Environmentally Friendly Adsorbents

Eko Siswoyo, Yingjie Dai, Masanobu Mori, Nobuhiko Wada, and Hideyuki Itabashi

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E. Siswoyo (✉)
Department of Environmental Engineering, Universitas Islam Indonesia, Yogyakarta, Indonesia
e-mail: eko_siswoyo@uii.ac.id

Y. Dai
College of Resources and Environment, Northeast Agricultural University, Harbin, China
e-mail: yingjiedai@neau.edu.cn

M. Mori
Faculty of Science and Technology, Kochi University, Kochi, Japan
e-mail: mori@kochi-u.ac.jp

N. Wada and H. Itabashi
Graduate School of Science and Technology, Gunma University, Kiryu, Gunma, Japan
e-mail: t15807009@gunma-u.ac.jp; itabashi@gunma-u.ac.jp

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Abstract Contamination of organic and inorganic substances in water, such as heavy metal ions and dyes, is found in almost every country, including developed and developing countries. The presence of these pollutants in the environment frequently resulted in negative effects on the human body and also ecosystem. So far, many technologies to remove pollutants, filtration, precipitation, ion exchange, phytoremediation, adsorption, and so on have been developed. Among these, adsorption is regarded as one of the most promising methods due to its high adsorption capacity and easiness of operation, and then many kinds of adsorbent materials have been researched. The most common adsorbent material used in many places is activated carbon; however, this adsorbent is quite expensive. This chapter introduces some environmentally friendly adsorbents, which are low-cost, safe, and non-harmful adsorbents based on natural products and solid waste materials. Especially, natural materials like plants, solid waste, and agricultural waste investigated in our laboratories are described here. Most of them have the large surface area and some useful functional groups for adsorbing, and then they originally have the high adsorption capacity for pollutants. The treatment of the adsorbents with chemicals like citric acid and phosphoric acid improved their adsorption capacities for metal ions. Some agricultural waste, such as konjac glucomannan, spent coffee grounds, and biochar, have the ability to remove organic compounds and dyes from water. Furthermore, it is introduced that the fermented bark amendment from the thinning of cedar can suppress the uptake of cadmium ion in rice.

Keywords Biochar, Drinking water treatment sludge, Environmentally friendly adsorbent, Fermented bark, Konjac glucomannan, Platanus leaf, Spent coffee ground

1 Introduction

Many water and wastewater treatment technologies have been developed in order to solve the contamination of heavy metal, including membrane filter [1], bio-sorption [2], neutralization [3], phytoremediation [4], ion exchange [5], precipitation [6], and adsorption [7]. Adsorption is known as one of the most effective for water and wastewater treatment, especially activated carbon is frequently employed. It is considered as the most common long-term adsorbent and has been used for the removal of many organic pollutants and also metal ions in water. Due to its large surface area and the presence of certain functional groups that are significant for metal binding, it has the high adsorption ability even for metal ions. However, its comparatively high cost puts it at a disadvantage for other sorts of adsorbents, such as biosorbents [8, 9]. Therefore, the development of low-cost and environmentally friendly adsorbent has been required. The term "environmentally friendly" literally means friendly for the earth and not harmful to the environment. Then environmentally friendly adsorbent is the safe and not-harmful adsorbent, in a narrow sense which is prepared from natural or waste materials and useful for removing pollutants

Table 1 Classification of the environmentally friendly adsorbents

Category	Adsorbent materials	Target	Characteristic	References
Natural material	Scallop shell	Metal ions	The large surface area	[10]
	Freshwater snail shell	Metal ions	The main functional groups responsible for chelation are OH, C=O, C=C, and C–C	[11]
Plant	Platanus leaf	Cadmium	Main element is cellulose with carboxylate group	[12]
	Eucalyptus camaldulensis	Metal ions	The thick wall structure along with a well-developed wider porosity	[9]
	Jujube	Metal ions	The irregular and inflexed surface morphology	[13]
	Auricularia auricularia	Neutral red (NR)	Has –OH/NH, –COH, C=C, –CO, and benzene ring skeletons	[14]
	Mango peel waste	Metal ions	The carboxyl and hydroxyl functional groups	[15]
Solid waste	Paper sludge	Cadmium	The phosphate functional group	[16]
	DWTP sludge	Cadmium	Main elements are Al and Si	[17]
	Coal fly ash	Metal ions	The large surface area	[8]
Agricultural waste	Konjac glucomannan	Organic compounds	Contains activate carbon	[18]
	Spent coffee ground	Metal ions and dye	The large surface area	[19, 20]
	Biochar	Tetracycline	The porous surface	[21]
	Carbon material from the combustion of forest branches	Methyl orange (MO) and methylene blue (MB)	Has a partial tubular or rope-like structure	[22]
	Bark	Cadmium uptake in rice	Consists of natural polymers, such as lignin and cellulose	[23]

from the environment. The environmentally friendly adsorbents are classified into several kinds as shown in Table 1.

The environmentally friendly adsorbents classified in Table 1 have a high ability in removing contaminants including heavy metal ions and organic substances from water and soil. The presence of some functional groups, porous structure, and large surface area of these adsorbents plays important role in removing the target contaminants. Considering the availability and cost performance of the environmentally friendly adsorbent, the development of these adsorbent materials is very promising for environmental remediation in the near future.

2 Adsorbent Based on Solid Waste Materials

Recently, the development of adsorbent for the removal of metal ions based on solid waste materials has been studied by many researchers because of its high ability in removing some metal ions, low cost in preparation, and easiness in getting these materials. Sludge from drinking water treatment plant and from paper industry and some kinds of biomass such as leaves and seeds have their potency to be utilized as environmentally friendly and low-cost adsorbent. The characteristic of each adsorbent material is so interesting to be examined to understand the adsorption mechanism and its adsorption capacity for the removal of metal ions in water. In this section, some adsorbents based on solid waste materials that we have developed are introduced.

2.1 Paper Sludge for Removal of Cadmium Ion in Water

The amount of pulp and paper production is rising every year in many countries around the world and the production process has still problems with the appearance of solid waste. The top ten pulp producers are the USA, China, Canada, Brazil, Sweden, Finland, Japan, Russia, Indonesia, and Chile. Approximately 40–50 kg of sludge (dry) is generated by the processing of 1 ton of paper at a paper mill, of which approximately 70% is primary sludge and 30% secondary sludge [24]. Japan's paper industry remains to produce a large paper sludge as solid waste material that is disposed of in landfills. The amount of paper sludge disposed of by the Japanese paper industry in landfills is about five million tons per year [25]. The treatment of paper sludge in landfill or incineration is expensive and may create newly environmental problems such as the elution of heavy metals and pollution with dioxins. The use of paper sludge as a raw adsorbent material has many benefits, decreasing the amount of solid waste and treatment costs and providing a low-cost adsorbent for the removal of heavy metals. Paper sludge as an adsorbent medium has a high capacity to remove metal ions from water [16].

The characteristics of the paper sludge are defined on the basis of SEM, surface analyzer (BET), and FTIR data. The surface structure of the paper sludge before and after treatment with phosphoric acid as a modifier for the surface is shown in Fig. 1. It is quite difficult to find out the effect of activation with some chemicals on adsorbent materials only by using SEM image because the images of these adsorbents are almost similar. However, from the image of both adsorbents we can state that the adsorbent becomes more porous after the treatment using phosphoric acid. The result of surface analyzer test based on BET strengthened the data of SEM. The surface area of raw paper sludge was 50 m^2/g and then increased into 83.5 m^2/g after treatment with phosphoric acid maybe because of the ability of this acid in releasing dirty particles from the paper sludge.

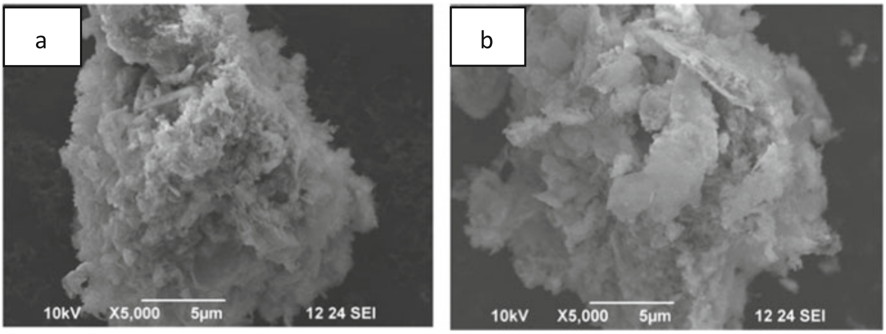


Fig. 1 SEM images of paper sludge before (**a**) and after treatment with H_3PO_4 (**b**)

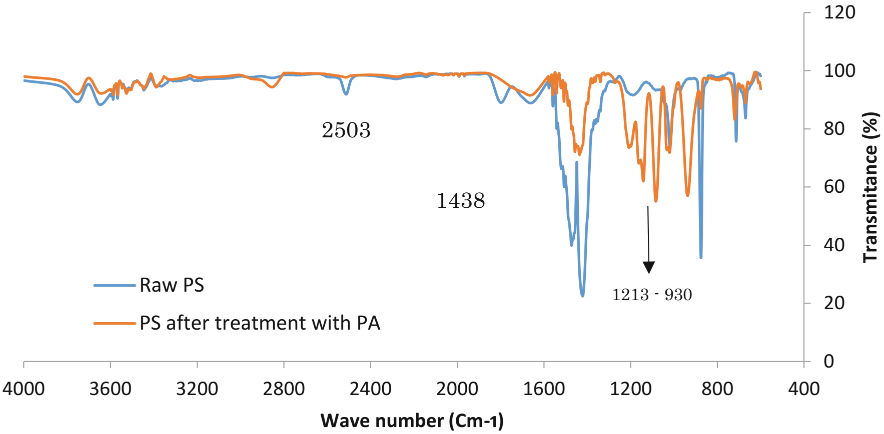


Fig. 2 FTIR spectra of paper sludge (PS) before and after treatment with H_3PO_4

Paper sludge has some functional groups which are important to bind metal ions. Based on the data of FTIR spectra as shown in Fig. 2, we can see that the activated paper sludge has some new peaks between 930 and 1,213 cm^{-1} and they indicate the presence of the functional groups generated by the activation process with phosphoric acid. These functional groups have an important role in binding some metal ion such as cadmium in water. Therefore, the adsorption capacity increased significantly after the modification with phosphoric acid.

Figure 3 clearly shows that the impregnation ratio during the activation process influences the performance of the adsorbent for removing metal ion in water. The impregnation ratio is the ratio between adsorbent material and the chemicals used for the activation (weight/weight). The best impregnation ratio for the removal of cadmium by using phosphoric acid is 0.5 (paper sludge: phosphoric acid = 50%: 50% of weight). The highest adsorption removal for 10 mg/L of cadmium ion by using 200 mg of the activated adsorbent at pH 6.0 was 97.74%.

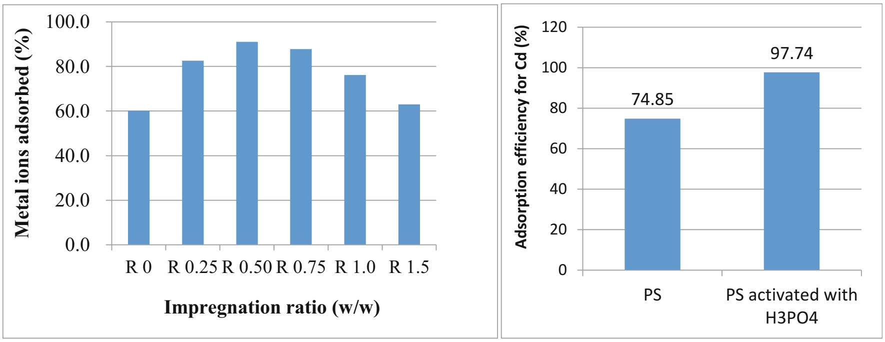


Fig. 3 The effect of the treatment with H_3PO_4 on Cd removal by the paper sludge

2.2 Adsorbent Based on Drinking Water Treatment Plant Sludge

Drinking water treatment plant sludge (DWTPS) is a by-product of the precipitation process that uses coagulant, and it is produced in large quantities in most municipalities around the world on a daily basis. In the developed countries, this sludge is mostly disposed as solid waste to the landfill, however, in some developing countries, it is discharged into the river because of the high processing cost at landfill. The quality of the drinking water source, the type of coagulant, and the treatment plant system all have an impact on the property of the DWTP sludge. If water sources for drinking water would be contaminated, DWTPS could contain some contaminants in it. However, ordinary clean water sources are preferred for drinking water production, and then the levels of contaminants or hazardous substances in DWTP sludge are low enough to use it as an adsorbent. As a result, using DWTP sludge as an adsorbent material may be feasible.

Adsorption of metal ion on the adsorbent is influenced by some factors, and among them pH of the solution is one of the most important factors [17, 26]. The surface charge of the adsorbent is strongly influenced by the pH of the solution. There are several ways how the initial pH of the solution can influence the adsorption capacity: (1) the electrostatic repulsion and affinity between adsorbent and adsorbate [8, 27, 28]; (2) the process of ion exchange between adsorbent and adsorbate [15, 29]; and (3) the distribution of metal species, such as soluble or insoluble and cationic or anionic [26, 30]. In extreme acidic conditions the surface of the adsorbent has dominantly positive charges, and therefore the adsorbent has the low adsorption capacity for metal ion with positive charge such as cadmium (Cd^{2+}), lead (Pb^{2+}), and cupper (Cu^{2+}) because of the electrostatic repulsion between the adsorbent and adsorbate.

