Manganese Nodules as Catalyst and Adsorbent (Part 7)

Adsorptive Characteristics of Manganese Nodule for Removal of Heavy Metal Ions from Aqueous Solution

Masahiro NITTA*, Yuko KUROKAWA* and Kazuo AOMURA*

In order to investigate applications of manganese nodules as adsorbents, the adsorption of heavy metal ions such as Pb(II), Cd(II), Zn(II), Hg(II), Cr(III), and Cr(VI) was carried out in an acidic aqueous solution and the results obtained were compared with those of some well-known adsorbents.

The results were as follows:

- (1) The initial pH of the solution containing a metal ion should be kept above 3.0 to prevent dissolution of the metals constituting the nodule.
- (2) Pb(II), Cd(II), Zn(II), and Hg(II), except for Cr(VI), were well adsorbed on the nodule. By applying the Langmuir isotherm equation to these adsorption data, it was shown that the order of activities of the ions for adsorption was: $\text{Pb(II)} > \text{Cd(II)} > \text{Zn(II)} > \text{Hg(II)} \gg \text{Cr(VI)} \approx 0$
- (3) The adsorption capacity of the nodule was almost the same as that of bone charcoal and of zeolite, and much larger than the capacity of activated carbon and of activated clay. The adsorption of metal ions on the nodule was partly irreversible and the complete recovery of the metal ions was much difficult.
- (4) The saturated adsorption capacity of the nodule was related to the amount of the surface excess oxygen on the nodule. It was strongly suggested that the excess oxygen may play an important role in the adsorption of heavy metal ions.

1. Introduction

Waste waters containing heavy metal ions from the factories should be treated to prevent pollution. Although the adsorption method seems to be one of the most effective methods for removal of heavy metal ions, there is hardly any report concerning it available in the literature^{1)~4)}. Thus, the development of an effective adsorbent associated with the method is desirable.

In recent years, manganese nodules, which consist of various metal oxides, have attracted considerable attention as a new resource of metals; moreover, they seem to be available extensively cheaply⁵⁾. At the same time, utilization of the nodules as catalyst^{6),7)} and adsorbent^{8),9)} could be expected, because they have a porous structure. However, no attempt has been made for the removal of heavy metal ions from waste water by using the nodules. The purpose of this study is to show that the nodules are available as ad-

sorbents for heavy metal ions. In the present paper, adsorption of Pb(II), Zn(II), Hg(II), Cr(III), Cr(VI), and Cd(II) by the nodules was carried out in acidic aqueous solution. The amount of surface excess oxygen on the nodules was measured and the mechanism of adsorption was discussed. A comparison under the same conditions was made with other well-known adsorbents.

2. Experimental

2.1 Adsorbent

The manganese nodules used in this experiment were collected from the open sea off Hawaii. The nodules were dried in an oven at 100°C for 24hr after washing with distilled water until no chloride ions were detected, and then grounded to different particle sizes. The chemical composition of the nodule, which is ground to pass through a 150-mesh sieve, is given in **Table 1**.

Zeolite-Y SK-40 (Nishio Industry, Ltd.), Activated Carbon (Nakarai Chemicals Co., Ltd.), Activated Clay, and Bone Charcoal Powder (Kanto Chemicals Co., Inc.), which were used to compare their adsorption capacities with that of the nodule, were pretreated similarly.

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* Department of Chemistry, Faculty of Engineering, Hokkaido University (Kita 13 Nishi 8, Kita-ku, Sapporo 060).

Table 1 Components of Manganese Nodule in This Study (on a Wet Basis)

Component	wt%
MnO ₂	49.20
Fe ₂ O ₃	8.66
NiO	1.78
CuO	1.79
CoO	0.23
MgO	3.03
CaO	1.26
Na ₂ O	3.07
Silica, Alumina and Others	17.98
H ₂ O*	13.00

* Removed after 4hr heating at 150°C

For the purpose of investigating the changes in adsorption capacity brought about by pretreatment temperature, the crushed nodule was preheated in the temperature range from 110°C to 800°C for 4hr in air. All the samples were placed in a desiccator, which stored NH₄Cl saturated solution, at room temperature before use.

