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Research paper

Determination of key components and adsorption capacity of a low cost adsorbent based on sludge of drinking water treatment plant to adsorb cadmium ion in water

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ABSTRACT

A low cost adsorbent based on sludge of drinking water treatment plant (DWTP), solid waste by-product of sedimentation process in the DWTP, was studied for adsorption of cadmium ion in water. Some parameters such as dose of the adsorbent, pH of solution, and shaking time were investigated in the batch system in order to know the optimum condition and adsorption ability of the adsorbent. Artificial sludge was prepared by following the process of DWTP and the effect of humic acid extracted from the DWTP sludge was examined in order to clarify the key component and adsorption capacity of the adsorbent. This study found that humic acid and iron oxide were the key components of the adsorbent material for adsorption of cadmium ion in water. The Langmuir isotherm adsorption model was fit and the adsorption capacity of the adsorbent based on sludge of Miyamchi and Nishino DWTP for Cd(II) was 5.3 and 9.2 mg/g, respectively. The finding of this study is important for further development of a low cost adsorbent material in the near future.

1. Introduction

Pollutions with heavy metal ions have attracted public concern because of its potential damage to human health and environments. 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 (Clabeaux et al., 2011). 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, metal plating and textile (Rao et al., 2006; Wang et al., 2009). It adversely affects several important enzymes to cause bone disease and kidney damage (Manahan, 2010). 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 (Kawano et al., 1986). It is known that heavy metals such as cadmium and lead are accumulated in the human body and their influences might be found after several years. Therefore, even the low concentration of cadmium in water is still potential for human damage due to the accumulation effect.

Many methods have been developed to remove heavy metal ions in water, i.e. membrane technology, ion exchange, phytoremediation and adsorption (Namasivayam and Ranganathan, 1995). Adsorption is one of the common methods that have been widely applied for water and wastewater treatment. Activated carbon is a common adsorbent in many countries, however, it is quite expensive (Papandreou et al., 2007). The high cost of the activated carbon has inspired many researchers into the development of alternative low cost adsorbent.

Sludge from DWTP is a sort of by-products in the precipitation process using coagulant, and it is produced daily in large quantities in most municipalities worldwide. The characteristic of the DWTP sludge is influenced by the quality of the source of drinking water, a type of coagulant and the system of treatment plant. The sludge of DWTP is directly disposed to landfill or is recently used as a soil improver (Ishikawa et al., 2007). The quantity of contaminants or hazardous substances in the DWTP sludge is relatively low, since the clean water resources are preferentially used for drinking water production. Therefore, the utilization of the DWTP sludge for adsorbent material may be favorable. The studies on the reuse and recovery of the DWTP sludge for phosphorus removal have been conducted (Babatunde et al., 2011; Ishikawa et al., 2007; Razali et al., 2007; Yang et al., 2006), however, the study on the DTWP sludge as a material of adsorbent for heavy metal ions is still very limited. Aluminum, silica, iron and humic

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substances usually exist in the sludge of DWTP. Humic acid, one of the humic substances, can increase the ability of adsorbent if the surface of adsorbent was covered with humic substances to adsorb heavy metal ions such as copper and cadmium ions in water (Santoso, 2006). Namasivayam and Ranganathan (1995) mentioned that iron hydroxide produced from waste of fertilizer industry was considered as a low cost adsorbent.

The development of adsorbent using the DWTP sludge is one of potential methods in terms of cost, preparation of adsorbent, process of adsorption and removal efficiency (Hovsepyan and Bonzongo, 2009). The reuse of the sludge will give benefits, reducing the amount of solid waste from DWTP as well as producing a low cost adsorbent for removal of heavy metal ions.

The purpose of this study was to determine the key components and adsorption capacity of the DWTP sludge for adsorption of cadmium ion in water. The humic acid was extracted from the sludge according to the method of International Humic Substances Society (IHSS) (Stenven, 1994) and several artificial sludges were synthesized by following the process in DWTP in order to determine the key components due to adsorption of cadmium ion in water.

2. Materials and methods

2.1. Preparation of adsorbent and stock solutions

Adsorbents were developed by using sludge taken from Miyamachi and Nishino DWTP in Sapporo city, Hokkaido, Japan. The sludges were collected from a sludge drying bed, a part of the processes in the DWTP to dry the sludge generated from the sedimentation tank, before the disposal to a landfill. Poly-aluminum chloride (PAC) is used as a coagulant in Miyamachi and Nishino DWTP. Especially, Nishino DWTP utilizes activated carbon to adsorb metal ions and odor compounds in the raw water so that the color of the sludge from the DWTP is black, which is different from the color of the common sludge.

The sludge was washed with distilled water and dried at 100 °C for 24 h. After cooling it at room temperature, the sludge was crushed into a powder form and then sifted with a 1 mm sieve. The powdery sludge was used as the adsorbent to adsorb cadmium ion in water.

