

Sorption of Chromium Oxy-Anions onto Cationized Ligno-Cellulosic Material

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ABSTRACT: Quaternary ammonium groups were grafted onto ligno-cellulosic material (cotton, wood sawdust, and maize-cob flour) to obtain a support able to adsorb oxy-anions containing chromium atoms (chromate and dichromate). For both anions in aqueous solutions, adsorption proceeded very quickly and reached a limit value dependent on the rate of ammonium grafting; at saturation, the Cr/N⁺ ratio was always close to 1/1 for chromate anions, but two

ammonium sites were needed to link a dichromate anion in a stable structure, resulting in the same 1/1 Cr/N⁺ ratio. Tentatives for modeling the adsorption process were performed with the Langmuir, Freundlich, and Jossen equations. A nearly total desorption occurred only when these saturated supports were treated with solutions of high ionic strength (4M potassium chloride). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1660–1665, 2003

INTRODUCTION

Industrial plants are likely to discharge a lot of pollutants in the soil, rivers, and ground waters from their waste waters. Among these pollutants, heavy metals are very toxic, even at low concentrations, due to their possible storage in the food chain. Primary treatment by precipitation in a basic medium allows the elimination of a major part of the aqueous metal load, but legislation generally requires residual concentrations lower than 1 ppm, typically 0.1 mg/L.^{1,2} Methods to reach these levels involve ion exchange, adsorption onto activated carbon, membrane filtration, and inverse osmosis, which are efficient but expensive.

Ligno-cellulosic byproducts from the raw biomass or arising from agriculture (e.g., stems, fruit shells) or wood processing (e.g., wood chips, sawdust, flour) are available at large rates and exhibit interesting capacities as pollutant adsorbents. When ligno-cellulose is chemically modified, it may present still higher capacities with a specificity to catch a particular kind of pollutants. For heavy metals, for instance, various supports have been successfully used: dyed cottons or agricultural waste,^{3–6} carboxymethyl cellulose,^{7,8} and celluloses modified with nitrogen-containing groups.^{9–12}

In previous studies, cellulose modified through amidoximation^{13,14} has been used for metal-ion com-

plexation [among them, Cr(III)], and cationized cellulose has been used for anionic dye adsorption.^{15–17} In this study, particular attention was devoted to chromium, a highly toxic metal, whose pollution sources include surface treatments such as electroplating, wood preservatives, pigment manufacturing, and tanneries. Hexavalent chromium is frequently used as an oxidative reagent or corrosion inhibitor, and many attempts have been made to catch this polluting species from aqueous medium onto mineral supports [e.g., activated carbon, ferric and chromium(III) hydroxides] or vegetal byproducts after eventual treatment: Table I summarizes some literature results with the adsorption capacities of various ligno-cellulosic materials.^{18–23} This study concerned the adsorption of anionic forms of Cr(VI), namely, the chromate and dichromate moieties, onto different cationized materials and also their desorption from such supports.

EXPERIMENTAL

Materials

Syrian cotton fibers were furnished by Société Internationale Tunisienne de Textile (SITEX, Tunisia). Wood sawdust and maize-cob flour were furnished by Société Parisienne des Sciures (France). Wood sawdust had a particle size range of 1.6–0.9 mm. It consisted of mainly spruce (85%) and also pine, fir, and poplar. The particle size range for maize-cob flour was 0.53–0.20 mm. Before use, the various materials were dried at 100°C for 24 h and Soxhlet extracted with ethanol.

Potassium chromate and dichromate were purchased from Aldrich (Sigma-Aldrich Chimie Sarl,

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TABLE I
Adsorption of Cr(VI) as $\text{Cr}_2\text{O}_7^{2-}$ onto Various Ligno-Cellulosic Materials

Adsorbent	Adsorption capacity (mg/g)	Reference
Raw material		
Sawdust	4.4	18
Coconut fibers	29	19
Palm fibers	14	19
Barks (<i>Acacia arabica</i>)	12	20
Coniferous leaves	5	21
Modified material		
Carbonized tea leaves	43	22
Quaternized cellulose derivatives	7	23
Cationized cellulose	64.5	This work
Cationized wood sawdust	39.5	This work
Cationized maize-cob flour	41.6	This work

Saint-Quentin Fallavier, France) and used at concentrations up to $35 \times 10^{-3} \text{ M}$ in deionized water. For these concentrated mother liquors, the pH of the deionized water (5.6) was lowered when dissolution of dichromate occurred (new pH = 4.0) and increased when chromate was solubilized, reaching a value of 8.8. This was due to the shift of the chemical equilibrium involving chromate, dichromate, and water. The pollutant solutions were all used at the final pH values obtained at the high concentration or after adequate dilution. 1,5-Diphenyl carbazide was purchased from Acros (Acros Organics France, Noisy-le-Grand, France).