The specific surface area of the nodule was determined by the BET method using N₂ gas as an adsorbate.

2.2 Solutions

Aqueous solutions containing Cd(II), Pb(II), Zn(II), and Cr(III), respectively, were prepared from guaranteed reagents of their chlorides except for Pb(II) which was prepared from its nitrate (E. Merck A. G.). Solutions of Hg(II) and Cr(VI) were made from HgCl₂ and K₂CrO₄ (Wako Pure Chemical Industries, Ltd.), respectively. Purified water was used. All pH values of the solutions were adjusted with HCl and NaOH (Wako Pure Chemical Industries, Ltd.).

2.3 Adsorption

One hundred milliliters of a solution containing a definite amount of heavy metal ions was put in an Erlenmeyer flask equipped with a stop cock. A nodule sample was added and the suspension was shaken back and forth (175 times per minute) at room temperature for a given period of time. The supernatant solution centrifuged was analyzed with an atomic absorption spectrophotometer (Hitachi 208-model). No attempt was made to maintain the level of pH value of the suspension during the reaction.

3. Results and Discussion

3.1 Effect of initial pH of solution

It is known that various metals which constitute manganese nodules can be extracted with acid¹⁰⁾, and their dissolution into the adsorbate solution is undesirable for the purpose of the present inves-

Fig. 1 Dissolution of Metals of Manganese Nodule in Acidic Solution

tigation. The influence of the initial pH of the solution on the dissolution of manganese, iron, nickel, copper, and cobalt from the nodule after shaking for 24 hr at room temperature was determined for a 150–325 meshed nodule in the absence of adsorbate metal ions. The results obtained are shown in **Fig. 1**. Amounts of the dissolved metals abruptly increased in the solution having the initial pH below 3.0. There is no precipitation due to hydrolysis of the metal ions dissolved out from the nodule. In preliminary experiments, a rise in the pH was observed during the reaction in the presence of an adsorbate. It is necessary in the adsorption experiments to adjust the initial value of pH of the solution to above 3.0 when the nodule is used as an adsorbent.

3.2 Effect of Particle Size

Effects of particle size of the nodule on the adsorption of Cd(II) were investigated at the initial pH=5.4 of the adsorbate solution. The results are presented in **Table 2**. Although the adsorption amount increased with finer grinding of the nodule, the amount by the sample ground above 150 mesh remained constant. This indicates that the adsorption rate of the sample below 150 mesh is controlled by diffusion rate. From the result, 150–325 mesh sample of the nodule was used in

Table 2 Effect of Particle Size of Manganese Nodule on Adsorption of Cd(II)

Mesh	Amount Adsorbed (mg/g)
10- 16	7.5
16- 20	8.3
20- 24	11.7
24- 48	17.0
48- 80	19.8
80-150	27.1
150-325	28.3
>325	28.3

Shaking time : 1hr
Adsorbent : 100mg pretreated at 400°C for 4hr in air
Adsorbate : Cd(II), 100 ppm/100 ml
Initial pH of solution : 5.4

subsequent experiments.
3.3 Adsorption Equilibrium

The Kinetics of adsorption of Cd(II) from the solution at initial pH=4.0 is presented in Fig. 2. The initial rate of adsorption of Cd(II) on the nodule was quite rapid. About 83% of the equilibrium adsorption capacity of Cd(II) took place in the first hour of the run; however, about 18hr were required to attain equilibrium. As a result, the shaking time required for determining the full adsorption capacity at equilibrium was 24 hr.

The highly complex structure of the manganese nodules suggests the existence of various adsorption sites. Then, the reversibility of all heavy metal ions adsorbed was investigated. After Cd-(II) ions had reached at adsorption equilibrium, the suspension was centrifuged and 90% of the supernatant solution was removed. Distilled water, which its pH was adjusted, was added to the residue

Manganese nodule : 100 mg pretreated at 150°C for 4 hr
Adsorbate : Cd(II), 50 ppm/100 ml
Initial pH of solution : 4.0

Fig. 2 Effect of Shaking Time on Adsorption of Cd(II)

until the original volume of the solution was re-stored. This suspension was shaken again at room temperature for 24 hr, and again the concentration of Cd (II) in the supernatant solution was determined. The results are shown in Fig. 3. The broken line is the desorption isotherm obtained by this method for perfectly irreversible adsorption. The result indicates that Cd (II) adsorbed on the nodule is partly irreversible. The amount of desorption of Cd (II) increased with decrease in the pH value of the distilled water added. However, as described above, desorption at lower pH values cannot be visualized, because the dissolution of the metals of the nodule occurs at the same time. This result reveals that complete regeneration of used nodule is quite difficult.