The results of the adsorption study using the DWTPS for removal of Cd^{2+} at different pH are shown in Fig. 4. For all types of the adsorbents (powdery raw sludge, powdery treated sludge, treated sludge encapsulated in alginate gel and

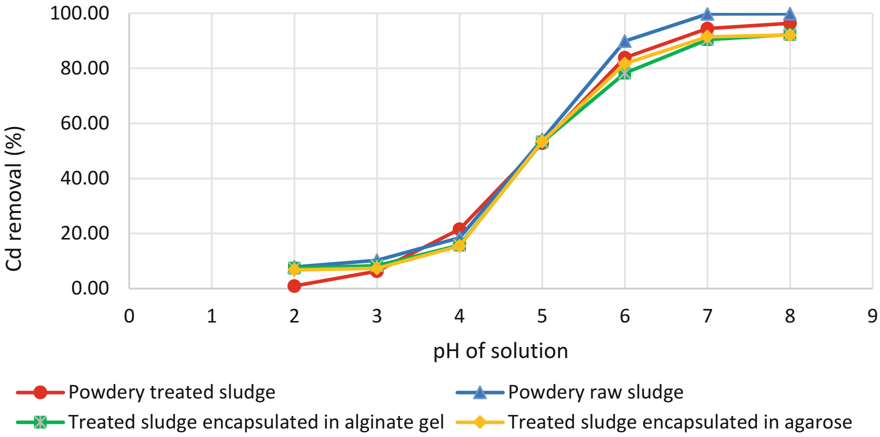


Fig. 4 The influence of pH solution on the adsorption of Cd ion in water

treated sludge encapsulated in agarose adsorbents), the removal efficiency increased as pH of the solution increased. Under pH 5, the adsorbent has positive charges, therefore it has a low cadmium adsorption removal due to the electrostatic repulsion between the adsorbent and cadmium ion. The favorable pH for cadmium removal was 6–7. The adsorption removal of cadmium becomes constant around pH 8 and cadmium ion in water will be precipitated at higher pH than pH 8.2 [17].

The adsorption potential of the adsorbent for metal ions can be evaluated using the Langmuir isotherm model. The Langmuir isotherm model was used to achieve the constant balance of the adsorption equilibrium by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{1}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of metal ion adsorbed at the equilibrium (mg/g), q_m and K_L are the Langmuir isotherm constants related to the adsorption capability and adsorption energy, respectively. From the above equation, a plot of C_e/q_e versus Ce will be employed to calculate the values of q_m and K_L as the tangent of the estimated straight line and its vertical axis intercept.

Beside Langmuir isotherm model, the Freundlich isotherm model can also be used to evaluate the isotherm process of adsorption. The equation of this model is:

$$q_e = K_f \, {C_e}^{1/n} \tag{2}$$

$$\mathrm{Log}\ (q_e) = \log\ (K_f) + 1/n\ \log\ (C_e) \tag{3}$$

where q_e is the amount of metal ion adsorbed at the equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), and K_f and n are the constants. We can determine the amount of K_f and n by plotting between log C_e and log q_e.

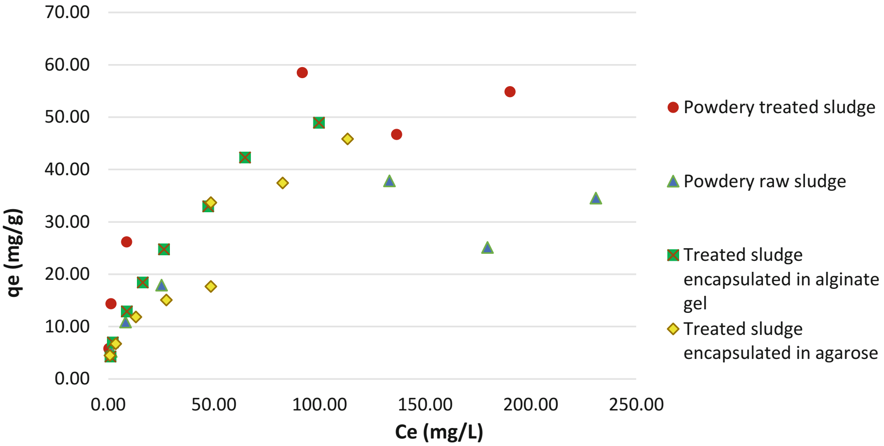


Fig. 5 Langmuir adsorption isotherm for Cd removal

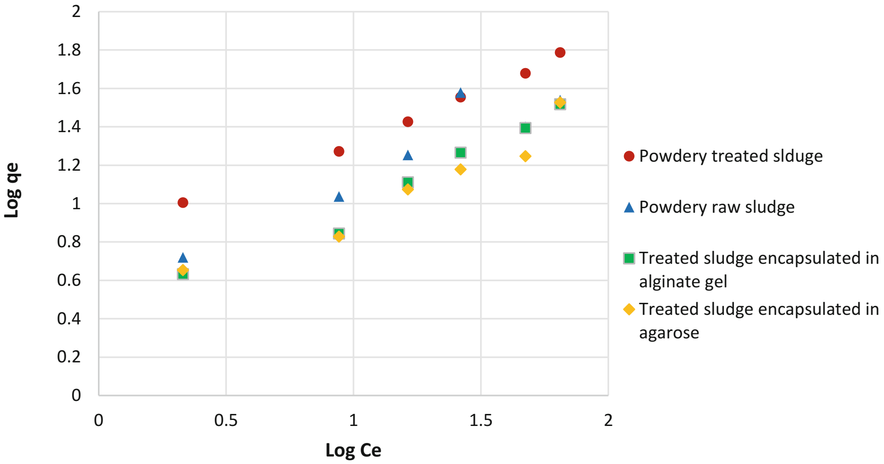
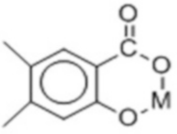


Fig. 6 Freundlich adsorption isotherm for Cd removal

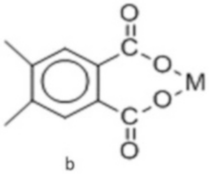
Figures 5 and 6 show the Langmuir and Freundlich isotherms of those adsorbents based on sludge of drinking water treatment plant for the removal of cadmium ion in water.

Most drinking water treatment plants in many countries use river water as their raw water because of its high quality, the stable supply in quantity and continuity. Compared to other water sources, river water is better in terms of the above criteria. In order to use the river water as the raw water for the drinking water treatment plant (by public water company) sustainably, the government needs to protect the river from contamination. The turbidity of raw water is one of the key parameters to be treated in the sedimentation tank. Most public water providers use some coagulants to minimize the turbidity to meet drinking water requirements. The condition of the raw water and the type of coagulant affected the quality of the sludge from the sedimentation tank. Humic substances (natural organic matters) and iron hydroxide (from iron including in the coagulant) are commonly present in the DWTPS. Both components play an important role in the adsorption of metal ions by using an adsorbent obtained from a drinking water treatment facility.

The possible binding mechanism of cadmium ion with the DWTPS is suggested by considering the functional groups in the structure of humic substances: (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups, and (c) by complexation with a carboxyl group.



a



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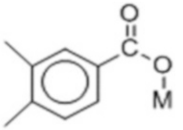


c

The presence of iron hydroxide as explained in the above paragraph also is suggested to have an important role in adsorption of metal ions. The possible mechanisms of adsorption by iron hydroxide are shown as follows.

$$\mathrm{RO^- + M^{2+} \rightarrow ROM^+}$$

$$\mathrm{RO^- + MOH^+ \rightarrow ROMOH}$$

$$\mathrm{ROH + M^{2+} \rightarrow ROM^+ + H^+}$$

$$\mathrm{ROH + MOH^+ \rightarrow ROMOH + H^+}$$

where $\mathrm{RO^-}$ denotes a negatively charged surface of iron hydroxide, ROH denotes a neutral surface, and M denotes metal such as Cd. The mechanism of cadmium adsorption by using DWTP sludge is investigated by preparing the sludge similar to the DWTPS artificially. The artificial sludge were constructed by using the following process, in which kaolin, a white clay mineral, was used as the sludge's basic material and then combined with other elements such as Fe(III), Mn(II), and humic acid. In order to make a flock from these components, aluminium sulfate ($Al_2(SO_4)_3$) was used instead of coagulant (PAC) in the real drinking water treatment plant. Several types of artificial sludge were generated using various types and amounts of chemicals in order to search for the key constituents of the adsorbent for cadmium ion adsorption in solution. The amounts of each substance were determined by referring to the actual DWTPS as follows. In 1,000 mL of distilled water, 10 g of kaolin, 10 g of $Al_2(SO_4)_3$, 0.2 mg of Fe(III), 0.05 mg of Mn(II), and 1.2–2.4 mg of humic acid were added. A jar test using the mixed solution containing those components was carried out at 150 rpm for 5 min, and followed by a 10-min jar test at 40 rpm. The mixed solution was then rested for around 30 min until

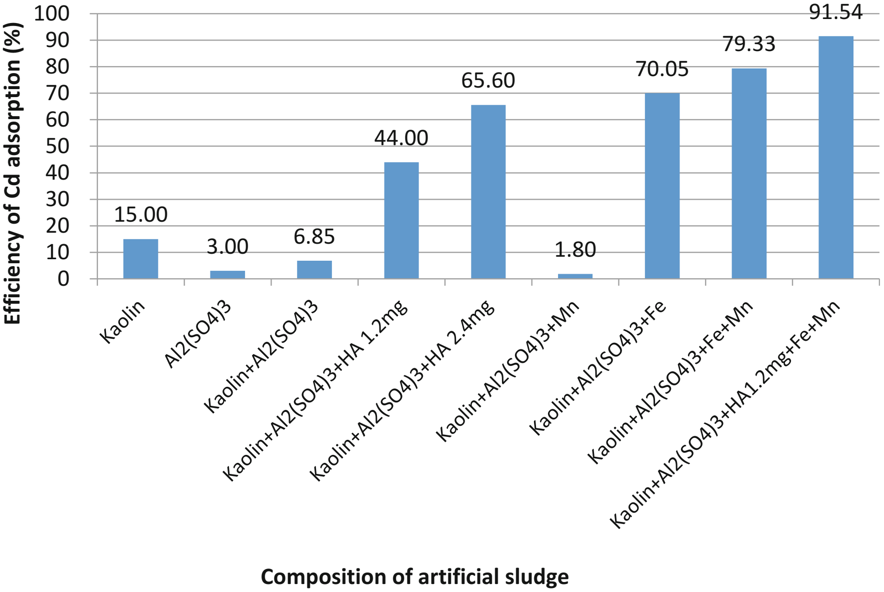


Fig. 7 Cd removal of some artificial sludge

precipitation occurred entirely to form sediment. According to the original sludge treatment, the sediment was removed from the solution by decantation, dried at 100°C for 24 h, and then crushed into powder. The amounts of humic substances and iron hydroxide are adjusted and then some kinds of the prepared artificial sludge were applied to the removal of cadmium ion in water. The results of the cadmium removal are shown in Fig. 7. The artificial sludge with the higher amount of humic substances and iron hydroxide showed the higher adsorption capacity, and therefore two components of the artificial sludge are suggested to play the most important role in the adsorption process [17].

2.3 *Adsorbent Based on Platanus Leaf*

The Platanus tree is common in Japan and many other Northern Hemisphere countries, where it is used as an ornamental and roadside tree. In Japan, the fall leaves of this tree are typically collected and discarded as garbage. The leaf of this tree has the potential to be a low-cost and environmentally friendly adsorbent material. However, the research on the use of the leaf of the Platanus tree as an adsorbent material is still limited. It is known that the modification of plant based adsorbents with citric acid is effective to improve the adsorbing ability for metal ions [31]. Therefore, in this section, the adsorbing ability of Platanus leaf modified with citric acid is introduced.

Table 2 The main elements of Platanus leaf before and after citric acid modification

	Type of adsorbent	
Element (%w/w)	Raw adsorbent	Citric acid modified adsorbent
Carbon (C)	49.98	49.90
Hydrogen (H)	5.78	6.14
Oxygen (O)	23.03	40.22
Nitrogen (N)	1.10	1.95
Ash	20.11	1.79

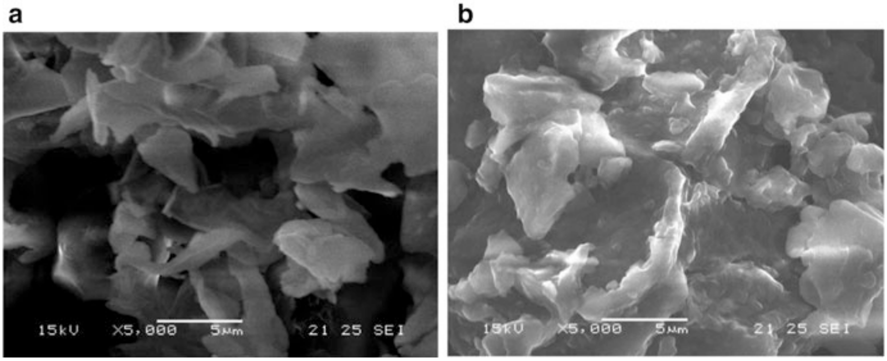


Fig. 8 SEM images of Platanus leaf before (**a**) and after treatment (**b**) with citric acid

Table 2 shows the contents of principal elements of Platanus leaf before and after the treatment with citric acid. The content of oxygen (O) increased significantly after the treatment with citric acid because carboxyl groups (COOH) of citric acid are probably bound to the leaf by the reaction shown later. The presence of the carboxyl group in the adsorbent material is important for the adsorption of metal ions due to the complex formation.

The micromorphology of Platanus leaf before and after the treatment with citric acid can be seen in Fig. 8. The surface of Platanus leaf after treatment with citric acid seems to be brighter and more porous compared to that of the raw Platanus leaf. The increase in the porosity is also proved by the data obtained from the BET analysis. The surface area and pore volume of the raw leaf and treated leaf are 19 $m^2\ g^{-1}$ and 4 $cm^3\ g^{-1}$, and 32 $m^2\ g^{-1}$ and 7 $cm^3\ g^{-1}$, respectively. The surface area and pore volume are important to improve the adsorption capacity of the adsorbent, and therefore the larger surface area and pore volume of the adsorbent are, the higher adsorption capacity the adsorbent has usually.

