Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution

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Abstract

The capability of carbon nanotubes (CNTs) to adsorb lead (Pb) in aqueous solution was investigated. Batch mode adsorption experiment was conducted to determine the effects of pH, agitation speed, CNTs dosage and contact time. The removal of Pb(II) reached maximum value 85% or 83% at pH 5 or 40 mg/L of CNTs, respectively. Higher correlation coefficients from Langmuir isotherm model indicates the strong adsorptions of Pb(II) on the surface of CNTs (adsorption capacity X_m = 102.04 mg/g). The results indicates that the highest percentage removal of Pb (96.03%) can be achieved at pH 5, 40 mg/L of CNTs, contact time 80 min, and agitation speed 50 r/min.

Key words: lead removal; carbon nanotubes; kinetic modeling; adsorption

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Introduction

Carbon nanotubes (CNTs), a new member of the carbon family, have good anion and cation adsorption materials for water treatment, as they exhibit exceptionally large specific surface area. In addition to the remarkable mechanical properties, their hollow and layered nanosized structures make them a good candidate as absorbers. Various technologies are currently employed in industry to deal with heavy metals such as chemical precipitation, reverse osmosis (Ahalya *et al*., 2007) and adsorption or ion exchange (Lu *et al*., 2007).

In wastewater treatment, nanomaterials especially CNTs have been developed in remediation and end-of-pipe treatment technologies (Masciangioli and Zhang, 2003). Lead in wastewater comes mainly from the discharge of battery manufacturing, printing, dying and other industries (Li *et al*., 2002). Other major sources of lead in the environment include lead-based paint, household dust and food containers. Lead has been found to be acute toxic to human beings when present in high amounts in water. Studies have shown that young children, infants and pregnant women are particularly susceptible to unsafe lead levels (http://www.safe-drinking-water.com). For adults, increased levels of lead have been linked to high blood

pressure and damaged hearing. Drinking, eating, inhaling even at low level of lead can cause other serious health effects. The aim was to study the removal of lead from synthetic water using CNTs by optimizing the process parameters to maximize the removal.

1 Materials and methods

1.1 Experimental

The production of carbon nanotubes was conducted in two horizontal tubular reactors, using chemical vapor deposition (CVD) technique, which has been developed from Muataz (2005) technique. The horizontal reactors are a ceramic tube of 50 mm in diameter and 1200 mm in length and heated by silicon carbide heating element. The ferosine ($C_{10}H_{10}Fe$) catalyst of 100 mg was fixed at the first reaction chamber at 150°C for 10 min, while the second reaction chamber was used for the reaction with H_2O_2 and for growth processes at 800°C for 30 min. Hydrogen was used as a reacting gas and the argon was used for flushing the air from the system. Both of them were controlled by a flow meter.

1.2 Batch mode adsorption experiment

Experiments were conducted at 25°C to study the effects of initial solution pH, CNTs dosage, contact time, and

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agitation speed on the adsorption of Pb(II). Each test was conducted in volumetric flask and the initial and final concentration of Pb(II) were analyzed using atomic adsorption spectrometer (AAS) (AAnalyst 400, Elemer Precise, USA) at wavelengths of 283.3 nm for lead. The final concentration of each study was use to determine the Pb(II) removal percentage. The run orders for complete batch mode adsorption experiment were determined using matrix analysis (Levine, 2001).

2 Results and discussion

2.1 Effect of pH on the uptake of lead

The differences in percentage removal indicate that the initial pH would play a vital role in Pb(II) removal as shown in Fig. 1, where the percentage uptake of Pb(II) varied at different pH values (3–7). Previous study has stated that the adsorption of Pb(II) increases with an increase in solution pH from 3 to 7. This is because oxidation of CNTs with oxidized acid can introduce many functional groups such as hydroxyl, carbonyl and carboxyl on the surface of CNTs (Li *et al.*, 2002).

The decrease in percentage removal at pH 7 reflects a reduction of negative surface charge density on CNTs. Therefore, the presences of a negative charge on CNTs surface over the pH range were the main reason for Pb adsorption. H^+ should be considered as competitive ones in ion-exchange processes and consequently, ion exchange of metals favored by high acidity, which should, however, be lower than the minimum acidity of precipitation.

