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A review on toxic cadmium biosorption from contaminated wastewater

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ABSTRACT

The presence of cadmium(II) in water possesses human health risks. Cadmium(II) has the harmful effects of high toxicity to the living organism in water. This review presents a compilation of biosorption of cadmium(II) by different biomaterials for the efficient removal of cadmium(II) from contaminated water. Kinetic models and adsorption isotherms have been discussed. The aim of this review is to present a broad view of adsorbents that have been identified and used for cadmium(II) removal from contaminated waters. The removal efficiency and adsorption of different biosorbents have been compared in this review. The influence of pH on removal of cadmium(II) efficiency has also been discussed.

Keywords: Toxicity; Cadmium; Biosorption; Kinetic models; Adsorption isotherm

1. Introduction

Water coming from industries and municipalities is highly polluted with heavy metals such as cadmium [1,2], arsenic [3], lead [4], copper [5,6], and chromium [7,8]. Due to toxicity, their presences in aquatic ecosystem possess human health risk. Among these toxic metals, cadmium(II) causes most harmful effects to human health.

The EU Directive, World Health Organization and US Environmental Protection agency have set the maximum contaminant concentration level for cadmium(II) in domestic water supplies as $5 \,\mu g \, L^{-1}$ [9]. Excess cadmium is mainly responsible for bone degeneration, liver damage, lung insufficiency, hypertension, and renal dysfunction in human [10].

Cadmium has been marked as Category-I carcinogen by International Agency for Research on Cancer. US Environment Protection Agency has also classified cadmium(II) as Group B1 carcinogen. This metal is highly toxic for diverse organisms including human beings. We invite many harmful incurable diseases by taking polluted drinking water that is especially rich in cadmium. The important sources of cadmium in contaminated water are from electroplating, pigment manufacture, printing and photographic industries, plastic, alloy preparation, ceramics and silver/ cadmium batteries. For the removal of cadmium(II) in contaminated wastewater, several popular methods are known, such as chemical oxidation or reduction, electrochemical treatment, chemical precipitation, reverse osmosis, solvent extraction, ion exchange, and evaporation, but these methods are applicable only when water is enriched with high metal concentration

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(e.g. greater than 100 mg L^{-1}) [10], and these techniques are not very attractive, when metal concentration is very low due to high chemical costs or low removal efficiencies. On the other hand, biosorption technique is very fruitful to remove or reduce low metal concentration in wastewaters showing a high efficiency [8].

2. Chemistry of cadmium

The element cadmium has low abundance in nature (of the order of 10^{-6} of the earth's crust). Cadmium minerals are scarce, and it occurs by isomorphous replacement in almost all zinc ores [11]. Cadmium reacts readily with nonoxidizing acids, releasing hydrogen and giving the divalent ions [11]. Cadmium exists as crystal having closely packed hexagonal arrangement, and it is usually combined with other elements in mineral compounds (e.g. cadmium oxide, cadmium sulfate, and cadmium sulfide).

Cadmium dust can ignite spontaneously in air in both flammable and explosive, when exposed to heat, flame, or oxidizing agents. Toxic fumes are emitted, when cadmium metal is heated to high temperatures. It was discovered as an impurity in zinc carbonate by Friedrich Stroh Meyer in Germany in 1817. Most cadmium is obtained as a by-product of the chemical treatment of copper, lead, and zinc ores, although it is a naturally occurring element in Earth's crust. Food and cigarette smoke are the most likely source of cadmium exposure for the general population. The total daily intake of cadmium from food, water, and air for an adult living in North America or Europe is estimated to be between 10 and 40 g (3.53×10^{-7}) and 1.41×10^{-6} ounces). Cadmium is formed on burning the metals in air or by pyrolysis of the carbonates or nitrates; oxide smokes can be obtained by combustion of the alkyls, those of cadmium being exceedingly toxic. The aqua ions are quite strong acids, and salts are hydrolyzed in water. In ClO_4^- solutions, the only species for cadmium below 0.1 M are the MOH⁺ ions, for example,

$$Cd^{2+}(aq) + H_2O \rightarrow Cd(OH)^+(aq) + H^+$$

For more concentrated cadmium solutions, the principal species is Cd_2OH^{3+} [11].