The concentration of carboxylic acid of adsorbent materials was determined by titration method using NaOH as a titrant. The concentration of carboxylic acid of Platanus leaf before and after treatment with citric acid were 0.26 and 1.4 mmol/g,

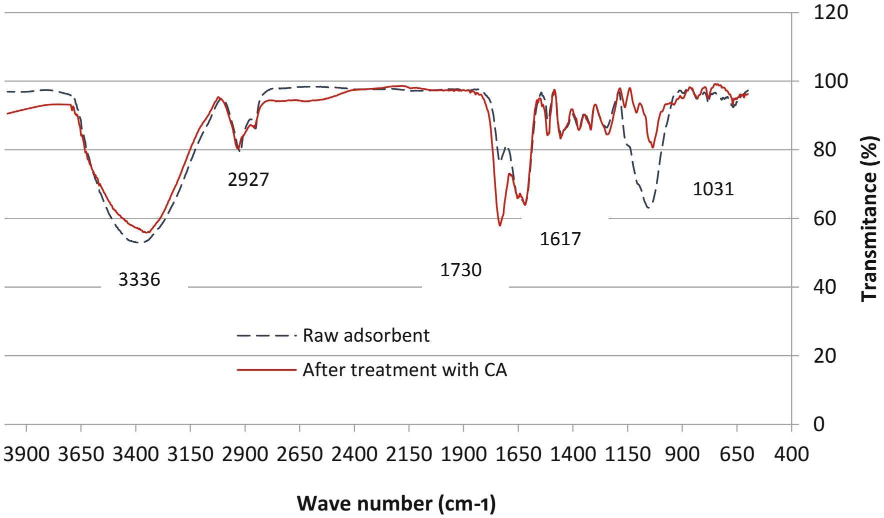


Fig. 9 FTIR spectra of Platanus leaf before (**a**) and after treatment (**b**) with citric acid

respectively. It was clear that the amount of carboxylic acid increased almost five times as the effect of treatment with citric acid.

The concentration of carboxylic acid in citric acid used for activation was 15.6 mmol/g and few parts of them (about 1.14 mmol/g) were bonded with Platanus leaf. Figure 10 presented the possible mechanism of the modification for Platanus leaf treated with citric acid. Cellulose, a main component of Platanus leaf, was bonded with carboxylic acid of citric acid to form the citric acid modified cellulose that has some carboxyl groups, which is important for metals binding. As shown in Fig. 9, the strong absorption band at 1,730 cm^{-1} of the modified adsorbent indicates the presence of carboxyl groups in Platanus leaf as the result of citric acid modification.

Powdery adsorbent has a larger surface area than granular adsorbent. However, the separation of the powdery adsorbent after adsorption process is difficult in comparison with granular adsorbent. Therefore, granular adsorbent is suitable for the application to real samples. The encapsulation of powdery adsorbent into alginate or agarose gel sometimes gives a solution for the separation of the adsorbent after adsorption. In this study, the adsorbent treated with citric acid was encapsulated in agarose gel. The adsorption capacities of the adsorbent before and after encapsulation are shown in Table 3. The adsorption capacity decreased largely after the encapsulation because of covering of the adsorbing sites with the gel. However, the encapsulated adsorbent still has enough adsorption capacity in comparison with that of the untreated adsorbent.

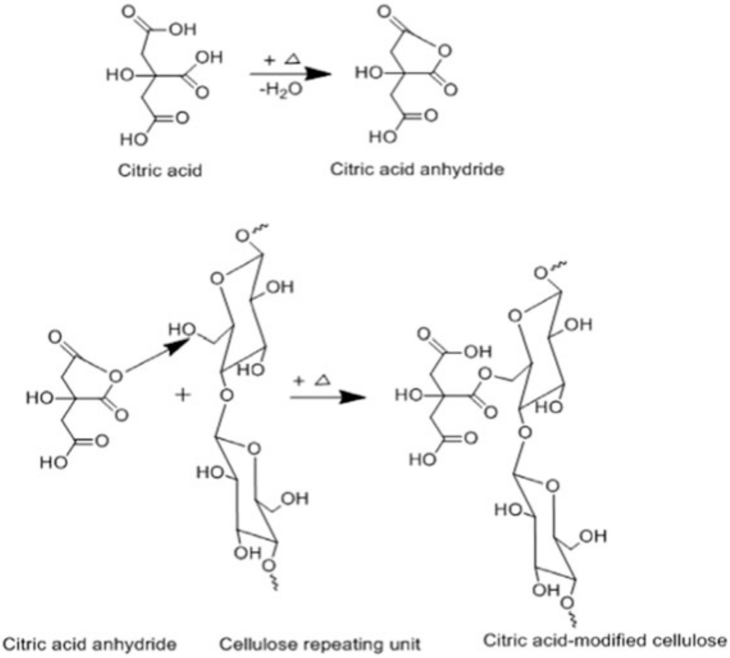


Fig. 10 Possible mechanism of modification for Platanus leaf with citric acid

Table 3 The adsorption capacities of Platanus leaf before and after encapsulation

Adsorbent	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (l/mg)	R^2	K_f	n	R^2
Raw Platanus	3.69	6.29	0.978	4.403	2.61	0.972
Platanus treated with CA	15.31	1.36	0.939	6.725	3.27	0.993
Platanus treated and encapsulated in agarose	6.89	2.48	0.948	4.709	2.64	0.991

The basic features of the Langmuir isotherm can be described by the dimensionless separation factor constant or by the equilibrium parameter R_L defined as: $R_L = 1/(1 + K_L C_0)$, where K_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in the solution. The R_L value shows the shape of the isotherm:

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

The R_L value between 0 and 1 is favorable for adsorption [32]. The R_L values of raw, treated (powdery), and encapsulated adsorbents for 10 mg/L of cadmium ion are 0.016, 0.069, and 0.039, respectively. It was proved that Platanus leaf-based adsorbents are favorable for the removal of cadmium ion in water.

2.4 Conclusion

The adsorbents based on paper sludge, drinking water treatment plant sludge, and leaf of Platanus have good performance in reducing cadmium ion in water. The presence of some functional groups, humic acid, and iron (for DWTPS) are considered as the major elements for metal adsorption. These developed adsorbents are suggested to be the low-cost and environmentally friendly adsorbents for the removal of heavy metal ions in water.

3 Agricultural Products and Waste-Based Absorbents

There have been many kinds of the adsorbent that can effectively adsorb harmful and toxic substances in the environments. Moreover, with the vigorous development of environmental protection technologies, many new adsorbents have emerged in an endless stream. For the application of these adsorbents to the actual polluted sites, adsorbents should be low cost, easy to obtain, and environment-friendly in addition of the conventional functions like the high capacity and selectivity. Especially, among agricultural products and wastes, there are many candidates for the adsorbents having these properties, which illustrate significant benefits in the environmental field, and some of them surpass the traditional adsorbents. In this section, the author’s recent researches on the development of the adsorbents based on agricultural products and waste are introduced. Five kinds of the adsorbents developed by authors, konjac glucomannan gel embedded with activated carbon, spent coffee ground, *Auricularia auricularia*, biochar and carbon material, are described.

3.1 Konjac Glucomannan Gel Embedded with Activated Carbon

Konjac plant is grown in some Asian countries for its edible use. Konjac glucomannan (KGM) is a high-molecular weight water-soluble nonionic natural polysaccharide isolated from the konjac plants, which is nontoxic and low cost, and the chemical structure is shown in Fig. 11 [33]. KGM gel (KGMG) is formed by heating a KGM solution in the presence of alkali compound or higher amount of neutral salt [34]. In the food industry of China and Japan [35–37], KGMG has been used widely as a non-caloric health-care food. The KGM itself has a low adsorption

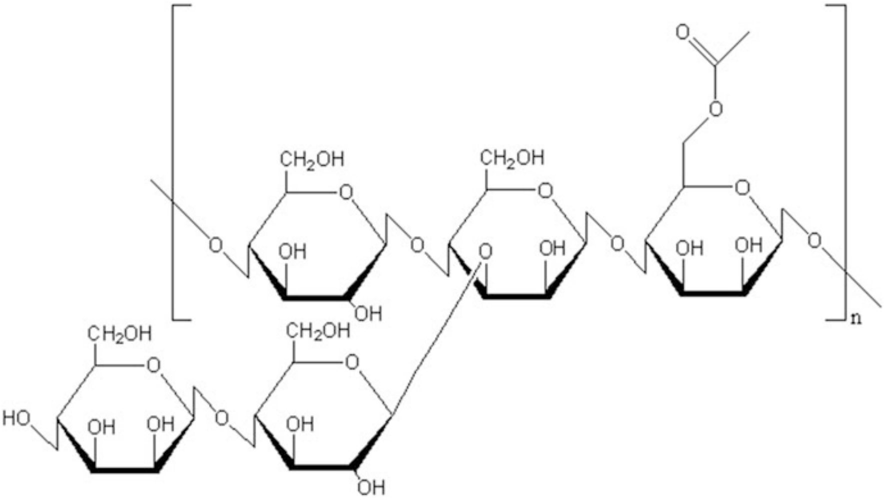


Fig. 11 Chemical structure of konjac glucomannan (KGM) [32]

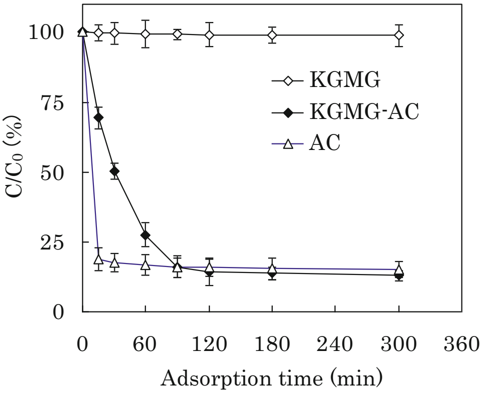


Fig. 12 The removal ratio of nitrobenzene (NB) as a function of time using AC(10 mg), KGMG (1 g) and KGMG-AC(1 g containing 10 mg AC)

ability, but can act as a carrier for the adsorbent by the encapsulation of the adsorbent like activated carbon with the KGM's gel network structure (KGMG-AC). The encapsulation of adsorbent with the gel network can make only small molecules participate in the adsorption process but block macromolecules like humic substances as pointed out in the study using alginate gel beads by Fugetsu et al. [38]. Therefore, it can improve the selectivity of adsorption and consequently extend the lifetime of the adsorbent.

The experimental results using the KGMG-AC showed that the KGMG-AC adsorbed NB well, slightly better than AC itself as shown in Fig. 12. Some organic dyes such as Methylene Blue (MB) and Rose Bengal (RB) in solution could be removed by KGMG-AC. Humic substances play an important role in supplying nutriments to plants and microbial organisms and also in maintaining the crumb structure of soil. The use of AC to remove pollutants in agriculture water sometimes leads to the removal of precious humic substances. Therefore, we attempted to avoid the adsorption of humic acid by the encapsulation of AC with KGMG.

100 mg/L humic acid solution was shaken with 10 mg of AC or 1 g KGMG containing 10 mg AC for 5 h at 25°C. As a result, 47% of humic acid in the solution adsorbed on AC, however, it is noteworthy that humic acid did not adsorb at all KGMG-AC. The gel structure of KGM around the AC might suppress the transport of humic acid to the AC entrapped within the KGMG. It shows that KGMG-AC has the potential for the selective removal of agricultural chemicals from the wastewater [18].

In conclusion, KGMG-AC prepared from a safe food processing material showed the high efficiency in the adsorption of some organic contaminants, slightly higher than that of AC itself. More importantly, it provided the possibility of selective adsorption for small molecules avoiding the adsorption of large molecules such as humic substances. Consequently, KGMG-AC will be a complete safe, low-cost, and environment-friendly adsorbent.

3.2 Spent Coffee Ground

Coffee is one of the most consumed beverages in the world. According to the latest International Coffee Organization (ICO) statistics, global coffee consumption for the year 2019–2020 has reached 10 billion kg [39], which cause a release of a notable amount of solid and liquid residues. About 90% in weight of coffee berries is discarded during manufacturing as agricultural waste and by-products. Spent coffee ground (SCG) is a waste residue from the ground coffee beans after extracting them with hot water and the porous structure of the SCG can act as the adsorbing sites. The dry SCG has been used for the removal of the moisture and smell in a refrigerator and room. In this study, the ability of the SCG to absorb tetracycline (TC) in water was investigated. TC is widely used in aquaculture as the antibiotics. Since not degradable easily in environment, it stays for a long time in environment and has a possibility to affect the ecosystem. In this section, we introduce the removal of TC with the SCG as an adsorbent. In this study, two kinds of the SCG were used; SCG-1 produced from coffee Arabica beans of Hainan Province of China and SCG-2 produced from coffee Arabica beans of Yunnan Province of China.

It can be retrieved from Fig. 13 that the adsorption reaction reached equilibrium quickly within about 20 min. At the initial stage of adsorption, the removal ratio of TC was high, and the adsorption ratio slowed down over time until the adsorption equilibrium reached. The pseudo-first-order model and the pseudo-second-order model were used to analyze the kinetic experiment data, the R^2 of pseudo-second-order had a higher degree of fitting compared the correlation coefficients of pseudo-first-order with that of pseudo-second-order kinetic. Therefore, it was concluded that

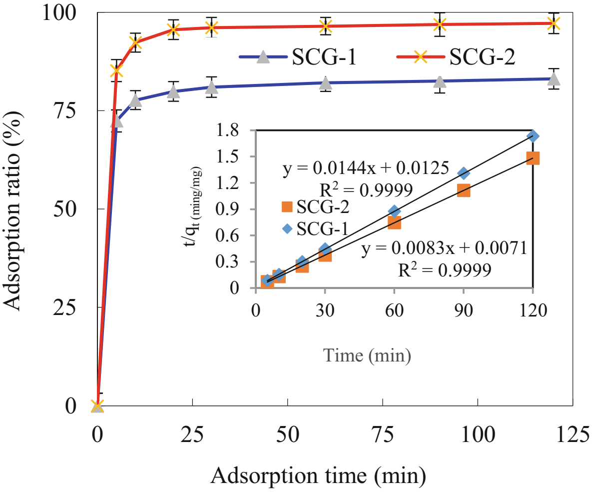


Fig. 13 Effect of adsorption time and Pseudo-second-order kinetic plots of TC by SCG-1 and SCG-2

the adsorption of TC by the SCGs progresses according to the pseudo-second-order model.

Although the BET surface area of SCG-1 (451 m^2/g) was slightly larger than that of SCG-2 (419 m^2/g), the adsorption equilibrium constant of TC by SCG-2 was almost twice as high as that of SCG-1. This indicated that the adsorption capacity of SCG-2 to TC depended mainly on the chemical properties of the surface, rather than the BET surface area [19, 20, 40]. The SCG-2 surface has a large amount of oxygen-containing functional groups in which the carboxyl group, the lactone group, and the phenol group can form a hydrogen bond on the TC molecules with the hydroxyl groups of C10 and C12 (see Fig. 14) [41]. The adsorption mechanism is through the hydrogen bond, and also the π-π interaction occurs at the interface between the TC molecule and the SCG. The results showed that second-hand coffee grounds had a great potential to be an inexpensive alternative adsorbent for tetracycline removal in wastewater treatment.