3.4 Adsorption Isotherm

Different amounts of the nodule pretreated at 150°C were added to the solutions which contained 50 ppm of each of heavy metal ion. In the present investigation, the Langmuir isotherm¹¹⁾ was applied to the experimental data obtained. The Langmuir expression has the form:

$$V=\frac{V_m bC}{(1+bC)}$$

where *V* is the amount adsorbed per unit quantity

A : Adsorption isotherm : Initial pH of solution 4.0
B : Desorption isotherm : Solution of pH 4.0 was added for desorption
C : Desorption isotherm : Solution of pH 4.0 was added for desorption
D : Theoretical irreversible desorption isotherm

Fig. 3 Reversibility of Cd(II) Adsorption

of the adsorbent (mg/g), V_m is the saturated adsorption capacity of the adsorbent (mg/g), b is a constant related to the energy of adsorption, and C is the residual concentration (ppm) of the adsorbate in the liquid phase at equilibrium. To facilitate the evaluation of the characteristic constants, V_m and b can be estimated from the experimental measurements of V and C . The Langmuir expression written in a linear form is:

$$\frac{C}{V} = \frac{C}{V_m} + \frac{1}{bV_m}$$

If the adsorption is of the Langmuir type, the plot of C/V vs. C will give a straight line with a slope of $1/V_m$ and will intercept with $1/V_m b$. It should be noted that a satisfactory fit of the experimental data to the equation does not necessarily imply that the assumed model is reasonable. The Langmuir plot of the adsorption data is presented in **Fig. 4**. From the results of **Fig. 4**, the saturated adsorption capacity of the adsorbent, V_m , the energy parameters, b , and the final pH values for Pb(II), Cd(II), Zn(II), and Hg(II) are summarized in **Table 3**.

The adsorption behavior of chromium ion differs considerably from the other cations investigated here. That is to say, Cr(VI), which exists as an anion (dichromate ion) under the conditions of the present investigation, was hardly adsorbed on the nodule. This suggests that the manganese nodule

Table 3 Maximum Adsorption Capacity of Manganese Nodule

Species	V_m (mg/g)	Final pH	b (mole/l)
Zn(II)	26.1	5.76 ± 0.24	0.11
Pb(II)	103.7	4.75 ± 0.37	0.39
Hg(II)	49.0	6.43 ± 0.53	0.11
Cd(II)	41.7	6.14 ± 0.31	0.18

adsorbs cationic species preferably. Cr(III), which is a cation, was adsorbed as well as other metal ions and to a considerable extent. The dissolution of a large amount of manganese from the nodule was observed in the adsorption of Cr(III). And the color of the solution changed from light green due to Cr(III) to yellow. This indicated that Cr(III) remaining in the solution after adsorption was oxidized to Cr(VI), and this observation was confirmed colorimetrically. These experimental observations could reasonably be explained as follows: since the existence of excess oxygen on the manganese nodule is known⁷⁾, the oxidation of Cr(III) is due to the excess oxygen. As a result, the surface excess oxygen is consumed in the oxidation of Cr(III), and the surface of the nodule collapses and finally the manganese dissolves out in the solution. Manganese nodules would not be a suitable adsorbent for chromium ions.

3.5 Adsorption Sites

Since the manganese nodule was pretreated in the temperature range from 200°C to 800°C, its specific surface area and saturated adsorption capacity for Cd(II) were determined. The adsorption experiment was carried out at initial pH=4. The results are shown in **Fig. 5**. The saturated adsorption capacity of the nodule decreased uniformly with rising pretreatment temperature. This suggests that unpretreated nodule have the largest adsorption capacity and that it is much desirable for practical use. On the other hand, the specific surface area showed in **Table 4** has its maximum at 400°C and then it decreases with temperature. In other words, other important factors than the specific surface area may be involved in the adsorption.