$$2Cd^{2+}(aq) + H_2O \rightarrow Cd_2(OH)^{3+}(aq) + H^+$$

3. Biosorption equilibrium and kinetics

3.1. Equilibrium modeling

Biosorption is considered as solid phase and an aqueous phase containing dissolved species to be sorbed (Cd²⁺ ions) is treated as the sorbent. Due to higher affinity of the sorbent for the ionic species, they are attracted and bound to the solid biomass. This process takes place until equilibrium between the amount of solid-bound ions and their concentration in solution is reached. Classical adsorption models (Langmuir and Freundlich) are used to describe the equilibrium between the adsorbed metal ions (Cd²⁺) on the solid (q_{eq}) and metal ions in solution (C_{eq}) at a constant temperature. The Langmuir equation is applicable to monolayer sorption onto a surface with a finite number of identical sites and is given by Eq. (1):

$$q_{\rm eq} = (q_{\rm max}bC_{\rm eq})/(1+bC_{\rm eq}) \tag{1}$$

where C_{eq} and q_{eq} represent the residual metal concentration in solution and the amount of the metal adsorbed on the biosorbent at equilibrium, respectively. The q_{max} represents a practical limiting adsorption capacity, when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases when the sorbent did not reach its full saturation in experiments and b represents a coefficient related to the affinity between sorbent and metal ions. The above model is best fit, for example, divalent cadmium removal by green coconut shell powder [12] and so on.

The empirical Redlich–Peterson equation was proposed to improve the Langmuir model and is given by

$$q_{\rm (eq} = (a_{\rm RP}C_{\rm eq})/(1 + b_{\rm RP}C_{\rm eq}^n)$$
⁽²⁾

where a_{RP} , b_{RP} , and n are empirical parameters without physical meaning. The parameter n is dimensionless and lies between 0 and 1. If n = 1, Eq. (2) becomes the Langmuir form. These Eqs. (1) and (2) do not reflect the physicochemical underlying principles of the biosorption process because sorption mechanism is more complex. The uptake capacity (q) evaluates the performance of biosorbents. Maximum uptake capacity (q_{max}) is one of the parameters of Langmuir equation. The initial slope of the sorption isotherm curve is very meaningful. A curve with an abrupt initial slope signifies a biosorbent with a high affinity for the ionic species at low concentration. The affinity is measured by the coefficient b in the Langmuir equation; the high value of b indicates high affinity. This method is best fit for Cd²⁺ removal by algae Gelidium and agar extraction algal waste [13].

3.2. Kinetic modeling

In order to investigate the controlling mechanism of biosorption process and to understand the biosorbate–sorbent interactions, various kinetic models have been used. The pseudo-first-order model derived by Lagergren has found wide application [14]. Pseudosecond-order kinetics can also very well describe these interactions in certain specific cases such as biosorption of metal ions, oils, dyes, herbicides and organic substances from aqueous solutions [15–18]. The pseudo-first-order rate equation is generally expressed as in Eq. (3):

$$dq_t/dt = K_{\rm ad}(q_{\rm e} - q_t) \tag{3}$$

It is the first equation of sorption (16,17). Where q_t and q_e are the amount sorbed at time t and at equilibrium, and K_{ad} is the rate constant of the pseudo-first-order biosorption process. After integration and applying boundary conditions, t = 0 and $q = q_{e}$, the integral from of Eq. (3) becomes:

$$\log(q_{\rm e} - q_t) = \log(q_{\rm e}) - (K_{\rm ad}t)/2.303 \tag{4}$$

Plot of log $(q_e - q_t)$ vs. *t* gives a straight line for first-order kinetics, which allows computation of the biosorption rate constant, K_{ad} .

If the experimental results do not obey the Eq. (3), pseudo-second-order kinetics [15] are used.

This is expressed as:

$$dq_t/dt = K(q_e - q_t)^2 \tag{5}$$

For boundary conditions t=0 to t=t and $q_t=0$ to $q_t=q_t$, the integrated form of the equation is:

$$q_t = q_e^2 \cdot K_t / (1 + q_e \cdot K_t) \tag{6}$$

Or, in the linear form,

$$1/q_t = 1/h + (1/q_e) \cdot t \tag{7}$$

when *t* approaches to 0 the biosorption rate q_t/t becomes the initial biosorption rate $h = Kq_e^2$.