3.3 *Auricularia Auricularia*

In China's textile mills, as the working environment is full of cotton wadding, the factory often distributes fungus (such as *Auricularia auricularia*) free of charge. Because the colloid of *Auricularia auricular*(*AA*) has strong adsorption capacity, it can adsorb and gather the dust and dregs remaining in the human digestive system and discharge them out of the body. It has the function of cleaning the stomach. Based on this fact, we came up with the idea of using *AA* in dye removal. *AA,* one of the four most important cultivated edible fungi in the world, is nutrient-rich and has pharmacological functions. *AA* grows on the rot and is like a gelatinous sheet. The

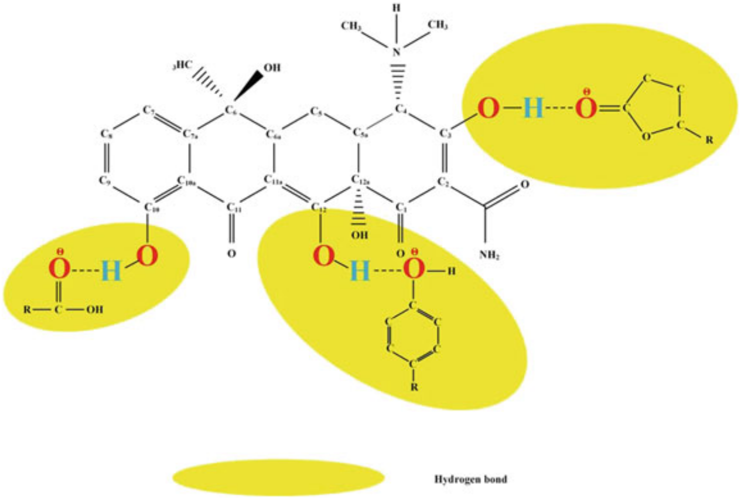


Fig. 14 The mechanism of hydrogen bonds for TC adsorption on SCGs

origin of *AA* is mainly in China, Thailand, Japan, and other countries in Asia. AA not only plays an important role in the field of food, but also can be used in the field of environment.

Two kinds of *AA, AA-Se,* and *AA-1* were selected in our studies. The content of Se in *AA-Se* was significantly higher than that of *AA-1*. As one of the essential micronutrients for humans and animals, Se is involved in the synthesis of more than 30 proteins and enzymes in mammals. Selenium deficiency can cause a variety of diseases in human body. By eating selenium enriched *AA*, we can supplement the selenium needed by human body. The results of the adsorption experiments showed that the *AA-Se* adsorbed Neutral Red (NR) better than *AA-1*. After *AA-1* adsorbed NR, there was no change in the type of functional group, and only the position of the absorption peak of some functional groups changed. Figure 15 shows that the functional groups of *AA-Se* mainly include 3,418.81 cm^{-1} (–OH functional group), 2,926.18 cm^{-1} (lipid CH functional group), 1,735.78 cm^{-1} (–COH), and 1,655.06 cm^{-1} (C=O stretching or aromatic C=C and C=O/C=C stretching), 1,560.44 cm^{-1} (secondary amine group), 1,377.69 cm^{-1} (CH bending, symmetric bending of –CH), 1,254.48 cm^{-1} (CN. stretching)), 1,064.40 cm^{-1} (COH stretching), 605.45 cm^{-1} (Fe–O) [42, 43]. After adsorption of NR, some functional groups of *AA-Se* shifted or decreased. These results suggest that the –OH/NH, –COH, C=C, –CO, and benzene ring skeletons in *AA-Se* participate in the reaction with NR.

The adsorption mechanism diagram is shown in Fig. 16 [14]. The adsorption isotherm results showed that the adsorption of NR on *AA-1* and *AA-Se* was based on electrostatic adsorption. FTIR analysis showed that the functional groups in *AA-1* and *AA-Se* played a key role in NR adsorption, including aromatic skeleton vibration, C–H, C–O and Si–O–Si groups through π–π stacking and hydrogen bonding,

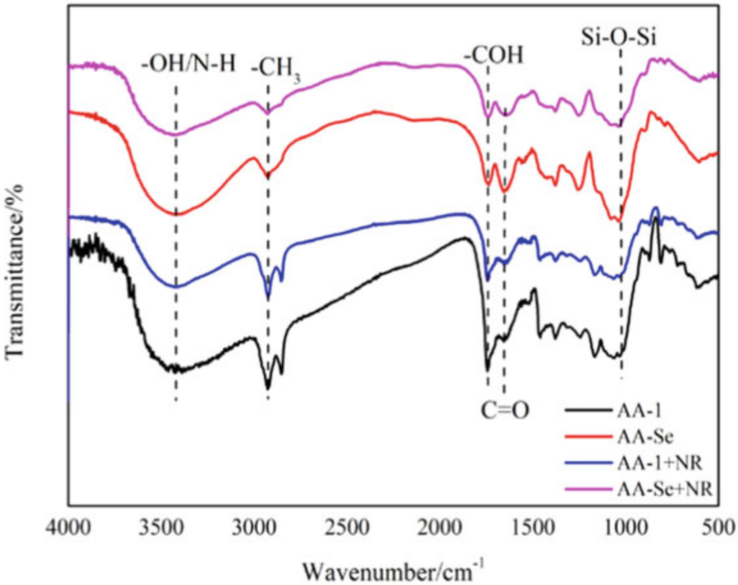


Fig. 15 FTIR spectra of AA-1 and AA-Se

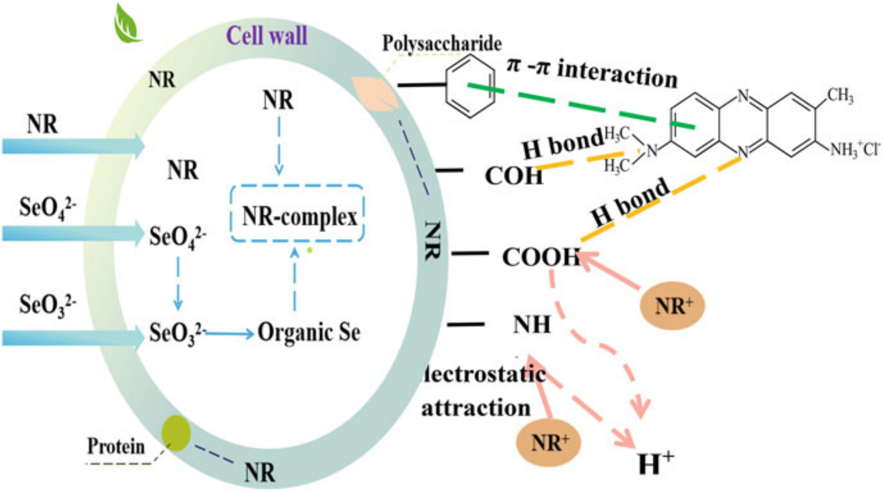


Fig. 16 Possible adsorption mechanism of NR on AA-1 and AA-Se

etc. The aromatic benzene rings of *AA-1* and *AA-Se* easily form π–π stacking with the benzene ring of NR. In addition, the chemisorption mechanism plays an important role in the adsorption of NR by *AA-1* and *AA-Se*. The mechanism involved in chemisorption is the formation of covalent bonds and ion exchange, and it is speculated that NR may cooperate with proteins and polysaccharides on the cell wall of the adsorbent to immobilize NR on the cell wall. The experimental data also speculate that NR can be removed by the above oxidation-reduction reaction.

AA is a nontoxic and harmless food material, which can effectively adsorb some chemical dyes. The *AAs are* an environmentally friendly adsorbent with low cost and easy to obtain.

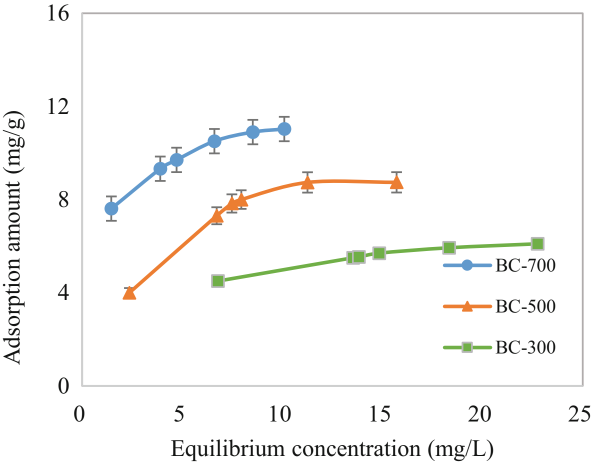
3.4 Biochar from AA *Dregs*

Biochar (BC) is a widely used adsorbent, because of its cost efficiency and adsorption properties [44]. The methods used for preparing raw materials to obtain BC are important, where the raw materials should not pollute the environment as well as being ready and available [45]. BC has a wide range of sources, such as Pinus taeda, rice husk, sawdust, tires, Fargesia leaves, and waste *Auricularia auricula* (*AA*) dregs.

AA dregs are a by-product of the edible *AA* industry, comprising a mixture of wood chips, wheat bran, corncob granules, lime and gypsum, which are used to cultivate *AA*. After bagging the mixture, it is sterilized at 100°C for 12 h, before inoculating the raw *AA*. The *AA* dregs are usually disposed of after harvesting the *AA*. China is the largest producer of edible *AA* with an annual output 22.6 million tons, which accounts for more than 75% of the total production [46]. Previous studies have showed that the production of 1 kg of edible *AA* generates 5 kg of waste *AA* dregs [47].

Waste *AA* dregs can be utilized as raw materials to produce BC for removing tetracycline (TC) from aqueous solutions in order to develop a cheap and readily available adsorbent. During the preparation process of BC from waste *AA* dregs, three different pyrolysis temperatures comprising 300, 500, and 700°C were tested. The results of adsorption isotherms obtained for the BCs are shown in Fig. 17 [21].

Fig. 17 Adsorption isotherm curves obtained for TC on BC-300, BC-500, and BC-700



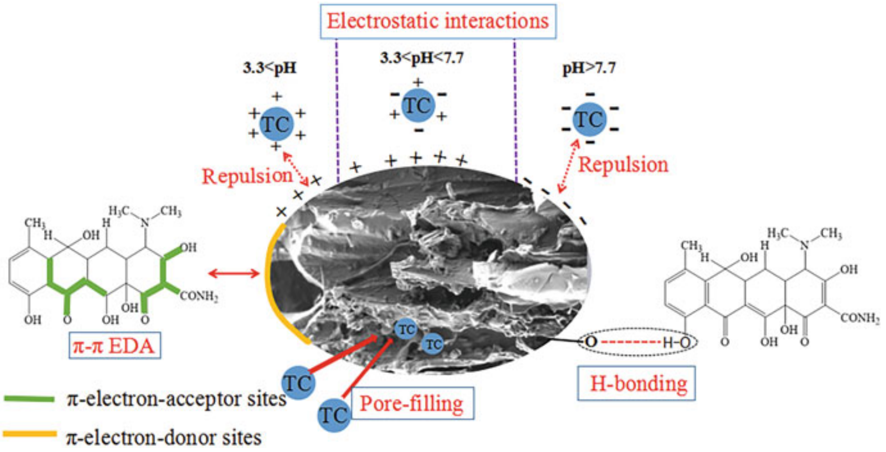


Fig. 18 Possible mechanisms responsible for adsorption of TC on BCs

Langmuir, Freundlich, Temkin, and D-R isotherm models were utilized to fit the isotherm data in order to explore the adsorption mechanisms [48]. The Langmuir model represents a process with monolayered adsorbents on a homogeneous surface [49], and obtained the best fit in previous studies of the adsorption of TC [50]. The results showed that the saturated adsorption capacities of BC-300, BC-500, and BC-700 were 7.22 mg/g, 9.90 mg/g, and 11.90 mg/g, respectively. After three cycles of ultrasonic vibration, the TC removal rates decreased for the three BCs. But given the low cost and ready availability of the waste *AA* dregs used as the raw material to produce the BCs, the dosages of the BCs could be increased during the reusability process to achieve the higher removal efficiencies.

The TC adsorption mechanisms for the BCs are shown in Fig. 18. The adsorption isotherm data fitted well with the D-R model and the Temkin isotherm model. H-bonds form readily when TC is adsorbed on BC. It is indicated that the pore filling effect, the formation of hydrogen bonds, and electrical recycling are all the principles of adsorption of TC. Finally, π-π electron-donor acceptor (EDA) interactions may have played a major role in the adsorption of TC onto the BCs according to the FTIR results. BC from *AA* dregs is a possible economical and environment-friendly adsorbent for the removal of TC from wastewater. Through the experiment, we knew that the BC prepared at the higher temperature had the greater capacity for removing TC.

3.5 *Carbon Material*

Carbon material (CM) derived from the combustion of forest branches has been widely used for the adsorption of nitrobenzene [51]. In this section, we are going to introduce the removal of Methyl Orange (MO) and Methylene Blue (MB) from an aqueous solution using a CM derived from the combustion of forest branches. The CM used in this study was produced during combustion of wood chips in a gasification power plant (Thomas Koch Corporation, Denmark) in Oshu City in Japan. The wood chips were obtained from logging or thinning of trees (Japanese cedar and red pine after approximately 25 years of growth) during the summer of 2006. After dried and pyrolyzed, the part of the wood chips is inverted into CM. In order to observe the adsorption characteristics of the CM and the effect of the functional groups on the surface of the CM on the removal of dyes more clearly, we oxidized the CM for 4 h to obtain the oxidized version (Ox-CM), whose adsorption properties were compared with those of the CM.

