kanagawa－it.ac.jp

The processing of the acid drainage, which was industrial waste using rice bran was examined. Rice bran showed the good pH buffer action for acidic aqueous solution of pH=2 which prepared the sulfuric acid. Because the phosphorus element is included in rice bran, it was indicated that the pH buffer action by the phosphate was occurred. And, the Cu(Ⅱ) ion was adsorbed in rice bran, and in addition, $Cu(OH)_2$ was formed by the progress of the acid-base reaction. By the sintering reaction at 1200℃, $CuSO_4 \cdot 5H_2O$ and $Cu(OH)_2$ which adsorbed in rice bran were reduced to CuO, Cu_2O and Cu. The possibility of the effective recycling of the Cu(Ⅱ) ion included in the acid drainage to the copper materials were indicated.

Key words: Acid waste water, Rice bran, pH buffer action, Cu(Ⅱ) ion Adsorption, $Cu(OH)_2$, CuO、Cu_2O, Cu, Reduction, 1200℃sintering, Recycling

1. INTRODUCTION

From a background of various problems such as tightening of final disposal space of the refuse, environmental damage by unlawful throw, dioxins pollution etc., "waste disposal and public cleaning law" is revised and is promulgated in June, 2000, and it is perfectly carried out since April, 2001. "Waste disposal and public cleaning law" incorporates weight reduction of a waste, promotions of the recycling, reviews of the industrial waste management system and penal regulation strengthening, etc.

The industrial waste has been classified into 19 types by the above-mentioned law. The acid drainage including heavy metal ions are one of them. The acid waste water including the Cu(Ⅱ) ion is large discharged from the factory of production of the printed circuit board concerning the IT industries. Ministry of Agriculture, Forestry and Fisheries issued "Food recycling low" in June, 2000, and it was enforced in May, 2001. Because the rice is staple food in Japan, rice bran is an agricultural waste in which stable supply is possible.

Authors discovered that rice bran had excellent characteristics as a pH buffer action and an adsorbent of Cu (Ⅱ) ion. From the viewpoint of "Waste disposal and public cleaning law" and "Food recycling low", we examined processing of the acid drainage including the Cu(Ⅱ) ion using rice bran and possibility of the recycling of the Cu element.

2. EXPERIMENTAL

Experiments were carried out in the constant temperature bath system at 30℃. Rice bran added 10.0g for the pure water of the 200ml volume. The water used the distilled water (WAKO Co.,Ltd). Rice bran used the commercial product. The sample solution was prepared using sulfuric acid (H_2SO_4) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). The reagents used the marketing prime class reagent (WAKO Co.,Ltd) without carrying out further purifications.

Time profile of the pH value was recorded in the computer, after analog voltage signal from pH meter (TOA Co.,Ltd : Type HM-7 E) was converted into the digital signal by A/D board which set a sampling time at 5s.

Rice bran was added to $CuSO_4$ aqueous solution prepared at the arbitrary concentration, and the agitation was carried out for 1h.

The sample after the agitation separated by the filter paper, and it dried after the washing under the room temperature.

Moreover, the dried sample sintered in electric furnace at 1200℃ for 1 h.

For rice bran, dried reaction sample after the filtration and the sintered sample, XRD measurement (Rigaku Co.,Ltd : RAD-ⅡVC CuKα), SEM observation and EDX elemental analysis (Shimadzu Co.,Ltd : SEM-SSX-550) were carried out.

3. RESULTS AND DISCUSSION

Fig.1 shows the time profile of pH value in adding 10.0g rice bran to 200ml aqueous solution. The initial pH value is prepared in 2.0 using sulfuric acid. Though the acquisition of the data is the interval of 5s, the graph is plotted in the interval of 1min. By addition of rice bran, the pH value of acidic aqueous solution rapidly shifted to the neutrality, and it became about 6.0 after 20 min.