Chemical treatment

Cationization of ligno-cellulosic material was performed as previously described,^{15,16} and the supports were characterized by nitrogen analysis (Table II). Depending on the reaction conditions, four values of the ammonium content (C_a) were obtained for cotton (between 0.31 and 1.32 mmol of ammonium sites/g of support), two were obtained for sawdust ($C_a = 0.50$

and 0.78 mmol/g), and only one was obtained for maize-cob flour ($C_a = 0.79 \text{ mmol/g}$).

Sorption procedure

Adsorption was realized in batch procedure by simple contact under stirring between the cationized material (0.1 g) and 10 mL of the aqueous solution of chromium derivative (bath ratio = 1/100 g/mL). The experiment temperature appeared to have no appreciable effect on the adsorption capacity for these two anions, contrary to the sorption of large organic molecules such as dyes,^{15,16,24} where an increase of the temperature generally induces a desorptive effect. Therefore, all assays, described later, were conducted at room temperature, that is, in the range $18 \pm 2^\circ\text{C}$. The amount of adsorbed chromium (Q_a) was deduced by the difference with the residual pollutant in the solution (Q_r). Spectrometric determination of chromium in solution was performed after obtention of the dichromate/diphenylcarbazine colored complex at 540 nm^1 with an Uvikon 941+ spectrometer. Titration of chromate was performed after chromate was transformed into dichromate in acidic medium (H_2SO_4 , pH = 1–1.3).¹ Calibration of the detector response in the concentration range 0.1–1.5 mg/L gave a straight line with a correlation coefficient of 0.999.

Tentatives for the desorption of these anions from the supports were performed with pure water or potassium chloride solutions.

RESULTS AND DISCUSSION

Adsorption of chromate and dichromate

When nontreated cotton was used in the conditions described previously, no adsorption of chromium derivative occurred. On the contrary, Figure 1 shows that the rate of adsorption onto cationized cotton was very fast; an equilibrium was reached within 10 min. Figures 2 and 3 represent the quantities adsorbed (Q_a)

TABLE II
Quantities of Chromate and Dichromate Anions Adsorbed by Cationized Material for Various C_a Values

	Treated cotton				Wood sawdust			Maize-cob flour	
					Nontreated	Treated	Nontreated	Treated	
Ligno-cellulosic support									
Nitrogen content ^a (%)	0.44	1.06	1.54	1.86	0.10	0.70	1.10	0.15	1.11
C_a (mmol/g)	0.31	0.75	1.10	1.32	—	0.50	0.78	—	0.79
Chromium derivative adsorption									
Q_a									
CrO_4^{2-} (mmol/g)	0.31	0.73	1.05	1.29	0.018	0.44	0.77	0.023	0.79
CrO_4^{2-} (mg Cr/g)	16.1	37.9	54.6	67	0.93	22.9	40.0	1.2	41.0
Q_a									
$\text{Cr}_2\text{O}_7^{2-}$ (mmol/g)	0.10	0.36	0.55	0.62	0.010	0.20	0.37	0.013	0.40
$\text{Cr}_2\text{O}_7^{2-}$ (mg Cr/g)	10.4	37.4	57.2	64.5	1.04	20.8	39.5	1.35	41.6

^a Determined by microanalysis.