The SEM pictures of the CM and the Ox-CM are shown in Fig. 19. These pictures show the surface texture and porosity of the adsorbents. A high porosity and large surface area are essential for highly efficient adsorbents. The SEM picture of the CM displays a partial tubular or rope-like structure, but the surface of the Ox-CM shows no such structure probably due to the oxidization with nitric acid. We have studied some factors affecting the adsorption, such as pH, ion concentration, and contact time. The removal ratio of MO decreased as the pH was increasing while the removal ratio of MB increased with the pH increased. The higher cationic strength and valence of salts showed the stronger adsorption of dye. An increase in temperature had a slight influence on the adsorption isotherms of this CM. The adsorption ratios of MO and MB on the CM after 3 h were 96.3% and 90.2%, respectively. The removal rates of the MO and the MB were quite fast during the initial 5 min, and then the removal ratio slowly increased and reached equilibrium after 3 h. This result is important because the equilibrium time is one of the considerations for application to the removal of dyes in a wastewater treatment plant [52]. The effect of the adsorption time on the MO and MB adsorption by the CM (initial concentration of MO (50 mg/L) and MB (50 mg/L), adsorbent dose = 0.40 g/L, pH = 7.0, at 25°C) was also investigated. The adsorbed dyes were almost completely released by the regeneration process, while the capacity for dye adsorption of the reused CMs remained unchanged. The adsorptive capacity was regained even after three cycles of

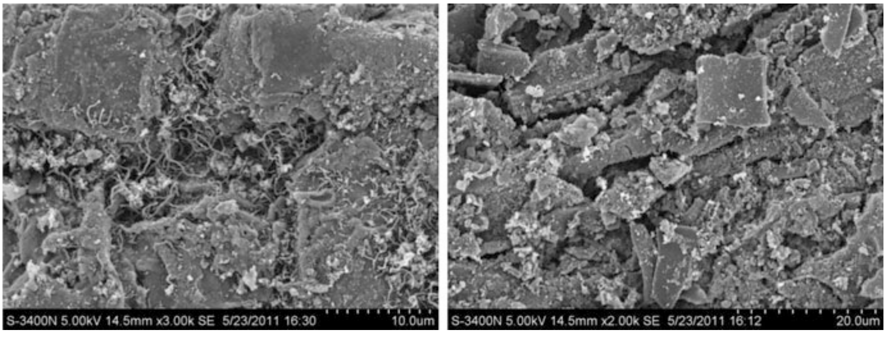


Fig. 19 SEM and FTIR images of the CM (left) and the Ox-CM (right)

adsorption and elution. So, the CM can be regenerated and reused many times [22]. The CM derived from the combustion of forest branches can be an inexpensive and environment-friendly adsorbent for the removal of organic dyes such as MO and MB from aqueous solutions.

3.6 Conclusion

It is very pleased to see that the discovery and application of environmental adsorbents are growing vigorously. But so far, there are still many pollution problems in the environments around us in spite of many efforts by various people. Therefore, more practical application, exploration and development of adsorbents still need to remediate our environments. Although the discovery of new adsorbents plays an important role in the field of environmental protection, it causes a new challenge to gradually improve the defects of adsorption process and give full play to the benefits of adsorbents to achieve maximum adsorption benefits. It is hoped that readers can understand the characteristics of these five types of adsorbents through this paper and promote the optimization and application of these five types of adsorbents, as looking forward to a greater breakthrough in the field of environmental adsorbents in the future.

4 Utilization of a Fermented Bark Amendment That Can Be Assimilated into Soil

We have investigated the properties of lignin in woody bark, which can adsorb heavy metals, and applied the fermented bark to fixing the heavy metals in soil and accelerating plant growth, considering as a mild recycle that woody biomass can be assimilated into soil.

Here, we introduce the suppression of cadmium uptake from soil to rice by the amendment produced from fermented bark (fermented bark amendment:FBA), and its application of FBA to large-scale rice farmland in China. In addition, we also describe simultaneous uptake suppression of arsenic and cadmium from a cultivation agar to radish by mixing a mixture of magnetic nanoscale powder (MNP) and FBA.

4.1 Suppression of Cadmium Uptake in Rice Using Fermented Bark

4.1.1 Introduction

We considered the potential of bark, an environmentally friendly material produced in abundance from the thinning of cedar in Gunma Prefecture, Japan, for soil restoration. Bark consists of natural polymers, such as lignin and cellulose, and has been primarily used for fuel production or as a soil substitute [53] in horticulture. Lignin, which represents about 20–35% of the cell wall of conifer wood, is particularly known for absorbing heavy metals [54, 55], since it is not easily decomposed by bacteria or hydrolyzed as happens with cellulose. However, white-rot fungus found in humic soil is known to decompose bark [56, 57]. The assimilation of bark in the soil can be accelerated by applying it in a decomposed state, instead of using it directly. Bark composts consist of decomposing bark that is rapidly assimilated into the soil to improve plant growth and soil quality [58]. However, the preparation of bark compost is time consuming and requires approximately 6–12 months for the decomposition to small organic compounds such as aliphatic carboxylic acids, aromatic carboxylic acids, or carbon dioxide (CO_2).

Our group has developed a soil amendment that could be used to reduce Cd uptake in brown rice. The fermented bark amendment (FBA) was produced by mixing recycled bark, rice bran, and white-rot fungus to accelerate the fermentation process and was obtained in 2–10 days using a rapid fermentation procedure (Fig. 20).

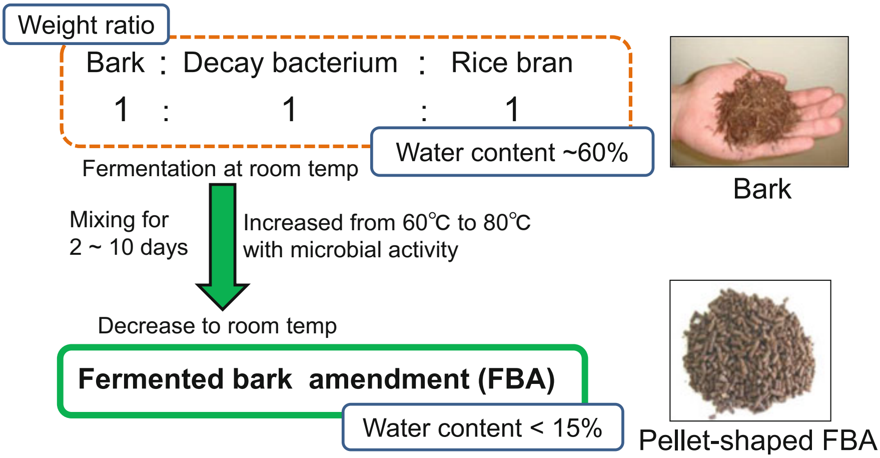


Fig. 20 Preparation process of FBA. Reproduced from Elsevier Copyright with permission

4.1.2 N, P, and K Contents in FBA

The N, P, and K contents in FBA were 3.2%, 0.6%, and 1.2%, respectively, giving a total content of less than 5.0%. Considering that the recommended total content of N, P, and K in commercial chemical fertilizers is 30%, the FBA has significantly lower N, P, and K levels and thus an inferior quality.

4.1.3 Rice Cultivation in Pot

Rice was cultivated for approximately 120 days between July and November in 2009–2014 on a rooftop at Gunma University, Gunma, Japan. The soil was collected from a site close to a Cu-Cd mine, with a Cd content of 2.2 ± 0.7 mg kg^{-1}, which was lower than the reference value of 150 mg kg^{-1} for contaminated soil.

The FBA was mixed with 5 kg of soil at weight ratios ranging from 0.1 to 2.0%. At the same time, a high-grade compound fertilizer (N:P:K, 1:1:1) was added to all test soil samples at a rate of 0.5 g per pot (530 cm^2). The water regime was applied under "water-filling with midterm drying" (approximately 5 cm water depth), which is a common method for rice cultivation in Japan, which strengthens the roots of plants by temporarily allowing the soil to dry-out during paddy cultivation.

4.1.4 Effects of FBA Application and Water Regimes

We studied the effects of different FBA application amounts (0.1–2%, w/w) under water-filling on soil pH and ORP and the uptake of Cu, Zn, Cd and Pb in brown rice. The pH of soil supplemented with chemical fertilizers and FBA increased from 4 to 7, however, no significant differences were identified between the treatments. On the other hand, the ORP in soil supplemented with chemical fertilizers and FBA rapidly declined, probably due to the activities of methanogens or sulfate-reducing bacteria in the soil and water, which promote oxidative decomposition and generate CO_2 [59]. In fact, the amount of CO_2 and CH_4 increased with the amount of FBA due to the rapid reduction of soil.

The suppression of Cd uptake was clearly dependent on the amount of FBA applied to the soil. Cd concentration in rice cultivated in FBA-supplemented (0.1–2%, w/w) soil was significantly lower ($P < 0.05$) than that of rice cultivated in soil without FBA supplementation (i.e., chemical fertilizer only). When FBA (2%, w/w) was applied, the level of Cd absorption was reduced to about one-tenth of that obtained when only chemical fertilizers were used (Fig. 21). However, rice growth was poor in soils supplemented with more than 1% FBA (Fig. 22).

We also investigated the application effect of 1% (w/w) fertilizer that ferments rice bran (RB) and 1% (w/w) compost that ferments bark by water (BC) on the uptake of heavy metals in brown rice. The results indicated that the content of heavy metals in rice cultivated with RB and BC was lower than that cultivated with

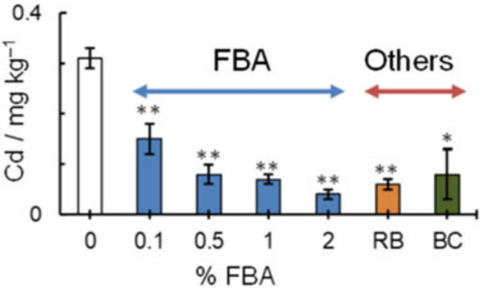


Fig. 21 Cd concentrations in brown rice after the application of FBA and other organic fertilizers to the soil under water-filling with midterm drying. RB, rice bran; BC, bark compost. RB and BC were applied to the soil at a rate of 1.0% (w/w). Asterisks indicate significant differences between bars at $P < 0.05$ (*), and $P < 0.01$ (**). Reproduced from Elsevier Copyright with permission

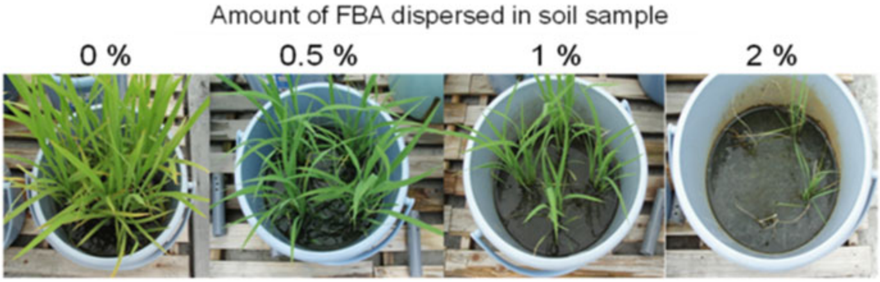


Fig. 22 Photos of paddies cultivated in FBA-supplemented soil for 30 days under medium drying conditions. Reproduced from Elsevier Copyright with permission

chemical fertilizers alone. However, the supplementation of RB provided strong odor during water-filling. The supplementation of BC did not obtain strong odor; however, the production of BC requires about 6–12 months.

4.1.5 Effect of a Timing for FBA Application

The application of FBA effectively suppressed the uptake of Cd in brown rice; when the roots of the paddy were still immature under water-filling conditions, it led to the failure of rice growth with a rapid decline in the ORP of the soil. Therefore, we applied 1% (w/w) FBA at 2, 4, 6, 8, and 9 weeks after rice planting and did not change the other conditions before. As the results, the crop failure could be minimized, because the roots are sufficiently grown to survive the reduction of ORP in the soil after 2 weeks after planting the seedlings.

Chino reports that the heavy metal uptakes into rice plants are maximal between 3 weeks before heading and 1 week after heading [60]. Based on the amount of Cd uptake in brown rice, the changes in soil ORP, and the growth of rice plants, we

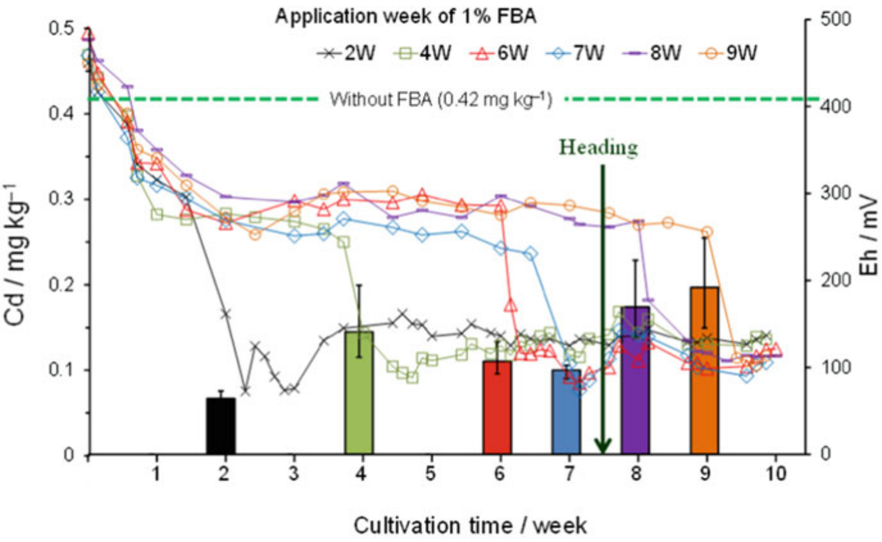


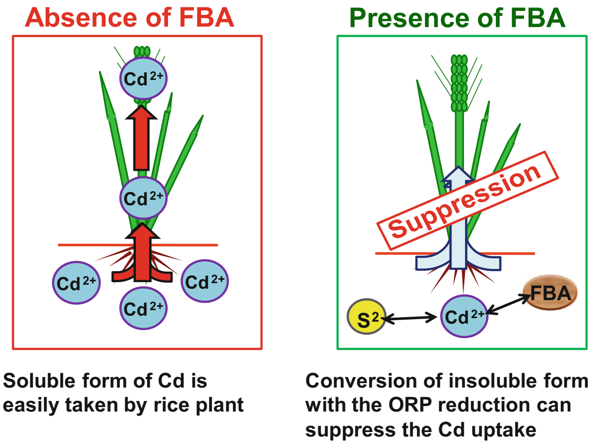
Fig. 23 Effect of FBA (1%) application timing (2, 4, 6, 7, 8, and 9 weeks after rice planting) on Cd concentrations and oxidation-reduction potential (OPR) in rice under water-filling with midterm drying conditions. Reproduced from Elsevier Copyright with permission

found that the optimum period for the application of FBA was 2 weeks after planting. The suppressions of Cd uptake in brown rice and the variation of ORP are shown in Fig. 23.