As shown in **3.4**, a large amount of heavy metal ions which exist as cationic species was adsorbed. Cr(VI), which exists as anionic species, was hardly adsorbed. And Cr(III) was presumably oxidized to Cr(VI) by the excess surface oxygen. These results suggest that the amount of the adsorbed ions is related to the amount of surface active oxygen on the manganese nodule. It is known that there is a wide variety of excess oxygen

Shaking time : 24 hr
 Adsorbent : Pretreated at 150°C for 4 hr in air
 Adsorbate : 50 ppm/100 ml
 Initial pH of solution : 4.0

Fig. 4 Langmuir Plot of Data for Adsorption of Heavy Metal Ions on Manganese Nodule

Table 4 Specific Surface Area of Manganese Nodule

Pretreatment Temp. (°C)	Specific Surface Area (m ² /g)
200	150
300	150
400	160
500	140
600	80
700	20

Fig. 5 Effect of Pretreatment Temperature of Manganese Nodule on Adsorption of Cd(II) and on the Specific Surface Area

which have different oxidation power on the surface of manganese nodules⁷⁾. Therefore, a volumetric method using hydrazine¹²⁾ was adopted for the determination of surface excess oxygen of the nodule. This method can successfully determine the surface excess oxygen. The change in the amount of excess oxygen with pretreatment temperature is shown in **Fig. 5**. Its change runs fairly parallel to that of the saturated adsorption capacity. It is apparent that excess oxygen plays the most important role in the adsorption of the cations. However the highly complex structure of manganese nodule suggests the existence of various adsorptive active also sites such as surface hydroxyl groups, lattice oxide ions and metal ions.

Concerning manganese dioxide which is a main component of manganese nodule, Murray¹³⁾ reported that only the alkali metal ions react electrostatically with the surface and the transition metal ions react more strongly with manganese dioxide than with alkaline earth metal ions. There is a possibility of adsorption due to the exchange of the adsorbate metal cations with alkali and alkaline earth metals which are minor components in manganese nodule. In the present investigation under lower pH condition, it is difficult to distinguish clearly between dissolution of the minor

components due to acid and release of them due to exchange with the adsorbate metal cation.

The extent of decline of the saturated adsorption capacity is severe for the samples pretreated at 700°C. In **Table 4**, the rapid decrease in the specific surface area of the nodule pretreated above 600°C, indicates the sintering of the sample. Therefore, the disappearance of adsorption sites is. On the other hand, Okada, et al.¹⁴⁾, reported about the heat transformation of manganese nodules collected from various locations. Their results showed that all samples were subject to heat transformation by heating above 600°C. With the nodule used here, the appearance of magnetism in a sample pretreated above 700°C was clearly confirmed with a hand-magnet. They concluded that the phenomenon was due to the growth of cubic (Fe, Mn)₃O₄. This suggests that these samples differ mineralogically from those pretreated below 600°C. In any case, the highly complex structure of the nodule makes it difficult to reveal all sites related to adsorption.

It is plausible that the adsorption capacities of manganese nodules collected from different locations are different because of their variations in the chemical composition and internal distribution of the components. The above results indicate that the adsorption capacity of manganese nodules collected from different locations can be estimated from the determination of the amount of the surface excess oxygen with the hydrazine method.

3.6 Comparison with Other Adsorbents

A comparison of the adsorption ability of the nodule with those of other adsorbents was made from the results of Cd(II) adsorption shown in **Table 5**. A direct comparison is difficult, because the mode of adsorption behavior is different for each. It can be said from **Table 5**, however, that manganese nodule is an efficient adsorbent as well as zeolite and bone charcoal. In case of zeolite, the dissolution of a large amount of cations in zeolite by ion exchange was observed. In this series of experiments with a solution of initial pH=4.0, manganese, which is the main component of the nodule, and other ions of nodule do not dissolve. This indicates that there is no danger of pollution due to the manganese nodule in the treatment of waste water.