In cases in which pseudo-second-order kinetics is applicable, the plot of t/q_t versus t gives a linear

relationship, which allows the computation of q_{e} , K, and h without knowing any parameter before hand. The model is very successfully applied for divalent cadmium removal by agents such as coconut copra meal [15], mulberry wood saw dust [17], poly aniline doped saw dust [18] and rice husk [19].

At low concentrations, adsorption sites took up the available metal more quickly. When the concentrations became high, the rate of diffusion became slow. This is because metal needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate.

The intraparticle diffusion equation given as:

$$R = K_{\rm s} t^b \tag{8}$$

In the linear form, Eq. (8) turns to Eq. (9):

$$\log R = b \log t + \log K_{\rm s} \tag{9}$$

where *R* is the percent metal biosorbed, *t* is the contact time of the biomass with the metal ions (min), *b* is the gradient of linear plots, and K_s is the intraparticle diffusion constant [16].

The multilayer biosorption kinetics study is explained by Elovich equation. This equation is generally suitable for systems with heterogeneous biosorption surface which explored that biosorbing sites increases exponentially with biosorption. The linear form of Elovich Eq. (10) is expressed as following:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \tag{10}$$

where q_t is the amount of Cd(II) ions biosorbed (mg g⁻¹) at time (t), α and β are known as the Elovich coefficients, α represents the initial biosorption rate (mg g⁻¹min⁻¹), and β is related to the extent of surface coverage [17] and activation energy for chemisorption (g mg⁻¹), respectively.

4. Biosorbent materials

The present review discusses about biosorbents for divalent cadmium removal. Properties and mechanism of different types of biosorbents investigated by different workers have been discussed. This review discusses about biosorbents such as (1) *Aspergellus niger*, (2) *Algae Gelidium* and agar extraction algal waste, (3) coconut shell powder, (4) *Bifurcaria bifurcata*, *Saccorhiza polyschides, Asphyllum nodosum, Laminaria ochroleuca, Pelvetia caniculata*, (5) blue-green algae *Spirulina*, (6) *Aeromonas caviae*, (7) coconut copra meal, (8) saw dust and neem bark, (9) nonliving *Egeria densa*, (10) Thermophilic Bacteria *Geobacillus stearothermophilus* and *Geobacillus thermocatenulatus* (11) dead streptomyces rimosus biomass, and (12) Alga *Sargassum muticum*. Biosorption, which uses the ability of biological materials to accumulate heavy metals is one of those technologies that have gained more importance, an increasing amount of research is being focused on it. There are several advantages of biosorption such as (1) environmental friendly, (2) Low cost or cost free biomaterial, (3) wide range of operating conditions such as pH, temperature, and metal concentration, and (4) recovery of adsorbed metal.

5. Comparison of adsorption capacities

Removal efficiency of adsorbents for the removal of cadmium(II) from aqueous solution is shown in Table 1.

6. Discussion

Among the various adsorbents that were taken into consideration, i.e. which have been selected, it is found that blue-green algae Spirulina sp., A. niger and saw dust are very efficient biosorbents as indicated by their high removal efficiencies. Chojanacka et al. [38] suggested that blue-green algae Spirulina sp. possessed a very high biosorption capacity. It was also reported that biosorption capacity depends on biomass growth conditions. Biosorbents are complex and variable materials. The composition of cell wall, to which cadmium(II) ions are bound, depends not only on the biosorbent species, but also on the environmental growth. The chemical composition of the cell wall, the presence and availability of metal-binding sites are not only associated with microbial species but depends also on growth conditions, availability of nutrients, stress, etc. The process of cadmium biosorption on NaOH-pretreated A. niger biomass was investigated in the batch mode by Amini et al. [20]. Twenty experiments designed by central composite design (CCD) were performed. Initial pH of the solution, biomass dosage, and initial cadmium(II) concentrations on the biosorption process was investigated, and the process was then optimized by means of response surface methodology (RSM). Conclusion was that biomass A. niger fungus particles are very efficient bioadsorbents for cadmium(II) removal from industrial wastewater effluents. Saw dust and neem bark are low cost and readily available natural adsorbents for the removal of cadmium(II) from aqueous solutions that are studied by Naiya et al. [23]. In their study, batch and sorption experiments have been carried out. Fourier Transform Infrared Spectrophotometer (FTIR) studies indicated the functional groups like C–O, C=O, and C–N are responsible for metal binding, and it was proved that cadmium(II) removal efficiency was very high (94.25% for saw dust and 84.5% for neem bark at pH 6). The adsorption of cadmium (II) ions on the surface of saw dust and neem bark probably explain by an ion-exchange mechanism based on surface complex formation model [23], which is facilitated by the dissociation of different functional groups present in wood tannin particles resulting in the formation of metal complex and is explained as follows:

 $m[RO_7(OH)_{11}] = m [RO_7(OH)_9(O^-)_2] + mH^+$ $Cd^{n+} + m [RO_7(OH)_9(O^-)_2] = Cd [RO_7(OH)_9(O^-)_2]_m^{n-m}$

The overall reaction can be represented as:

 $Cd^{n+} + m[RO_7(OH)_9(O^-)_2] = Cd[RO_7(OH)_9(O^-)_2]_m^{n-m} + mH^+$

where Cd^{n+} = cadmium ion with n + charge;

 $-RO_7(OH)_{11}$ = acidic part of wood surface, R represents the matrix part of the adsorbent mH⁺ = number of protons released.

7. Influence of pH on biosorption

It is known that pH is a key parameter, along with metal concentration and solution composition in determining biosorption levels. The efficiency of cadmium(II) removal was strongly affected by solution pH. Amini et al. [20] worked on A. niger and he showed the simultaneous effect of initial solution pH and the initial concentration of cadmium(II) in the aqueous solution on cadmium(II) removal efficiency. It was observed that an increase in cadmium(II) removal with increase in pH in the range of 2.8-6.2. Decrease in solution pH caused a reduction in the biosorption of cadmium(II). The reducing effect of acidic pH on the biosorption process could be explained by interference caused by high concentration of H⁺ which occupies the active metal binding sites and decrease cadmium(II) removal. The author showed that cadmium(II) removal (99.41%) was obtained at a solution pH of 6.12. Pino et al. [12] showed excellent removal capacities for Cd²⁺ by using coconut powder. They observed that the Cd^{2+} removal increased from 69% at pH 4 to 98% at pH 7. Solution pH is an important parameter affecting biosorption of cadmium(II) by algae. Lodeiro et al. [37] worked on marine macroal-