The stock and standard solution of cadmium ion (Cd^{2+}) for analysis with an atomic adsorption spectrophotometer (AAS HITACHI A-2000) were prepared with $Cd(NO_3)_2 \cdot 4H_2O$ and a pure standards solution of WAKO Pure Chemical Co (Osaka, Japan).

Based on the preliminary study by using SEM/EDS, it was shown that sludge has a similar main component with kaolin, a white clay mineral, i.e. O, Al, Si and C. Therefore, it was used as a basic material of the artificial sludge and mixed with other components such as Fe^{3+}, Mn^{2+} and humic acids. Aluminum sulfate ($Al_2(SO_4)_3$) was employed as coagulant instead of PAC used in the real drinking water treatment plant in order to form flock from kaolin. The amount of each component was adjusted according to the composition of the raw waters of DWTP. Ten grams of kaolin, 10 g of $Al_2(SO_4)_3$, 0.2 mg of Fe^{3+}, 0.05 mg of Mn^{2+} and 1.2 to 2.4 mg of humic acids were added in 1000 ml of distilled water. A jar test was employed on 150 rpm for 5 min and then followed by 40 rpm for 10 min. Then the mixed solution was rested around 30 min until the sludge was precipitated completely. The sludge was separated from the solution by decantation, dried on 100 °C for 24 h and then crushed into powder.

2.2. Characterization of adsorbent

Surface area and main components of sludge such as aluminum, silica and iron as a result of the addition of PAC were measured by a scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) (JEOL JSM-6360 LA, Japan). The amounts of carbon, hydrogen, nitrogen, sulfur, ash and oxygen in the sludge were examined by using elemental instrument (MICRO CORDER JM10, Yanaco, Japan). In order to identify the metals adsorbed in the sludge, inductively coupled plasma mass spectrometer (ICP-MS) (SPQ 6500 Seiko Instrument (SII)) was used according to the following procedure: 200 mg dried sludge was added to 3 ml of 16 M HNO_3 and then heated at 120 °C for 4 h. After cooling at room temperature, the solution was filtered using 0.45 μm of a membrane filter and then diluted to 50 ml with distilled water. This solution was then diluted 10, 20, and 50 times and analyzed by using ICP-MS.

2.3. Batch adsorption studies

In order to know the optimum adsorbent concentration corresponding to a maximum binding capacity, the adsorbent dose was varied from 1 to 20 g/L and put into 50 ml of cadmium solution with different concentrations (10, 50 and 100 mg/l). After 24 h of stirring, the solution was centrifuged on 4000 rpm for 10 min and then the concentration of Cd^{2+} was measured using atomic adsorption spectrophotometer (AAS HITACHI A-2000).

The effect of pH on the adsorption of Cd^{2+} was studied by using the solution at pH 2 to 10 with initial Cd^{2+} solutions 10, 50 and 100 mg/l. Acetic acid, HNO_3 and NaOH were utilized to adjust the desired pH values of the sample solutions. The duration of the adsorption process was 24 h with a constant stirring rate.

In order to know the influence of shaking time on adsorption capacity, the study was conducted in various shaking times from 30 to 1440 min. Shaker (EYELA CUTE MIXER CM-1000) was employed at 1000 rpm. The phase in which the adsorption capacity becomes stable was considered as an optimum shaking time and implemented for further experiments.

3. Results and discussion

3.1. Properties of adsorbent

Result of the elemental analysis is shown in Table 1. The result showed that the sludge from Nishino DWTP contained a higher amount of C (42%) than the sludge from Miyamachi (9%). The high amount of carbon in Nishino sludge was due to the addition of activated carbon in the process of drinking water treatment plant.

Based on another analysis using ICP-MS presented in Table 2, it was found that Cd concentrations in both sludges were below detection limit of the ICP-MS. The other heavy metals such as Hg and As were very low and less than the environmental standard of soil in Japan which are 0.5 mg/kg and 15 mg/kg in soil for agricultural land. The high concentration of As in some hot-spring water in Hokkaido contributes in the increase of the As concentration in some river water near the area of the hot spring (Tatsumi et al., 2006). Therefore, the high concentration of As in the sludge of Miyamchi DWTP may be influenced by the presence of hot-spring near the area.

The photograph of a scanning electron microscope of both sludge and activated carbon shown in Fig. 1 reveals the surface texture and porosity of these samples. The surface structure of the sludge of Nishino was similar to activated carbon because the Nishino drinking water treatment plant used activated carbon in their treatment plant.

Table 1
Elemental analysis of the sludge from Miyamachi and Nishino DWTP.

Element (%w/w)	Sludge	
	Miyamachi DWTP	Nishino DWTP
C	8.81	42.38
H	2.96	2.42
O	26.31	19.78
N	0.48	0.3
S	0.49	0.29
Ash	61.44	35.12