Fig.2 shows the time profile of pH value as it added 10.0g rice bran to 200ml aqueous solution , which prepared pH value in 2.0 by sulfuric acid and added 4.45mol・dm^{-3}NaCl for sample solution after 18h.

The pH value is shifting to acidic side from the time, which passes through 15h at time of the reaction start before the NaCl addition. It is considered that this originates from the discharge of the metabolite (pyruvic acid) with the activity of the yeast of which is included for rice bran

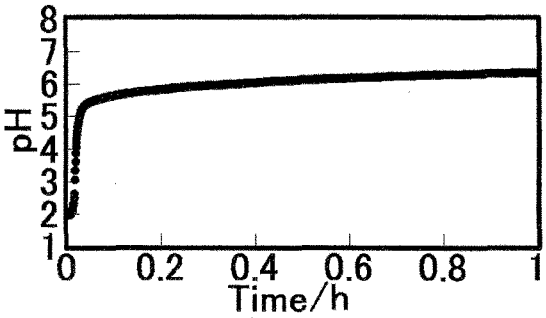

Fig.1 pH time profile of the 200ml aqueous solution which adjusted the initial pH value in 2.0 by sulfuric acid under the coexistence of 10g rice bran.

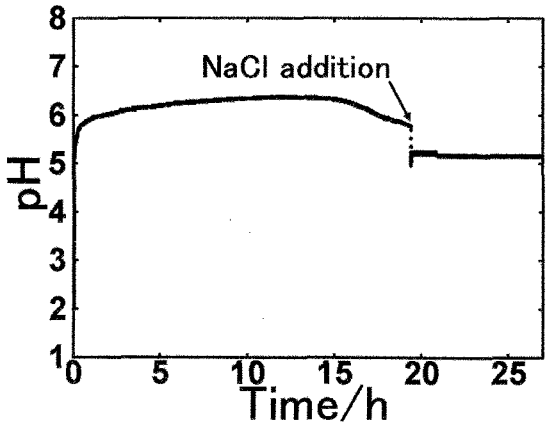

Fig.2 Change of pH value by the addition of NaCl . Concentrations of NaCl is 4.45moldm^{-3}. NaCl was added after about 18h since the reaction start. The pH adjustment was carried out by the sulfuric acid.

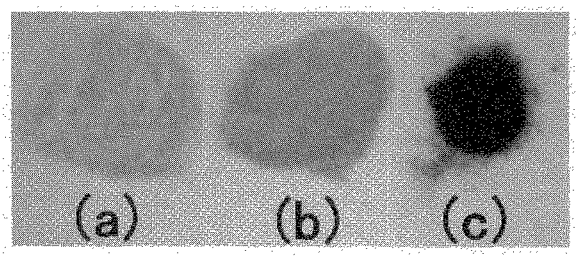

Fig.3 Color photographs of rice bran **(a)**, separation sample **(b)** and sintered sample **(c)**, respectively.

When NaCl was added after 18h, the pH value slightly shifted to acidic side. However, it was indicated that pH buffer action by rice bran could not be explained only in the simple mechanism of a cation exchange without confirming large acidic shift.

50.0g rice bran was added to 50.0×10^{-3}mol・dm^{-3} $CuSO_4$ aqueous solution, and it was stirred in a constant temperature bath at 30 ℃ for 1h.The rice bran component carried out the separation by the filtration after the agitation (reaction) end. After wash in water, it dried under room temperature. Also, the separation sample by the filtration after the drying sintered 1h in 1200℃.

Fig.3 shows the color photographs of rice bran **(a)**, separation sample **(b)** and sintered sample **(c)**, respectively. In comparison with rice bran of flesh tint color before the reaction, rice bran stirred in $CuSO_4$ aqueous solution changed to the color of sky blue. Also, the sintering sample mainly shows the black color.