Table 1 Removal efficiency of ads	orbents for the remo	val of cadmium(II) from aque	cous solution	
Name of biosorbents/ adsorbents	Sorption capacity (mg/g) (a) or removal efficiency % (b)	Initial cadmium ion concentration (mg/L)	Experimental conditions	References
Rice husk	26.73 (a)		Rice husk = 500 mg, $Cd^{2+} = 0.1 \text{ mM/L}$, $pH \sim 2.0-6.0$, $Temp = 25 ^{\circ}C$	[19]
Mulberry wood saw dust	403.73 (a)	5.0	Mulberry wood saw dust = 0.1 g, Cd^{2+} = 5 µg mg L ⁻¹ , pH -6.0 at room temperature	[17]
Poly aniline doped saw dust	136.05 (a)	50	Poli aniline = 4 g/L , $\text{Cd}^{2+} = 50 \text{ mg/L}$, pH -5.0 , Temp = $20-60 \text{ °C}$	[18]
Aspergellus niger (fungus	82.2% (b)	0.3 - 37.5	Aspergellus miger = 0.1–7.5 g/L, Cd^{2+} = 0.5–37.5 g/L, pH ~ 1.3–8.7	[20]
particle)	96.7% (b)	25.8 and dosage of biomass = 5.8 mg/L.		[20]
Gelidium	87% (b)	11.0	Gelidium = $90.7-7.5$ g/L, Cd ²⁺ = 91.8 mg/L	[13]
	71% (b)	28.9	I	
	58% (b)	50.0	1	
	38% (b)	91.8	1	
Algal waste	79% (b)	6.4	Algal waste = $91.8-7.5$ g/L, Cd ²⁺ = 91.8 mg/L	[13]
	70% (b)	22.0		
	50% (b)	45.8	1	
	50% (b)	2.06	1	
Green coconut shell	285.7 (a)	20-1,000	Green coconut shell powder = 5 g/L , Cd ²⁺ = 20.0 mg/L, pH -7,	[12]
powder Marine algae			Iemp=Z/C	
Bifurcaria bifurcata	61.02±0.3 (a)	250	Bifurcaria bifurcata = 2.5 g/L, Cd ²⁺ = 250 mg/L, pH \sim 4.8–5.6, Temp = 25 °C	[21]
Saccorhiza polyschides	71.82±0.06 (a)	250	Saccorniza polyschides = 2.5 g/L, Cd ²⁺ = 250 mg/L, pH \sim 4.8–5.6, Temp = 25 °C	
Ascophyllum nodosum	71.90±0.14 (a)	250	Ascophyllum nodosum = 2.5 g/L, Cd ²⁺ = 250 mg/L, pH \sim 4.8–5.6, Temp = 25 °C	
Laminaria ochroleuca	69.68±0.14 (a)	250	Laminaria ochroleuca = 2.5 g/L, Cd ²⁺ = 250 mg/L, pH \sim 4.8–5.6, Temv = 25 $^{\circ}$ C	
Pelvetia caniculata	67.62±0.13 (a)	250	Pelvetia caniculata = 2.5 g/L, Cd ²⁺ = 250 mg/L, pH \sim 4.8–5.6, Temp = 25 °C	
Aeromonas caviae particle (dead biomass) [a gram-negative bacteria]	155.32 (maximum) (a)	Biomass concentration 100 g/L at pH 7 and at 20°C Cd(II) concentration 5 mg/L	Aeromonus caviae particle = $(0.5, 1, \text{ and } 2 \text{ g/L}, \text{ Cd}^{2+} = 5 \text{ and } 50 \text{ mg/}$ L, NaNO ₃ = 0.01 and 0.5 M, pH 7.0, Temp = 20°C	[22]

(Continued)

Table 1 (Continued)				
Name of biosorbents/ adsorbents	Sorption capacity (mg/g) (a) or removal efficiency % (b)	Initial cadmium ion concentration (mg/L)	Experimental conditions	References
Saw dust	26.73 (a) 94.25% (b)	At optimum pH value 6	Saw dust = 10 g/L , Cd ²⁺ = 10 mg/L , pH 6.0	[23]
Neem bark	25.57 (a) 84.5% (b)	At pH 6	Neem bark = 10 g/L , Cd ²⁺ = 10 mg/L , pH 6.0	[23]
Olive stone carbon Sun flower stalks	5.91 (a) 42.18 (a)		Temp = 20 and 40°C Sun flower stalks = 50–1,000 ppm, Cd ²⁺ = 1,000 ppm, pH 5.16, Temp = 25°C	[24] [25]
Spent grain Carboxy methyl cellulose	17.3 (a) 28.7 (a)		- Carboxy methyl cellulose = $30-700 \text{ mg/L}$, Cd ²⁺ = 200 mg/L , pH 6.0, Temp = 20° C	[26] [27]
Sugar cane bagasse Wheat hran	10.7 (a) 21 0 (a)		Sugar cane bagasse = $0.02-1$ g, Cd ²⁺ = 20 mg/L , pH 5.8, Temp = 28° C	[28] [29]
Aspergellus niger Bone char	82.2% 61.72 (a)		Aspergellus niger = 0.1–7.5 g/L, Cd ²⁺ = 0.5–37.5 mg/L, pH \sim 1.3–8.7 Bone char = 0.25 g, Cd ²⁺ = 0.2–6.0 mM/L, pH 5.0, Temp = 20°C	[20] [30]
Tree fern Maize bran Grane stalk waste	16.3 (a) 7.43 (a) 27 9 (a)		Tree fern = 53-61 µm, $Cd^{2+} = 65.8-280 \text{ mg/dm}^3$, Temp = 25 °C -	[31] [30] [31]
Egeria densa (non-living biomass)	70% (b) at 30°C and at pH 5.2	0.40	pH 5.0, Temp=30°C	[32]
Geobacillus stearothermophilus and Geobacillus thermocatenulatus			G. thermocatenulatus = $(3.8 \pm 0.06) \times 10^8$ cells/mL, <i>Geobaciltus stearothermophilus</i> = ranged from $(4.8 \pm 0.06) \times 10^8$ to $(5.3 \pm 0.07) \times 10^8$ cells/mL, Cd ²⁺ = 5 ppm, pH ~ 3.5 -10.0. Temp = 55 °C	[33,34]
Streptomyces riomosus (dead biomass)	63.3 (a)	210.22 mg/L	Streptomyces riomosus = 3 g/L , Cd ²⁺ = 100 mg/L , NaOH = 0.1 M	[35,36]
Sargassum muticum (Invasive Alga in Europe)	65 (a) (raw biomass) 95 (a) (protonated biomass) at pH 10	250	Sargassum muticum = 10 g/L , $\text{Cd}^{2+} = 10-250 \text{ mg/L}$, pH 4.5, Temp = 25 °C	[37]