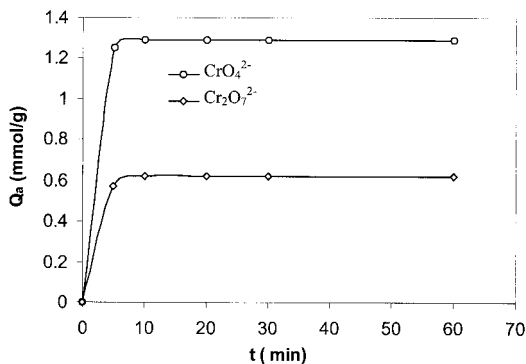


Figure 1 Adsorption of chromate and dichromate anions from a 6 g/L aqueous solution onto cationized cotton ($C_a = 1.32$ mmol/g) versus time.

and remaining in the solution (Q_r) when the initial quantity (Q_i) increased for chromate and dichromate anions, respectively. A saturation level was reached when about two times the actual adsorbed quantity was introduced. This behavior was quite different of that observed for interaction between the same cationized material and oleate anion:²⁵ In this last case, the curves for Q_a and Q_i were superimposed, and no oleate remained in the solution unless the saturation of the sorbent was attained. This was attributed to the presence of the hydrophobic tail, which conferred to the oleate anion a surfactant behavior (critical micelle concentration = 0.456 g/L), whereas chromate and dichromate were very soluble in water (629 and 110 g/L, respectively, at 20°C).

This saturation level for chromate and dichromate depended on the C_a value of the various supports (Table II), but in each case, it could be concluded that chromate adsorption corresponded to one anion per ammonium site, whereas dichromate adsorption required one anion per two ammonium sites. Nevertheless, the Cr/N⁺ ratio was always close to 1/1, as was previously observed for manganese when the adsorption of permanganate anion was performed onto cat-

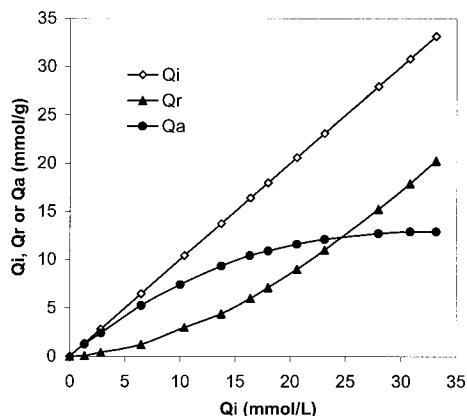


Figure 2 Proportions of Q_a and Q_r versus Q_i for chromate anions ($C_a = 1.32$ mmol/g).

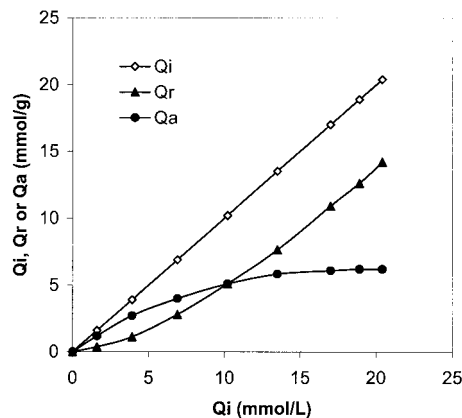


Figure 3 Proportions of Q_{ar} and Q_r versus Q_i for dichromate anions ($C_a = 1.32$ mmol/g).

ionized cellulose.¹⁷ When ammonium sites were more and more spaced by a decrease in the C_a value, it was expected that a dichromate anion would need only one ammonium site to be adsorbed, as was observed for the chromate anion. Unfortunately, this was not the case; at a low C_a value (0.31 mmol/g), only 0.10 mmol/g of $\text{Cr}_2\text{O}_7^{2-}$ was adsorbed onto cotton, whereas Q_a remained equal to C_a for chromate (Table II). It appears that the tetrahedral structure of chromate anion²⁶ allowed its fixation through an unique negative charge. On the contrary, the dichromate anion, with the same global charge, needed two ammonium sites to be effectively adsorbed. Its structure, where two tetrahedra are sharing one corner,²⁷ leads to an unstable interaction if not linked by the two negative charges. As a consequence, it is preferable to perform the adsorption of chromium oxy-anions at a high pH value where the chromate form is favored and to avoid a too acidic value where the dichromate form exhibits a high oxidative power toward all organic matter.