Sigworth et al.¹⁾ reported that adsorption of cadmium and zinc ions on activated carbon was slight. The result of Yoshida, et al.³⁾, indicates that the maximum amount of adsorption of mercury

Table 5 Comparison with Other Adsorbents*

Adsorbent	Shape	Amount Adsorbed (mg/g)	Final pH
Activated Carbon (110°C)**	Powder	2.5	4.17
Activated Clay (110°C)	Powder	5.2	3.80
Zeolite-Y SK-40 (110°C)	Powder	49.4***	6.44
Bone Charcoal (110°C)	Powder	47.0	6.66
Manganese Nodule(110°C)	150-325 mesh	41.9	6.20

* Conditions : Shaking time : 24 hr
Adsorbent : 100 mg
Adsorbate : Cd(II) 50 ppm/100 ml
Initial pH of solution : 4.0
** Pretreatment temperature
*** Dissolution of 2.8 mol of sodium ion per 1 mol of Cd(II) adsorbed was observed

ion on activated carbon is about 20 mg/g. The nodule in this study showed a saturated adsorption capacity of 49 mg/g for Hg(II) at the initial pH value of 4.0 (**Table 3**). Yuki, et al.⁴⁾, reported that the amount of cadmium ion adsorbed on waste clay was nearly 10 mg/g at equilibrium concentration of 5 ppm, while the amount adsorbed at the same concentration was 37 mg/g with the nodule pretreated at 150°C (**Fig. 3**). As a result of their comparison, it was found that manganese nodule is a great adsorbent for metal ions. Furthermore, from the results of **3.5**, the manganese nodules, which have a large amount of surface excess oxygen than the nodule used in this experiment, are expected to have a better adsorption ability.

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要 旨

マンガンノジュールの触媒作用および吸着作用に関する研究 (第7報)
水溶液中からの重金属イオンの除去のためのマンガンノジュールの吸着特性

新田 昌弘*, 黒河 雄幸*, 青村 和夫*

新しい金属資源として注目されているマンガン団塊は、種々の金属を含有し、多孔質であることから、触媒^{6)~7)}、および、吸着剤^{8)~9)}としての用途が期待される。本報では、工場廃水などに含有される汚染物質の一つである有害重金属イオンの吸着剤としての利用を目的として、酸性水溶液内における吸着特性を調べ、さらに、他の吸着剤との比較検討を行った。

マンガン団塊は溶液の初期 pH=3.0 以下でその構成成分である金属を多量に溶出するため、吸着は初期 pH=3.0 以上で行う必要がある (Fig. 1)。粒度の影響を検討したところ、150 メッシュ以上では、吸着速度は拡散が律速となった (Table 2)。吸着平衡に達するのに約 18 時間を要したが、初期の吸着はすみやかであり、吸着開始後、1 時間で平衡吸着量の約 83% が吸着される (Fig. 2)。吸着は部分的に不可逆であり、吸着された重金属イオンの完全な回収は難しい (Fig. 3)。水溶液中にアニオン種として存在する Cr(VI) は吸着されなかった。Cr(III) は吸着されるものの、溶液内残留イオンの Cr(VI) へ

の酸化と、団塊を構成するマンガンの多量の溶出が観測された。これは団塊表面に存在する過剰酸素⁷⁾によって Cr(III) が酸化され、それに伴って団塊の構造破壊が起こったことを示唆した。他方、溶液内にカチオン種として存在する Pb(II), Cd(II), Zn(II) と、HgCl₂ の形態を取っている Hg(II) は良く吸着され、ラングミュア等温式に従った (Fig. 4)。これらの飽和吸着量 (Table 3) は、他の吸着剤との比較 (Table 5) および他の研究者ら^{1), 3), 4)}の結果に対してそんな色なく、マンガン団塊の重金属イオンの吸着剤としての有用性を示している。処理温度の異なる団塊について Cd(II) の飽和吸着量は比表面積に依存しなかった (Fig. 5, Table 4) ことから、吸着量は主に団塊表面に存在する過剰酸素量と相関関係を有することが推定された。処理温度の変化に伴う両者の変化は一致しており (Fig. 5)、明らかに重金属イオンが主に過剰酸素上に吸着することを示し、団塊の吸着能は過剰酸素の定量によって予測しうることを示した。

* 北海道大学工学部 (060 札幌市北区北 13 条西 8 丁目)

Keywords

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