4.1.6 Suppression Mechanism of Cd Uptake with FBA

Cd uptake in brown rice was suppressed when rice plants were grown in FBA-supplemented soil under ordinary water-filling conditions, mainly because: (1) the complexation of Cd with the decomposed materials of bark and (2) the generation of sulfide form, e.g., CdS, with generation of sulfide ion in the soil (Fig. 24). Under no water-filling conditions, FBA did not reduce the mobility and uptake of specific heavy metals as occurred under water-filling conditions. In FBA-supplemented soil under water-filling conditions, the microbial decomposition of bark on the soil surface consumes O_2 and generates CO_2 and CH_4. At that time, SO_4^{2-} content in the soil is reduced with activation on sulfate-reducing bacteria in soil, causing the generation of S^{2-}, which combines with heavy metals and forms insoluble sulfide precipitates.

Fig. 24 Suppression mechanism of Cd expected by this study. Reproduced from Elsevier Copyright with permission



4.2 *Application of FBA to Large-Scale Crop Cultivation*

4.2.1 Introduction

Next, we investigated whether the variations of the Cd concentration in harvested brown rice and rice yields were affected by adding the FBA derivative onto a large-scale farmland soil contaminated by Cd continuously for 3 years.

A schematic representation of the farmland used in the study is shown in Fig. 25. A field trial was conducted in the western part of Jiangsu Province, China at ~5 m altitude. Both rice and wheat were cultivated there annually. The area of the experimental farmland was 9,635.4 m^2 (90.9 m E–W and 106.0 m N–S). The farmland was situated both east and west of a 20-m-wide canal. Several pottery and chemical factories are located to the south of the farmland.

The experimental farmland consisted of six plots (A–F) and an embankment passage 30–40 cm wide. For each plot, the rice plant samples were collected within the 1 m $\times$1 m of area of three equal parts (1–3) per each plot (Fig. 26). The rice plants were pulled out from the center and for corners in each plot.

The fermented bark was produced from woody and food wastes locally obtained in China, so-called fermented botanical waste-based amendment (FBWA), which is a kind of FBA. Before evaluating the effect of FBWA spraying on the Cd uptake in rice, the heavy metal concentration was measured in irrigation water pumped from canals adjacent to the farmland. The average Cd concentration was <0.20 μg L^{-1}, which was well below the environmental quality threshold for farmland used for edible agricultural product cultivation in China (5.0 μg L^{-1}). However, the Cd concentrations in the farmland soil were 7–10 times higher than the environmental quality standard (0.30 mg kg^{-1}) and also exceeded the averages for farmlands in Hunan Province (0.73 mg kg^{-1}), Guangxi Province (0.70 mg kg^{-1}), and Sichuan Province (0.46 mg kg^{-1}).

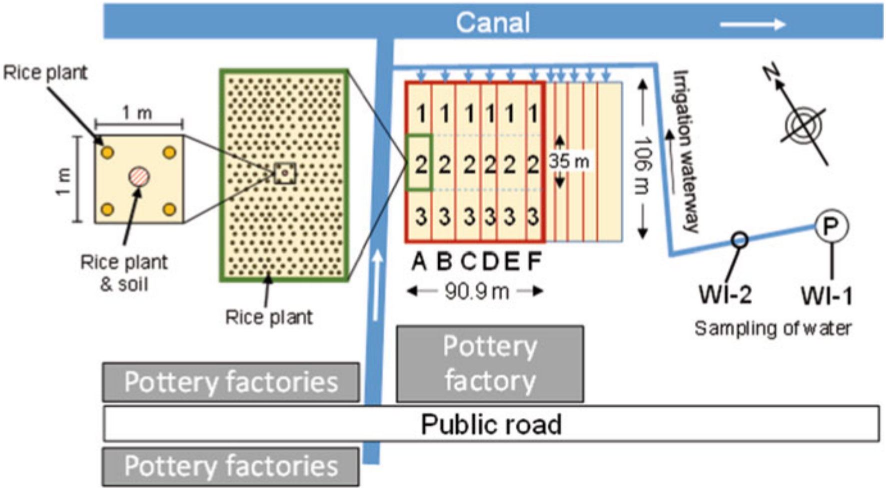


Fig. 25 Location of the farmland in Jiangsu Province, China. P: Pumping facilities. WI-1 and WI-2: water intake positions. The numbers in the experimental farmland represent the sampling points divided in three equal parts per plot. Reproduced from the Japan Society for Analytical Chemistry Copyright with permission

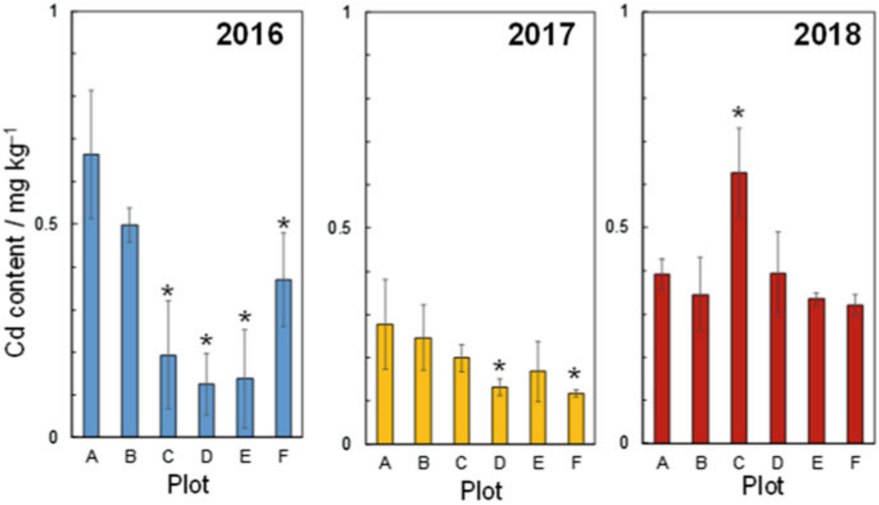


Fig. 26 Cd content in rice harvested from the farmland. Farmland was divided into blocks according to the irrigation water inflow. FBWA was sprayed onto the paddy soil at the following rates: A, 0%; B and F, 0.1%; C and E, 0.5%; and D, 1.0%. The variety of rice seed sprayed on the experimental farmland in 2017 was different to those in 2016 and 2018. Asterisks indicate significant differences between the Cd levels in the rice harvested from amended soil and those in the rice harvested from unamended soil at $P < 0.05$ (*). Triplicate samples were taken for each plot. Reproduced from the Japan Society for Analytical Chemistry Copyright with permission

4.2.2 Variations of Cd Content in Rice after Spraying FBWA onto Contaminated Soil

The effects of the FBWA application rate on soil were assessed in terms of the Cd uptake in rice and yield. On August 11, 2016, FBWA was sprayed about 2 weeks before the rice was headed. The quantities of FBWA sprayed were determined from the soil weight calculated using the depth of a rice root (15 cm) and the area in each plot, based on the soil specific gravity (1.2 g cm^{-3}). 0.1% FBWA was applied in plots B and F, 0.5% FBWA was applied in plots C and E, and 1.0% FBWA was applied in plot D. FBWA was not sprayed onto plot A (control plot). The variations in the Cd contents in brown rice were compared between plots amended with FBA and the control plot over a period of 3 years.

In 2016, the Cd concentration of the rice harvested from control plot A was 0.66 mg kg^{-1}, and those from plots B and F (where 0.1% FBWA was sprayed) were 0.50 mg kg^{-1} and 0.37 mg kg^{-1}, respectively (Fig. 29). Those in rice harvested from plots C and E (where 0.5% FBWA was sprayed) were 0.19 mg kg^{-1} and 0.14 mg kg^{-1}, respectively, lower than that of the rice harvested from plot A. Furthermore, the Cd concentration in rice harvested from plot D (0.13 mg kg^{-1}), where 1% FBA was sprayed, was reduced by 80% compared with that in plot A. Accordingly, rice harvested from plots amended with 0.5–1% FBWA had 66–80% less Cd than that derived from control plots, while rice harvested from plots B and F amended with 0.1% FBWA had 24% and 44% less Cd, respectively, than that derived from control plots.

In 2017, the rice crop was sown after the wheat harvest and soil conditioning. FBWA was not added to the cultivation soil to determine the longevity of its initial application. Because the rice variety seeded in that year was different to that in 2016, the Cd contents taken up by brown rice were lower than those in 2016 but the trends in the Cd contents among plots were similar. Because the Cd concentration in rice also decreased in plot A, the differences between the FBWA-amended plots and the control plot in 2017 were smaller than those in 2016.

In 2018, the suppressive effect of FBWA on the Cd uptake by rice was almost eliminated, that is, there were no significant differences between the amended plots and the control plot A. In addition, the Cd concentration in rice harvested from plot C amended with 0.5% FBWA was higher than that in plot A.

As mentioned above, we concluded that the longevity of the suppression of Cd uptake by rice was 2 years from the initial application of FBWA.

4.2.3 Rice Yield

Applying the technique evaluated in the present study to real farmland restoration requires not only decreases of the Cd content in rice, but also validation of the rice yield. The variation in the theoretical rice yield (Y_t) estimated from Eq. (4) for each year is plotted in Fig. 27.

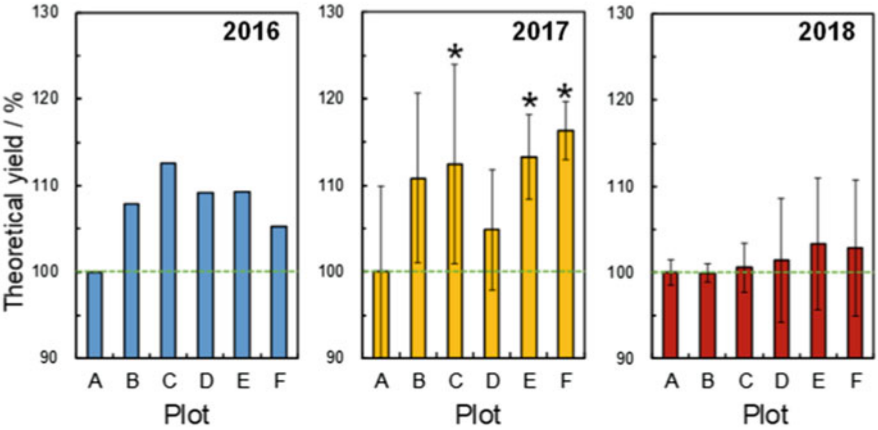


Fig. 27 Rice yield in each FBWA-sprayed farmland plot relative to that for the unamended control (plot A) in 2016–2018. FBWA was sprayed onto the paddy soil at the following rates: A, 0%; B and F, 0.1%; C and E, 0.5%; and D, 1.0%. Asterisks indicate significant differences between rice yields in soils amended with FBWA (B–F) and the unamended (A) at $P < 0.05$ (*). Statistical analyses were conducted using three replicates per plot. In 2016, the rice yield was calculated by collecting all the rice harvested in each plot. Reproduced from the Japan Society for Analytical Chemistry Copyright with permission

$$Y_{\mathrm{t}}(\mathrm{kg}) = N_{\mathrm{p}}\left(\mathrm{m}^{-2}\right) \times N_{\mathrm{r}} \times G_{1000}\,(\mathrm{g})/10^6 \times 0.85 \tag{4}$$

where N_{P} is the number of panicles to unit of surface area, N_{r} is the number of rice grains, G_{1000} is the 1,000-grain weight of ripe rice, and 0.85 is the weight loss ratio of the samples after drying.

When the yield in control plot A, which was a normal chemical fertilizer only, was compared with those for plots B–F after the FBWA treatment in 2016, plots C and E (0.5% FBWA) in 2016 had the maximum yields of 13% higher rice yields than all other plots ($P < 0.05$). Therefore, FBWA-amended soils promoted higher yields than unamended soil.

The rice yield trend obtained in 2016 did not change in 2017, though the species of rice seed in 2017 was different to that in 2016 and 2018. Because the cultivation situation, such as crop rotation, soil type, and water flow, except for rice species, remained, the soil remediation with spraying FBWA would lead to the acceleration of plant growth. In 2017, the rice yields in the amended plots were increased by 5–16% over that of the control plot A. The rice harvested from plots C–F had lower Cd concentration than the standard level (<0.2 mg kg^{-1}) in China. However, in the third year, no significant differences in yields were observed.

4.3 Simultaneous Suppression of Magnetic Nanoscale Powder and Fermented Bark Amendment for As and Cd Uptake by Radish Sprouts Grown in Agar Medium

4.3.1 Introduction

We here attempted to hybridize multiple compounds to simultaneously reduce the uptake of As and Cd, considering the influence of plant growth.

Honma et al. describes that it is difficult to simultaneously reduce As and Cd uptakes using a single countermeasure, such as water management practice or soil amendment application [61]. For example, filling water to paddy fields reduces the Cd concentrations in the rice under the anaerobic conditions in paddy soil. However, because it consequently accelerates the As uptake by rice due to the increases of solubilities of arsenite or arsenate in the water [62]. Thus, it has become widely recognized that there is a trade-off between the uptake of arsenic and cadmium by rice [63].

We attempted the suppression of the inorganic species uptake by plant in the agar medium including magnetic nanoparticle powder (MNP, α-Fe_3O_4) and FBA [64].

4.3.2 Preparation of MNP

MNP was prepared in Kanto Denka Kogyo Co., Ltd. (Shibukawa, Japan). Briefly, 0.6 mol $FeCl_2$ and 4.8 mol $FeCl_3$ were added to 1.0 L of pure water. Next, 500 mL of an aqueous solution containing 0.1 M NaOH was added, after which a colloid suspension was obtained. During this procedure, nitrogen gas was flowed over the mixture at a rate of 10 L min^{-1} at 60°C, and air was then bubbled into the sample at 20 L min^{-1} to oxidize the iron species for 6 h. The suspension was separated into particles and aqueous solution by centrifuging at 3,000 rpm for 3 h. The nanoparticles were washed with 200 L of deionized water at 60°C. The MNP obtained was dried at 120°C under a nitrogen stream.

4.3.3 Adsorption Capabilities for Arsenate, Arsenic, and Cadmium

The adsorption-saturation capacities of As(III), As(V), and Cd(II) to MNP and FBA at pH 6 were estimated from the adsorption amounts (q_e) reached during the saturated state after mixing for 30 min into the residual concentration (C_e).