Adsorption on nontreated wood sawdust or maize-cob flour showed a very low value, which increased

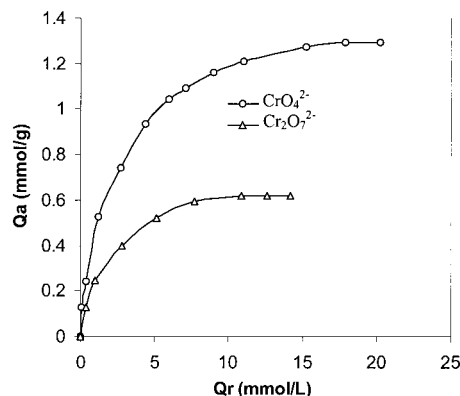


Figure 4 Adsorption isotherms of chromate and dichromate anions onto cationized cotton ($C_a = 1.32$ mmol/g).

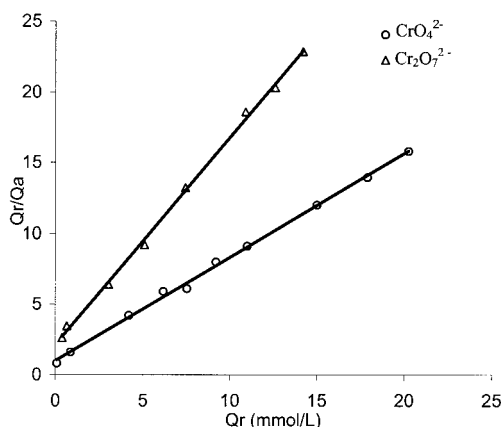


Figure 5 Langmuir plots for the sorption data of chromate and dichromate anions onto cationized cotton ($C_a = 1.32$ mmol/g).

considerably when the supports were cationized (Table II), also leading to a Cr/N⁺ ratio of 1/1.

Adsorption isotherms

Figure 4 represents the adsorption isotherms Q_a versus Q_r for chromate and dichromate anions onto cationized cotton ($C_a = 1.32$ mmol/g). Both curves corresponded to a Langmuir-shaped L₂ type in the classification system proposed by Giles et al.,²⁸ as was often observed for the adsorption of molecules bearing ionic sulfonate groups (e.g., dyes) onto cellulose.²⁹ Thus, three attempts for the modeling of the experimental data were performed.

Analysis through the langmuir isotherm

The Langmuir equation in its linear form is given as

$$\frac{Q_r}{Q_a} = \frac{1}{Q \cdot b} + \frac{Q_r}{Q}$$

where Q represents the adsorbate concentration in the solid phase for a complete monolayer coverage or, if not possible, for the limit adsorption capacity (mmol/g) on sites and b is the Langmuir constant related to adsorption energy (L/mol). The product $Qb = K_L$ is the Langmuir equilibrium constant. Plotting the ratio of concentrations in the solution and in the solid versus the solution concentration gave straight lines (e.g., Fig. 5) from which the Langmuir constants for all the studied systems were estimated (Table III).

For CrO_4^{2-} , the three values of C_a , Q_a and Q were always very close to each other, whatever the support considered and for all capacities tested. For $\text{Cr}_2\text{O}_7^{2-}$, the same observation was made for $C_a/2$, Q_a , and Q values (except for the lowest C_a value). All these results confirm a strong ionic interaction between the anionic moieties and the cationized support, with a 1/1 ratio for chromate and a 1/2 ratio for dichromate.

This modeling involved K_L [$K_L = Qb$ (L/g)]. K_L represented the volume of polluted solution, which could be purified ($Q_r = 0$) by 1 g of support. When only the relatively well-defined cotton support is considered, the data in Table III indicate that K_L was around two times higher for chromate than for dichromate, with the same restriction as described previously for the low C_a value.

TABLE III
Langmuir, Freundlich, and Jossen Constants for the Sorption of Chromate and Dichromate Anions onto Cationized Materials