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gae and showed that the uptake being almost negligible at $pH \leq 2$ and reaching a plateau at around pH 4. Chojnacka et al. [38] worked on blue-green algae Spirulina sp. and showed that overall biosorption process is strongly pH-dependent, and it was confirmed experimentally. The worker Ofomaja et al. [15] proved that biosorption of cadmium(II) by coconut copra meal depends on initial solution pH and initial cadmium concentration. The author in his study showed that as the initial solution pH is reduced from 5.53 to 3.53, the equilibrium biosorption of cadmium (II) on copra meal is reduced. The author Naiva et al. [23] in his study on biosorption of cadmium(II) by saw dust and neem bark showed that the optimum pH for the adsorption of cadmium(II) was found to be six. The author Modenes et al. [32] in their study on nonliving Egeria densa biomass showed that the pH threshold for cadmium adsorption was 5.2. Hetzer et al. [33] in their studies showed that at a given biomass concentration, increase in the pH results increased Cd²⁺ adsorption. Lodeiro et al. [37] worked on biosorption of cadmium(II) by algae, Sargassum muticum and found that at pH value lower than two, the cadmium(II) uptake capacity is almost negligible and maximum uptakes were found for pH higher than 4.5.

8. Instruments used in analytical method in the biosorption of cadmium(II)

Several instruments and analytical methods have been used to study cadmium(II) binding to biomaterials. Scanning electron microscope was used to study the outer surface, microporosity, and pore size of nonviable *A. niger* [20]. FTIR was used for the characterization of biosorbents.

8.1. Experimental design methodology

Optimum condition for the biosorption of cadmium(II) by *A. niger* [20] used CCD and RSM. In case of biosorption of cadmium(II) by green coconut shell powder the author, Pino et al. [12] used scanning electron microscope to evaluate the morphological characteristics of coconut. In order to determine the deprotonation constants and absolute concentrations of the specific functional groups present on the algal cell walls, potentiometric titration was performed by the author Chojnacka et al. [38]. In order to search the functional groups in the case of biosorption of cadmium(II) by saw dust and neem bark, author Naiya et al. [23] used FTIR. Hetzer et al. used surface

complexation models for quantifying cadmium(II) adsorption by thermophilic microorganism [33,34]. In order to know the functional groups that were responsible for cadmium(II) biosorption, IR analysis of the biomass was performed [39–45]. Kinetics investigation of the equilibrium data showed that the biosorption of Cd^{2+} onto algae followed well the pseudo-second-order kinetic model [40]. However, over the past few years, pseudo-second-order kinetic model has been considered to be among the most appropriate. Bioremediation using microorganisms offers an attractive option in treating wastewater containing composite pollutants of Cd(II) [42,43].

9. Conclusion

Among the various biosorbents blue-green algae *Spirulina* sp. [38] is the most efficient biosorbent. The authors Chojnacka et al. [38] quantitatively investigated the binding sites present at the surface of *Spirulina* sp., using both potentiometric titrations and adsorption isotherms. It was shown that blue-green algae *Spirulina* sp. possessed a very high maximum biosorption capacity. Among the saw dusts, mulberry has the highest adsorption capacity.

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