As the adsorption-saturation capacities (Q) of MNP and FBA were estimated from the intercept of the calibration curve in Eq. (1), the Q values of arsenic species to MNP were 10-fold higher than that of Cd(II), and the opposite tendency was observed for FBA, as summarized in Table 4. In addition, the Q value of As(III) to MNP was higher than those to the adsorbents cited in this paper [65, 66], though that of As(V) was lower than several materials complexing multiple adsorbents

Table 4 Adsorption-saturation capacity (*Q*) of arsenic and cadmium to MNP and FBA and the comparative data by adsorbents obtained from industrial wastes and iron oxide in previous researches [64]

Adsorbents	Analyte	*Q* (μmol/g)	References
MNP	As(III)	303 ± 12	
FBA		76.9 ± 5.3	
Pine cone-magnetite		227	[65]
Hematite-coated Fe_3O_4		13.3	[66]
MNP	As(V)	303 ± 10	
FBA		38.5 ± 7.2	
Hematite-coated Fe_3O_4		28.0	[66]
Granular ferric hydroxide		30.9	[72]
Synthesized magnetite		887	[67]
Chitosan-coated $Cu(OH)_2$		520	[68]
MNP	Cd(II)	27.4 ± 1.1	
FBA		558 ± 36	
Pinus halepensis sawdust		65.6	[70]
Magnetic biochar derived from kelp		207	[71]
Pyrolyzed coffee residues and clay		527	[69]

Average and standard deviations in MNP and FBA were estimated from three different samples

[67, 68]. The *Q* value of Cd(II) to FBA indicated much higher than biomass materials presented in reports by several researchers [69–71].

4.3.4 Determination of the As and Cd Concentrations in Radish Sprouts

Radish sprouts were cultivated in agar medium, according to the cultivation method described by [73]. Three different radish cultivations were performed for each condition. First, the FBA and/or MNP, 0.2 g agar powder, and 25 mL Tris (hydroxymethyl) aminomethane buffer containing both As(III) and Cd(II) (100 μg/L) were cooled to 25°C and then solidified by heating to 90°C. MNP and FBA were added in range of 0.025–2.5 g per 25 mL agar: the solid-to-liquid ratio (g/mL) was 0.001–0.1. The radish seeds were cultivated in agar medium for 18 days and then harvested. The radishes produced were dried in an oven at 80°C for 3 h, following the measurement of the length of the roots and edible portions. The dried radish samples were mashed using an agate mortar and completely dissolved in nitric acid. As and Cd concentrations in the solution were quantified by ICP-MS.

4.3.5 Suppression of As and Cd Uptakes into Radish Sprouts

When the radish sprouts were grown in the agar media with As and Cd (each initial concentration: 100 μg/L for As(III) (arsenite) and Cd(II)), the effects of MNP and FBA added to the medium were compared by determining the amounts of As and Cd

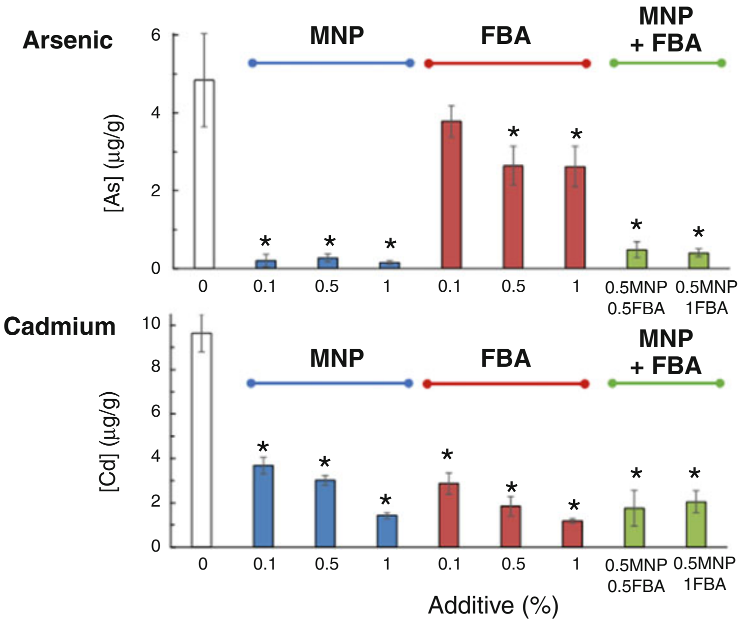


Fig. 28 Contents of arsenic (upper trace) and cadmium (lower trace) absorbed into radishes planted in agar medium supplemented with MNP, FBA, and a mixture thereof (0.5% MNP/0.5% FBA or 0.5% MNP/1% FBA). The initial concentrations of arsenic(III) and cadmium(II) in the agar were 100 µg/L. The error bars in bar graphs were estimated from the standard deviations of analytes in radishes, obtained in triplicate experiments. Significant differences ($p < 0.05$, $n = 3$) between the results of the blank and those of the treatments with MNP and/or FBA are indicated by asterisk above bar. Reproduced from Springer Copyright with permission

absorbed in the sprouts. In this experiment, they were co-mixed in the agar media. The amount of FBA and MNP added to the agar media ranged from 0.1 to 1.0%.

As shown in Fig. 28, the absorption of As into the sprouts was almost quantitatively suppressed by adding MNP in the medium at concentrations higher than 0.1% MNP. In addition, the As content decreased by approximately 50% in the blank condition by the addition of 1% FBA. The amount of Cd absorbed by the sprouts in the agar medium with FBA was reduced by approximately fivefold versus the blank. Interestingly, Cd uptake by the sprouts was also reduced by 60–85% by adding MNP, although Cd adsorption to MNP in aqueous solution was much lower than its As adsorption. The cation-exchanger or chelating complex site such as the carboxyl and hydroxyl groups in FBA promoted by decomposing bark by activation of white-rot fungus would relate to binding to metals. According to a report by [74], the carboxyl and phenolic hydroxyl groups in the humus bind to metal cations by forming complexes with the adsorption site. The suppression of As uptake by the radish sprouts in the agar media with FBA was lower than that of Cd. This would be because of the low binding capability for As (anionic species) to materials with carboxyl groups and phenolic hydroxyl groups in the FBA [75].

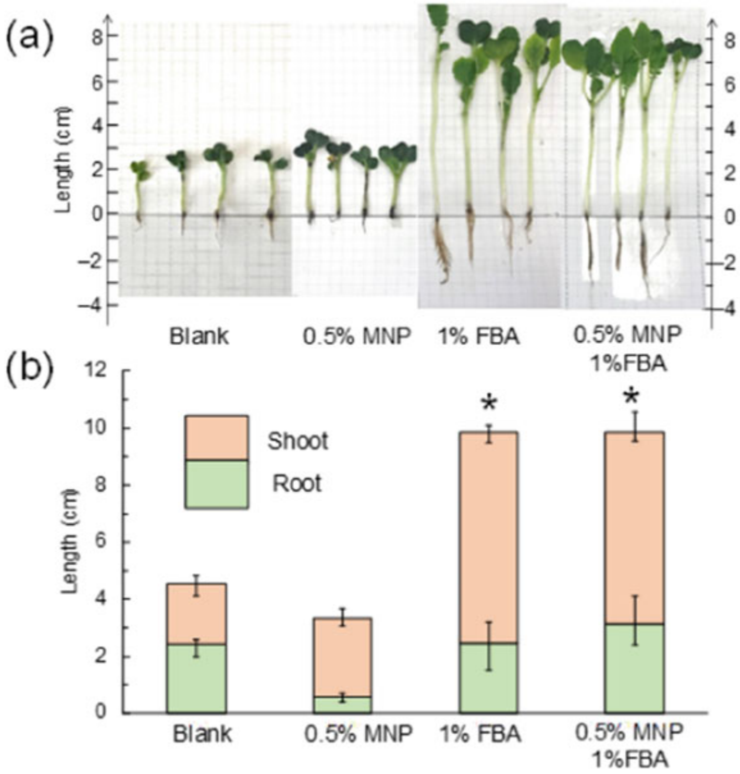


Fig. 29 Growths of radishes harvested after growth in blank medium, or medium containing 0.5% MNP, 1% FBA and 0.5% MNP, and 1% FBA. Trace: (**a**) photographs and (**b**) bar graphs. Significant differences ($p < 0.05$, $n = 4$) between the results of the blank and those of the treatments with MNP and/or FBA are indicated by asterisk above bar. Addition of As and Cd in the agar mediums used in the tests was not carried out. Reproduced from Springer Copyright with permission

Many researchers provided that iron hydroxides and oxides could efficiently bind and remove arsenic from aqueous solution [76–79]. In this study, MNP composed of iron oxide could bind negatively charged arsenic ions; thus, the binding mechanism of MNP to arsenic species is comparable to that for iron oxide.

Japanese radish was cultivated in the agar medium containing a mixture of 0.5% MNP/0.5% FBA or 0.5% MNP/1% FBA, of which concentrations were obtained after reasonable suppression of As and Cd. As shown in Fig. 29 their uptakes were suppressed by the presence of the mixed additive. However, the capability of the mixture for suppressing each analyte uptake was slightly lower than found for As with 1% MNP alone and cadmium with 1% FBA alone. This would be because the adsorption capabilities of MNP and FBA for analytes were offset. Indeed, the suppression of analyte uptake did not change even when the amount of FBA was increased to 1% and mixed with 0.5% MNP to further reduce the Cd contents in radishes. Inversely, when the MNP amount was increased to 1% and mixed with 0.5% FBA, As content was not different to that with 0.5% MNP and 0.5% FBA but the radish growth was largely suppressed (data not shown).

According to a report by [80] when both iron oxide and dissolved organic matter (DOM) co-exist in medium, the cadmium preferentially binds to functional carboxyl groups on aromatic rings in humic acid than to iron oxide. DOM contained in FBA may adsorb to both heavy metal cations and arsenite on mineral surfaces [81–83] demonstrated to reduce the arsenic content when iron and DOM coexisted in aqueous medium. Arsenic adsorption might be due to the formation of Fe-bridged As−Fe−DOM complexes and surface complexation of arsenic on DOM-stabilized Fe colloids [84, 85]. In this case, the FBA–MNP complex in agar might be formed dominantly over the complex with As or Cd in the agar medium.

Interestingly, the combination of MNP and FBA was found to be effective for the plant growth. In fact, the elongations of root and stem in radish cultivated in agar with FBA were larger than those in agars without FBA or with MNP only (Fig. 29a). As shown in Fig. 29b, in addition to the 0.5% MNP only, the growth of radish was obviously defected compared to other conditions, that is, the MNP might suppress the absorption of arsenic but cannot supply the nutrients such as potassium and phosphorus concerning the growth of plant. Also, the average length of stem and root cultivated in the agar with 0.5% MNP and 1% FBA were 2.7-fold and 3.4-fold longer, respectively, than those without additive, indicating almost comparative to those in the agar medium with 1% FBA.

4.4 Conclusion

The supplementation of FBA in the heavy metal-contaminated soil provides sustainable suppression of Cd uptake by rice plant, because the Cd is converted into insoluble form with the reduction of ORP on the soil surface. Also, since FBA is made from waste materials and food waste, it has a high affinity for soil and is considered to be an environmentally friendly amendment. Mixing different adsorbents such as a combination of FBA and MNP provides a synergy effect that can simultaneously suppress the uptake of different metal species by plant. As the further investigation, the FBA will be applied to soils contaminated by other toxic elements such as mercury or radioisotope cesium.

5 Conclusion

The environmentally friendly adsorbents proposed in the study, which is based on natural products, plants, solid waste material, and agricultural waste, have a high potential for removing organic and inorganic materials, including heavy metal ions and dyes, from water or soil. All of the adsorbent materials proposed in this chapter are widely available and easily developed by using low-cost and waste materials. Furthermore, they have a high capacity for metal ions and also some organic materials in water. The use of these adsorbents has many advantages, including low cost and easiness of production, safety for the environment, and the conversion of waste materials into valuable materials for the environmental remediation.

References

1. Khulbe KC, Matsuura T (2018) Removal of heavy metals and pollutants by membrane adsorption techniques. Appl Water Sci 8(19):1–30
2. Baysal A, Ozbek N, Akman S (2013) Determination of trace metals in wastewater and their removal processes wastewater – treatment technologies and recent analytical developments. Chapter 7. https://doi.org/10.5772/52025, ISBN: 978-953-51-0882-5
3. Markovic R, Bessho M, Masuda N, Stevanovic Z, Bozic D, Trujic TA, Gardic V (2020) New approach of metals removal from acid mine drainage. Appl Sci 10:1–16
4. Emiliani J, Oyarce W, Bergara CD, Salvatierra LM, Novo LAB, Perez LM (2020) Variations in the phytoremediation efficiency of metal-polluted water with Salvinia biloba: prospects and toxicological impacts. Water 12:1–15
5. Edebali S, Pehlivan E (2016) Evaluation of chelate and cation exchange resins to remove copper ions. Powder Technol 301:520–525
6. Pohl A (2020) Removal of heavy metal ions from water and wastewaters by sulfur-containing precipitation agents. Water Air Soil Pollut 231. 503:1–17
7. Namasivayam C, Ranganathan K (1995) Removal of Cd (II) from wastewater by adsorption on waste Fe (III)/Cr (III) hydroxide. Water Res 29:1737–1744
8. Papandreou AD, Stournaras CJ, Panias D, Paspaliaris I (2011) Adsorption of Pb (II), Zn (II) and Cr (III) on coal fly ash porous pellets. Miner Eng 24:1495–1501
9. Gebretsadik H, Gebrekidan A, Demlie L (2020) Removal of heavy metals from aqueous solutions using *Eucalyptus Camaldulensis*: an alternate low-cost adsorbent. Cogent Chem 6(1):1–16
10. Hasan AF, Hrdina R (2018) Chitosan/nanohydroxyapatite composite based scallop shells as an efficient adsorbent for mercuric ions: static and dynamic adsorption studies. Int J Biol Macromol 109:507–516
11. Hossain A, Bhattacharyya SR, Aditya G (2015) Biosorption of cadmium from aqueous solution by shell dust of the freshwater snail Lymnaea luteola. Environ Technol Innov 4:82–91
12. Siswoyo E, Nozomi E, Yoshihiro M, Shunitz T (2014) Agar-encapsulated adsorbent based on leaf of platanus sp. to adsorb cadmium ion in water. Water Sci Technol 70(1):89–94
13. Jae WC, Seung GC, Seok WH, Dong JK, Sang HL (2011) Development of an environmentally friendly adsorbent for the removal of toxic heavy metals from aqueous solution. Water Air Soil Pollut 2012(223):1837–1846
14. Dai Y, Li J, Sun Q, Liu Z (2020) Adsorption isotherm, kinetic modeling and mechanism of neutral red on *Auricularia auricularia*. Desalin Water Treat 198:335–344
15. Iqbal M, Saeed A, Zafar SI (2009) FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste. J Hazard Mater 164:161–171
16. Siswoyo E, Tanaka S (2013) Development of eco-adsorbent based on solid waste of paper industry to adsorb cadmium ion in water. J Clean Energy Technol 1(3):198–201
17. Siswoyo E, Mihara Y, Tanaka S (2014) 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. Appl Clay Sci 97–98:146–152