Chromium oxy-anion	Adsorbent	C_a (mmol/g)	Q_a (mmol/g)	Langmuir constants			Freundlich constants		Jossen constants			Correlation coefficient
				Q (mmol/g)	b (L/mmol)	K_L (L/g)	P	n	i (L/g)	j (L/mmol)	m	
CrO_4^{2-}	Cotton	1.32	1.29	1.36	0.66	0.90	0.38	1.60	0.744	0.614	0.941	0.998
		1.10	1.05	1.10	0.89	0.98	0.39	1.69	1.137	1.278	0.899	0.998
		0.75	0.73	0.77	1.55	1.20	0.36	1.73	1.075	1.412	0.967	0.997
	Sawdust	0.31	0.31	0.33	1.48	0.49	0.185	2.49	0.813	3.121	0.889	0.986
		0.78	0.77	0.82	1.10	0.91	0.33	1.83	1.293	1.946	0.913	0.990
		0.50	0.44	0.46	2.13	0.98	0.28	2.40	1.216	2.791	0.961	0.980
$\text{Cr}_2\text{O}_7^{2-}$	Maize-cob flour	0.79	0.77	0.81	0.93	0.76	0.33	1.43	1.257	1.767	0.934	0.991
		1.32	0.62	0.68	0.69	0.46	0.22	1.93	0.411	0.676	0.938	0.993
		1.10	0.55	0.59	0.81	0.48	0.19	1.51	0.397	0.681	0.961	0.994
	Cotton	0.75	0.36	0.36	1.47	0.53	0.19	1.94	0.449	1.033	1.040	0.986
		0.31	0.10	0.13	2.47	0.32	0.09	2.80	2.730	32.67	0.781	0.988
		0.78	0.37	0.39	1.51	0.59	0.19	1.98	0.466	1.140	0.996	0.987
Sawdust	0.50	0.20	0.21	2.95	0.62	0.14	2.42	0.730	3.727	0.938	0.979	
	0.79	0.40	0.42	1.09	0.46	0.18	2.14	0.523	1.447	0.964	0.989	
	0.79	0.40	0.42	1.09	0.46	0.18	2.14	0.523	1.447	0.964	0.989	

Analysis through the freundlich isotherm

The Freundlich equation

$$Q_a = P(Q_r)^{1/n}$$

where P and n evaluate the adsorption capacity and the adsorption intensity, respectively, gave generally two straight lines when used in its linear representation, $\log Q_a$ versus $\log Q_r$. Freundlich constants (Table III) were deduced from the slope and intercept with the axis of the line having the highest slope (Fig. 6).

When the various supports with the same C_a value (0.75–0.79 mmol/g) were compared, the P constants were very similar, and the n constants were in a restricted range. This also confirmed the major role of the cationic charge of the support in the adsorption phenomenon, independently of the nature of the support.

Analysis through the jossen isotherm

The modeling with Jossen equation

$$Q_a = \frac{i \cdot Q_r}{1 + j \cdot Q_r^m}$$

represents a combination between the two previous models with the three constants i , j , and m taken into account. These constants, obtained from adsorption data by an iterative procedure, are given in Table III. Figure 7 shows that this last model better fit the experimental data, as compared to Langmuir and Freundlich models, for both chromate and dichromate anions.

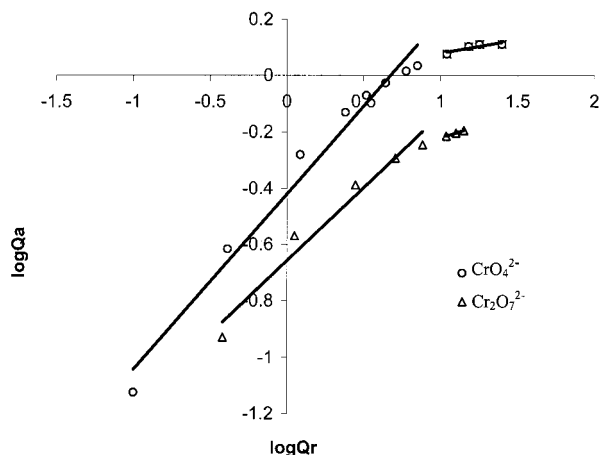


Figure 6 Freundlich plots for the sorption of chromate and dichromate anions onto cationized cotton ($C_a = 1.32$ mmol/g).