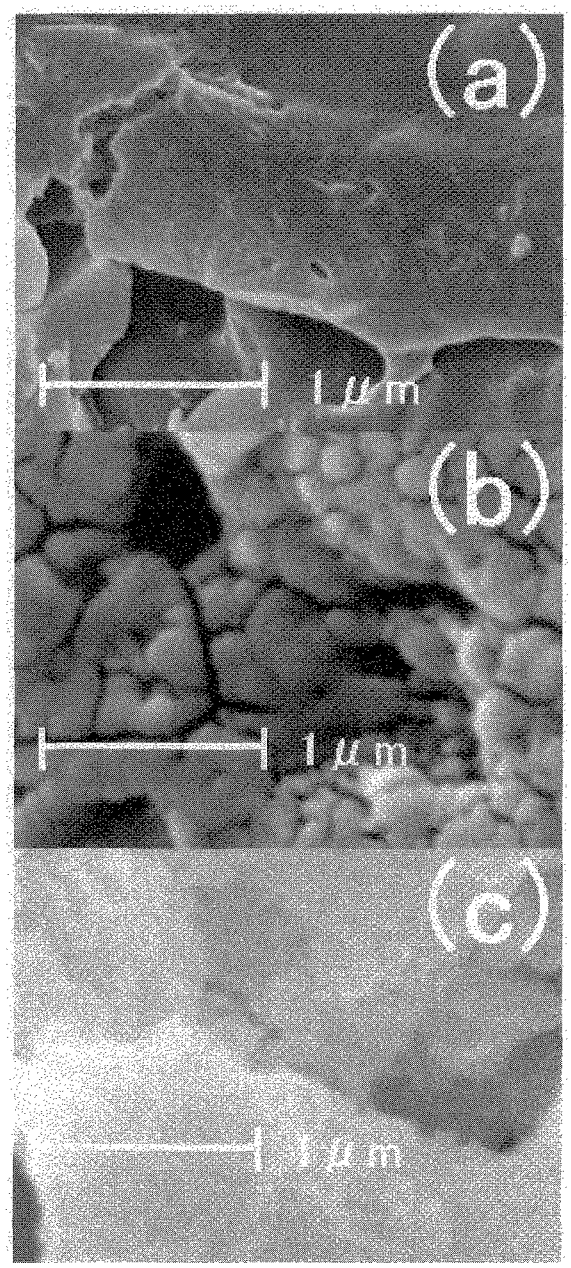

Fig.4 SEM image of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**. The magnification of photograph is 10000 time,

Fig.4 show the SEM image of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**, respectively. The magnification of photograph is 10000 time, respectively.

In comparison with the image of rice bran before the

reaction, it was not possible that the separation sample confirmed the rice bran surface, and the aggregation of a fine powder was confirmed. In addition, formation of the domain structure can be also confirmed. On the other hand, the surface of the sintering sample observed only the fine and flat surface.