18. Dai Y, Yan H, Zhang B, Wu W, Yang L, Li S, Li W, Li H, Yan L, Shan D, Feng Y, Terui N, Tanaka S (2014) A novel adsorbent obtained by caging activated carbon by konjac glucomannan gel for elimination of organic compounds. J Appl Polym Sci 131:40542
19. Dai Y, Du C, Yu H, Zhang D, Zhang K (2016) Influence of spent coffee ground treated by nitric acid on Pb (II)-biosorption from aqueous solution. Int Agric Eng J 25:20–28
20. Dai Y, Zhang D, Yan H, Ji Y, Wu W, Tanaka S (2016) Study on the mechanism of methylene blue adsorption on spent coffee grounds. Fresenius Environ Bull 25:3423–3429
21. Dai Y, Li J, Shan D (2020) Adsorption of tetracycline in aqueous solution by biochar derived from waste *Auricularia auricula* dregs. Chemosphere 238:124432
22. Dai Y, Li J (2020) Adsorption behavior of methyl orange and methylene blue onto carbon material in an aqueous solution. Desalin Water Treat 180:387–397
23. Mori M, Kotaki K, Gunji F, Kubo N, Kobayashi S, Ito T, Itabashi H (2016) Chemosphere 148: 487–494
24. Bajpai P (2015) Generation of waste in pulp and paper mills. In: Management of pulp and paper mill waste. Springer, Cham. https://doi.org/10.1007/978-3-319-11788-1_2
25. Prasetyo J, Naruse K, Kato T, Boonchird C, Harashima S, Park EY (2011) Bioconversion of paper sludge to biofuel by simultaneous saccharification and fermentation using a cellulose of paper sludge origin and thermotolerant saccharomyces cerevisiae TJ14. Biotechnol Biofuels 4: 35
26. Qin Q, Wang Q, Fu D, Ma J (2011) An efficient approach for Pb(II) and Cd(II) removal using manganese dioxide formed in situ. Chem Eng J 172:68–74
27. Rao M, Parwate AV, Bhole AG (2002) Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. Waste Manag 22:821–830
28. Vitela-Rodriguez AV, Rangel-Mendez JR (2013) Arsenic removal by modified activated carbons with iron hydro(oxide) nanoparticles. J Environ Manage 114:225–231
29. Su Q, Pan B, Wan S, Zhang W, Lv L (2010) Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water. J Colloid Interface Sci 349:607–612
30. Zhang Y, Jiang J, Chen M (2008) MINTEQ modeling for evaluating the leaching behavior of heavy metals in MSWI fly ash. J Environ Sci (China) 20:1398–1402
31. Zhou Y, Zhang R, Gu X, Lu J (2014) Adsorption of divalent heavy metal ions from aqueous solution by citric acid modified pine sawdust. Sci Technol 50(2):245–252
32. Mckay G, Blair HS, Gardener JR (1982) Adsorption of dyes on chitin I. Equilibrium studies. J Appl Polym Sci 27:3043–3057
33. Alonso-Sande M, Teijeiro-Osorio D, Remuñán-López C, Alonso MJ (2009) Glucomannan, a promising polysaccharide for biopharmaceutical purposes. Eur J Pharm Biopharm 72:453–462
34. Case SE, Knopp JA, Hamann DD, Schwartz SJ (1992) Characterisation of gelation of konjac mannan using lyotrophic salts and rheological measurements. In: Phillips GO, Willliams PA, Wedlock DJ (eds) Gums and stabilisers for the food industry 6. IRL Press, Oxford, pp 489–500
35. Gao S, Nishinari K (2004) Effect of degree of acetylation on gelation of konjac glucomannan. Biomacromolecules 5:175–185
36. Huang L, Takahashi R, Kobayashi S, Kawase T, Nishinari K (2002) Gelation behaviour of native and acetylated konjac glucomannan. Biomacromolecules 3:1296–1303
37. Nishinari K (2000) Konjac glucomannan. Dev Food Sci 41:309–330
38. Fugetsu B, Satoh S, Shiba T, Mizutani T, Lin Y, Terui N, Nodasaka Y, Sasa K, Shimizu K, Akasaka T, Shindo M, Shibata K, Yokoyama A, Mori M, Tanaka K, Sato Y, Tohji K, Tanaka S, Nishi N, Watari F (2004) Caged multiwalled carbon nanotubes as the adsorbents for affinity-based elimination of ionic dyes. Environ Sci Technol 38:6890–6895
39. Gokhan Z, Sinan K, Fawzi M, Mahomoodally., Simone, A., Ahmed, M., Mustafa., Sauro, V., Filippo, M., Giovanni, C. (2020) Chemical composition, antioxidant and enzyme inhibitory properties of different extracts obtained from spent coffee ground and coffee silverskin. Foods 9(6):713

40. Dai Y, Zhang D, Zhang K (2016) Nitrobenzenee adsorption capacity of NaOH modified spent coffee ground from aqueous solution. J Taiwan Inst Chem Eng 68:232–238
41. Kulshrestha P, Giese FR, Aga DS (2004) Investigating the molecular interactions of oxytetracycline in clay and organic matter: insights on factors affecting its mobility in soil. Environ Sci Technol 38:4097–4105
42. Liao YK, Li LX, Fan SS (2019) Removal behavior and mechanism of methylene blue in aqueous solution by rice straw and rice straw-Fe_3O_4 composite. Acta Sci Circumcision 39:359–370
43. Yao S, Zhang MS, Li LX, Liao YK, Zhou N, Fan SS, Tang J (2018) Preparation of tea waste-nano Fe_3O_4 composite and its removal mechanism of methylene blue from aqueous solution. Environ Chem 37:96–107
44. Ahmed M, Rajapaksha A, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33
45. Li YL, Ruan GD, Jalilov AS, Tarkunde YR, Fei HL, Tour JM (2016) Biochar as a renewable source for high-performance CO_2 sorbent. Carbon 107:344–351
46. Lou ZM (2016) Research on physio-chemical characteristics of spent mushroom substrate and its environmental impact during recycling process, Master thesis. Zhejiang University
47. Zhang L, Sun X (2014) Changes in physical, chemical, and microbiological properties during the two-stage co-composting of green waste with spent mushroom compost and biochar. Bioresour Technol 172:274–284
48. Ahmed M, Zhou JL, Ngo HH, Guo W (2015) Adsorptive removal of antibiotics from water and wastewater: progress and challenges. Sci Total Environ 532:112–126
49. Li Y, Wang Z, Xie X, Zhu J, Li R, Qin T (2017) Removal of norfloxacin from aqueous solution by clay-biochar composite prepared from potato stem and natural attapulgite. Colloids Surf, A 514:126–136
50. Fu B, Ge C, Yue L, Luo J, Feng D, Deng H, Yu H (2016) Characterization of biochar derived from pineapple peel waste and its application for sorption of oxytetracyclines from aqueous solution. Bio Resources 11(4):9017–9035
51. Dai Y, Mihara Y, Tanaka S, Watanabe K, Terui N (2010) Nitrobenzene-adsorption capacity of carbon materials released during the combustion of woody biomass. J Hazard Mater 174:776–781
52. Rocher V, Siaugue JM, Cabui V, Bee A (2008) Removal of organic dyes by magnetic alginate beads. Water Res 42:1290–1298
53. Yoshioka T, Hirata S, Matsumura Y, Sakanishi K (2005) Woody biomass resources and conversion in Japan: the current situation and projections to 2010 and 2050. Biomass Bioenergy 29:336–346
54. Guo X, Zhang S, Shan X (2008) Adsorption of metal ions on lignin. J Hazard Mater 151:134–142
55. Sciban MB, Klasnja MT, Antov MG (2011) Study of the biosorption of different heavy metal ions onto Kraft lignin. Ecol Eng 37:2092–2095
56. Tuomela T, Oivanen P, Hatakka A (2002) Degradation of synthetic ^{14}C-lignin by various white-rot fungi in soil. Soil Biol Biochem 34:1613–1620
57. Vane CH, Drage TC, Snape CE (2006) Bark decay by the white-rot fungus *Lentinula edodes*: polysaccharide loss, lignin resistance and the unmasking of suberin. Int Biodeter Biodegr 57: 14–23
58. Fukushima M, Yamamoto K, Ootsuka K, Komai T, Aramaki T, Ueda S, Horiya S (2009) Effects of the maturity of wood waste compost on the structural features of humic acids. Bioresour Technol 100:791–797
59. Asakawa S, Asagawa M, Koga Y, Hayano K (1998) Communities of methanogenic bacteria in paddy field soils with long-term application of organic matter. Soil Biol Biochem 30:299–303
60. Chino M (2006) The distribution of heavy metals in rice plants as influenced by the time and the path of supply. Jpn Soc Soil Sci Plant Nutr 77:119–124. In Japanese with English title

61. Honma T, Ohba H, Kaneko A, Nakamura K, Makino T, Katou H (2016) Effects of soil amendments on arsenic and cadmium uptake by rice plants (*Oryza sativa* L. cv. Koshihikari) under different water management practices. Soil Sci Plant Nutr 62:349–356
62. Koyama T (1975) Behavior of arsenic in soil and crops. Jpn J Soil Sci Plant Nutr 46:491–502. in Japanese
63. Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S (2009) Effects of water management on cadmium and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. Environ Sci Technol 43:9361–9367
64. Sun X, Mo H, Hatano K, Itabashi H, Mori M (2019) Simultaneous suppression of magnetic nanoscale powder and fermented bark amendment for arsenic and cadmium uptake by radish sprouts grown in agar medium. Environ Sci Pollut Res 26: 14483–14493
65. Ouma ILA, Naidoo EB, Ofomaja AE (2018) Thermodynamic, kinetic and spectroscopic investigation of arsenite adsorption mechanism on pine cone-magnetite composite. J Environ Chem Eng 6:5409–5419
66. Simeonidis K, Gkinis T, Tresintsi S, Martinez-Boubeta C, Vourlias G, Tsiaoussis I, Stavropoulo G, Mitrakas M, Angelakeris M (2011) Magnetic separation of hematite-coated Fe_3O_4 particles used as arsenic adsorbents. Chem Eng J 168:1008–1015
67. Iconaru SL, Guégan R, Popa CL, Motelica-Heino M, Ciobanu CS, Predoi D (2016) Magnetite (Fe_3O_4) nanoparticles as adsorbents for As and Cu removal. Appl Clay Sci 134:128–135
68. Elwakeel KZ, Guibal E (2015) Arsenic(V) sorption using chitosan/$Cu(OH)_2$ and chitosan/CuO composite sorbents. Carbohydr Polym 134:190–204
69. Boonamnuayvitaya V, Chaiya CY, Tanthapanichakoon W, Jarudilokkul S (2004) Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay. Sep Purif Technol 35:11–22
70. Semerjian L (2010) Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust. J Hazard Mater 173:236–242
71. Son E-B, Poo K-M, Chang J-S, Chae K-J (2018) Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass. Sci Total Environ 615:161–168
72. Saldaña-Robles A, Saldaña-Robles N, Saldaña-Robles AL, Damian-Ascencio C, Rangel-Hernandez VH, Guerra-Sanchez R (2017) Arsenic removal from aqueous solutions and the impact of humic and fulvic acids. J Clean Prod 159:425–431
73. Hatano K, Kanazawa K, Tomura H, Yamatsu T, Tsunoda K, Kubota K (2016) Molasses melanoidin promotes copper uptake for radish sprouts: the potential for an accelerator of phytoextraction. Environ Sci Pollut Res 23:17656–17663
74. Baker H, Khalili F (2005) A study of complexation thermodynamic of humic acid with cadmium (II) and zinc (II) by Schubert's ion-exchange method. Anal Chim Acta 542:240–248
75. Fakour H, Lin T (2014) Experimental determination and modeling of arsenic complexation with humic and fulvic acids. J Hazard Mater 279:569–578
76. Rahman IMM, Begum ZA, Sawai H, Maki T, Hasegawa H (2013) Decontamination of spent iron-oxide coated sand from filters used in arsenic removal. Chemosphere 92:196–200
77. Xu X, Chen C, Wang P, Kretzschmar R, Zhao FJ (2017) Control of arsenic mobilization in paddy soils by manganese and iron oxides. Environ Pollut 231:37–47
78. Mishra T, Mahato DK (2016) A comparative study on enhanced arsenic(V) and arsenic(III) removal by iron oxide and manganese oxide pillared clays from ground water. J Environ Chem Eng 4:1224–1230
79. Siddiqui SI, Chaudhry SA (2017) Iron oxide and its modified forms as an adsorbent for arsenic removal: a comprehensive recent advancement. Process Saf Environ Prot 111:592–626
80. Du H, Peacock CL, Chen W, Huang Q (2018) Binding of Cd by ferrihydrite organo-mineral composites: implications for Cd mobility and fate in natural and contaminated environments. Chemosphere 207:404–412
81. Wang S, Mulligan CN (2006) Effect of natural organic matter on arsenic release from soils and sediments into groundwater. Environ Geochem Health 28:197–214

82. Sharma P, Ofner J, Kappler A (2010) Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. Environ Sci Technol 44:4479–4485
83. Bauer M, Blodau C (2009) Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. Geochim Cosmochim Acta 73:529–542
84. Liu G, Fernandez A, Cai Y (2011) Complexation of arsenite with humic acid in the presence of ferric iron. Environ Sci Technol 45:3210–3216
85. Lin HT, Wang MC, Li GC (2004) Complexation of arsenate with humic substance in water extract of compost. Chemosphere 56:1105–1112