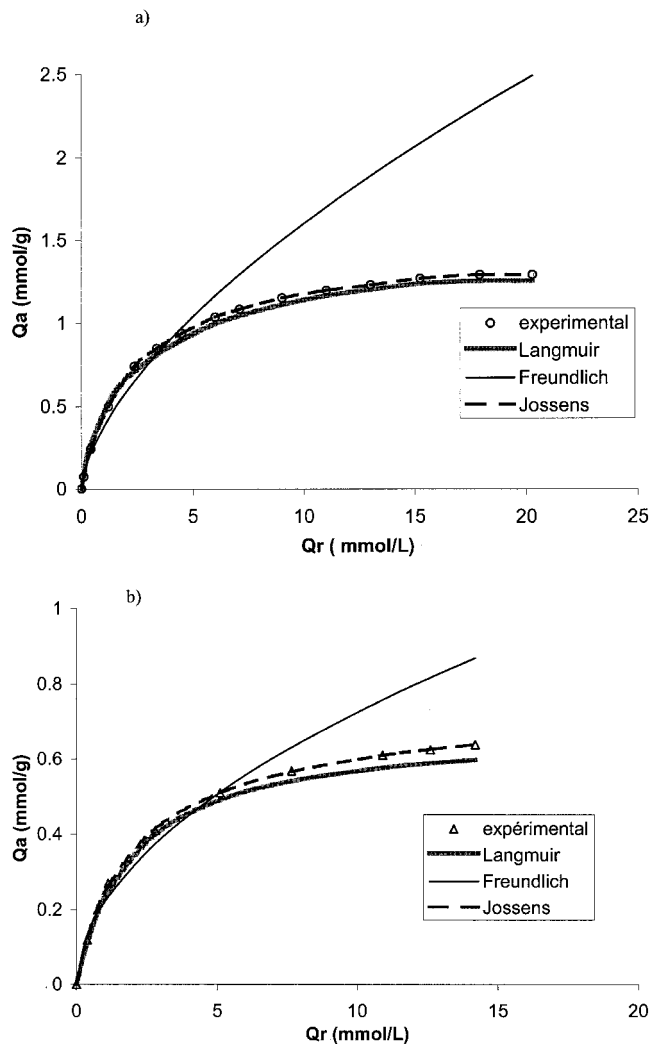


Figure 7 Comparison of theoretical isotherms with experimental data for the adsorption of (a) chromate and (b) dichromate anions onto cationized cellulose ($C_a = 1.32$ mmol/g).

Desorption of oxy-anions

To desorb these anions, washing with water appeared to be ineffective at a low or high bath ratio (Table IV). This result is of interest in the scope of water depollution because it indicates that the salting-out of the adsorbed pollutant will be avoided. The saturated supports had to be immersed in potassium chloride solution with a relatively high concentration (Table IV) to release the chromium oxy-anions. The percentage of desorbed anion increased with the ionic strength of the KCl solution, reaching a 90–95% value with 4M KCl. This meant that the quasitotal desorption of chromate anion, for instance, needed a quantity of chloride anion 150 times higher.

CONCLUSIONS

Cationized ligno-cellulosic materials were able to sorb chromium in the form of the anionic moieties CrO_4^{2-} or

TABLE IV
Desorption of Chromate and Dichromate Anions by Water Washing or by Potassium Chloride Solutions of Various Concentration (Bath Ratio = 1/50 g/mL)

Pollutant	Saturated cotton ^a Q_a (mmol/g)	Washing with water		Desorption by KCl solution ^b	
		Volume (mL)	Percentage of desorption (%)	Concentration (mol/L)	Percentage of desorption (%)
CrO_4^{2-}	1.29			2	70
		5	0	3	90
		100	18	4	95
$\text{Cr}_2\text{O}_7^{2-}$	0.62			2	55
		5	0	3	82
		100	19	4	90

^a 1 g of loaded support.

^b 50 mL of solution.

$\text{Cr}_2\text{O}_7^{2-}$. Adsorption occurred very quickly, and a plateau value was obtained according to the C_a of the adsorbent with the formation of a 1/1 Cr/N⁺ association. The Jossen model was the most adequate to describe these adsorptions. Desorption was possible by exchange with chloride anions used at a high concentration. As shown in Table I, such cationized supports were more efficient than nontreated ligno-cellulosic materials, with adsorption capacities ranging from 40 to 64 mg of chromium/g. In comparison with amidoximated cellulose, which could adsorb Cr(III) cations at a rate equivalent to the grafted sites ($Q_a = C_a = 3.9$ mmol/g or 200 mg/g¹³), the adsorption of chromium oxy-anions by cationized ligno-cellulose reached only a third of this value; it was not possible to increase the C_a of cationized ligno-cellulose because it may have lead to a partially soluble material, which is unfavorable in the scope of water depollution.

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