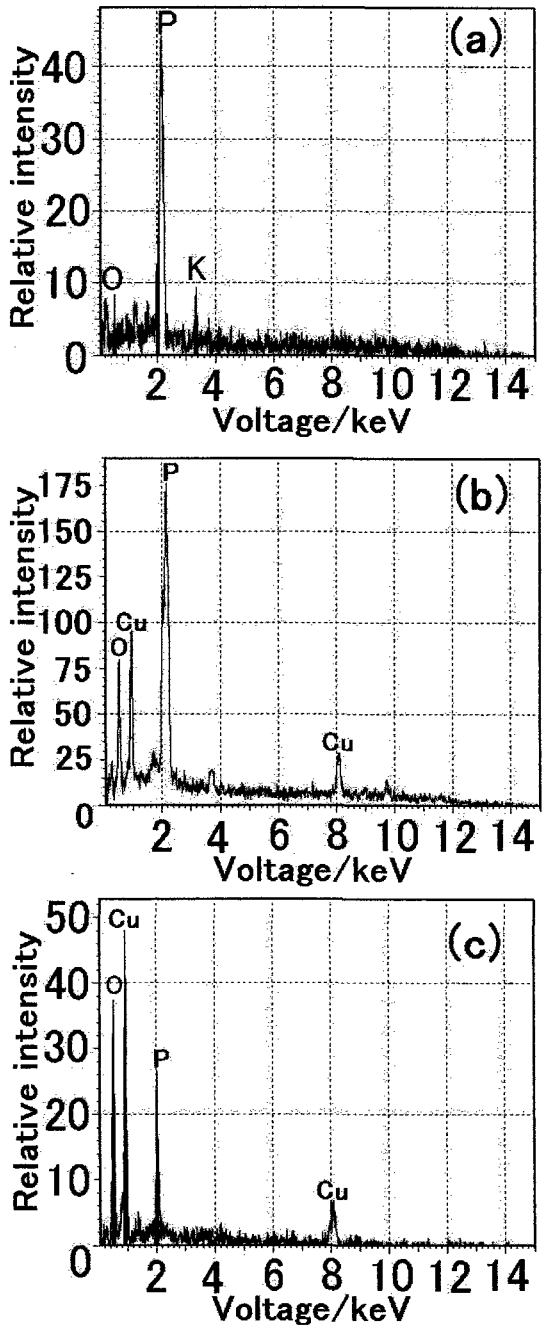

Fig.5 EDX elemental analysis of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**.

Fig.5 show the results of EDX elemental analysis of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**. It was detected that the elements of phosphorus (P) and potassium (K) existed in rice bran. This result is strongly indicated that the phosphate was included in rice bran. From the elemental analysis for the separation sample by the filtration, it can be confirmed that Cu element exists on the rice bran surface. Moreover, the existence of the Cu element was also similarly confirmed in the sintering sample. Also, the existence of phosphorus element were confirmed in all of three samples.

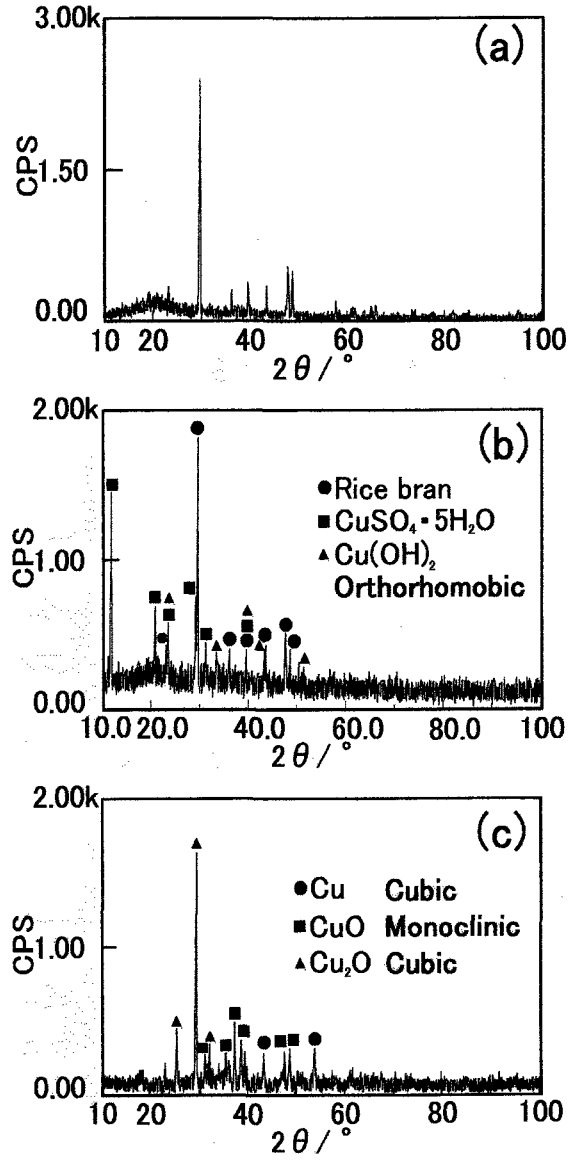

Fig.6 XRD paterns of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**.

Fig.6 show the results of XRD measurement of rice bran **(a)**, separation sample **(b)** and sintering sample **(c)**, respectively. Though the identification has not been done at present, it is proven that the diffraction pattern from rice bran has clear and strong peak intensity and that it contains chemical compound with a good crystallinity. For the separation sample, the diffraction peak of $CuSO_4 \cdot 5H_2O$ and $Cu(OH)_2$ with Orthorhomobic crystal system was identified[1,2]. From these results, rice bran seems to have the adsorption character for the Cu(II) ion. Simultaneously, it is indicated that Cu(II)

ion which adsorbed in rice bran changes to $Cu(OH)_2$ by the acid-base reaction. It is considered that the coloration of sky blue with the generation of $Cu(OH)_2$. The sintering sample identified the diffraction peak of CuO[3], Cu_2O[4] and Cu[5]. $CuSO_4 \cdot 5H_2O$ and $Cu(OH)_2$ in separation sample seemed to change to copper oxide (CuO and Cu_2O) and metallic copper by the sintering reaction.

Based on these results, the following descriptions are possible. The existence of elements of phosphorus and potassium were identified from the EDX measurements. From these facts, the existence of the phosphate in rice bran is strongly indicated. It is known that the phosphate has the peculiar pH buffer action by the type and combination. "Hasting-Sendroy" buffer solution is known as phosphate type which effectively actions in the vicinity of pH value≒6. This buffer solution is mixture of Hydrogenphosphate (HPO_4^{2-}) and Dihydrogenphosphate ($H_2PO_4^-$), and it has the buffer action between the pH value of 6.8~8.0 region. The HPO_4^{2-} ion actions as a weak base, and it reacts with H^+ ion discharged from the strong acid, and $H_2PO_4^-$ is formed (**eq (1)**).

$$HPO_4^{2-}+H^+ \rightarrow H_2PO_4^- \qquad (1)$$

From the result of **Fig.1**, the pH value gradually approaches to 6.0, and that it accepts the buffer action by **eq (1)**.

From the results of XRD measurement, rice bran has the adsorption character for the Cu(Ⅱ) ion. Also, it is consider that rice bran is the basic compound and the adsorbed Cu(Ⅱ) ion changes to $Cu(OH)_2$ by the acid-base reaction in rice bran.

By the sintering at 1200℃, progress of the following reactions are considered.

$$CuSO_4 \cdot 5H_2O \rightarrow CuO + SO_3 + 5H_2O \qquad (2)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \qquad (3)$$

$$2CuO + 2CuO \rightarrow 2Cu_2O + O_2 \qquad (4)$$

$$2Cu_2O \rightarrow 4\,Cu + O_2 \qquad (5)$$

CuO is formed by the **eq (2)** and **eq (3)** . In addition, CuO is reduced to Cu_2O by the **eq (4).** Further more, Cu_2O is reduced by the **eq (5)** and seems to finally form Cu.

4. CONCLUSIONS

"Green & Sustainable Chemistry" becomes the large social demand. At present, there seems to be the significance on the effective utilization for environment processing of rice bran of which most has been incinerated. pH control of the acid drainage and utilization as an adsorbent for the Cu(Ⅱ) ion using rice bran seem to be economical processing. And, the generation of CuO, Cu_2O and Cu by the sintering is also important on the viewpoint of useful recycling of resources.

References

[1] Powder Diffraction File, Card No.48-1548, International Centre for Diffraction Date, Network Square PA,1996.
[2] Powder Diffraction File, Card No.35-505, ibid.
[3] Powder Diffraction File, Card No.48-1548, ibid.
[4] Powder Diffraction File, Card No.34-1354, ibid.
[5] Powder Diffraction File, Card No.4-0836, ibid.
[6] Weiner, Fundamentals of Chemistry 4th edition, Academic press (1980), p.235.

(Received December 24, 2004; Accepted March 22, 2005)