$$(M(H_2O)_x)^{c+} + H_2O \longleftrightarrow (M(H_2O)^{x-1}(OH))^{(c-1)} + H_3O^+ \tag{1}$$
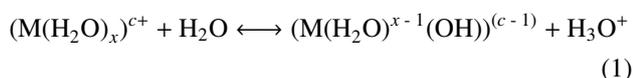
Consequently, the above equilibrium (Reaction (1))
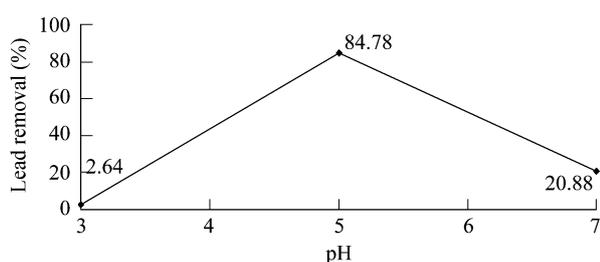
Fig. 1 Effect of pH on the uptake of lead. Conditions: contact time 20 min; adsorbent 20 mg/L; pH 3, 5, and 7.
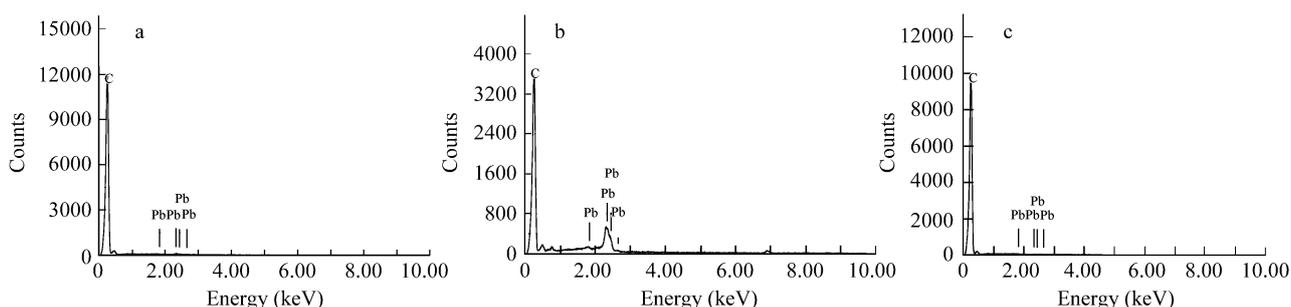
shifted to the left at lower acidity and more highly charged metal complexes are formed. This fact is beneficial for the exchange. Therefore, very low adsorption of the metal takes place from highly acidic solutions (Inglezakias *et al.*, 2007). The white crystal structure in the image was analyzed as Pb(II). This was supported by energy dispersive X-ray (EDX) analysis in Fig. 2, where CNTs at pH 5 obtained the highest peak.

The distribution of Pb at pH 5 was the highest (10.91%) compared to pH 3 (0.45%), and pH 7 (1.74%). Therefore, it can be concluded that Pb(II) have been adsorbed on the surface of CNTs. The maximum adsorption can be achieved at pH 5 with removal percentage of 84.78% (Fig. 1). The result agreed with the result by Bismarck and Wuertz (1999), that acidic surface sites give a negative zeta-potential, whereas basic sites give a positive zeta-potential. This implies that at low pH, a significant amount of basic groups which are able to induce a positive surface charge, are present on the surface.

2.2 Effect of agitation speed on the uptake of lead

As shown in Fig. 3, the removal percentage of lead is decreasing as the speed increases. The removal of lead reach to 37.76% at 50 r/min, while at 150 r/min only 3.49% of Pb(II) was removed from the solution.

It can be concluded that the effects of agitation speed on the uptake of lead are not significant for Pb(II) removal. As the speed increases, the suspension may not become homogeneous due to the rapid agitation. This will increase the boundary layer between the solid and liquid phase. Thus, the removal of Pb(II) could achieve maximum value at 50 r/min.

2.3 Effect of CNTs dosage on the uptake of lead

As shown in Fig. 4, the highest percentage removal (82.54%) occurred at high dosage (10 mg). The reason is that the high CNTs dosage provided more adsorption site for the attachment of Pb(II) and this accessibility greatly enhanced the adsorption of lead.

EDX analysis was conducted to verify the effect of dosage on the Pb(II) removal from aqueous solution (Fig. 5). It was observed that the high dosage of CNTs obtained a high peak. The Pb(II) distribution was 15.90% at 10 mg of CNTs compared to 1.74% at 5 mg. This verified Pb(II) have been adsorbed on the surface of CNTs.
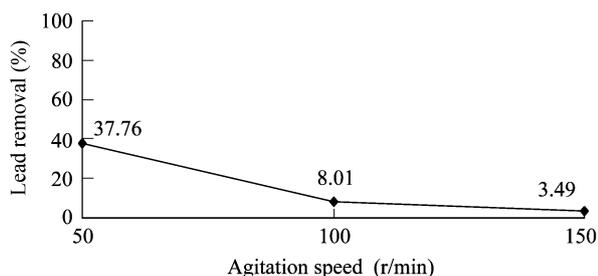

Fig. 2 Energy dispersive X-ray analysis of CNTs for pH 3 (a), 5 (b), and 7 (c).

Fig. 3 Effect of agitation speed on the uptake of lead. Conditions: contact time 120 min; adsorbent 40 mg/L; agitation speed 50, 100, and 150 r/min.
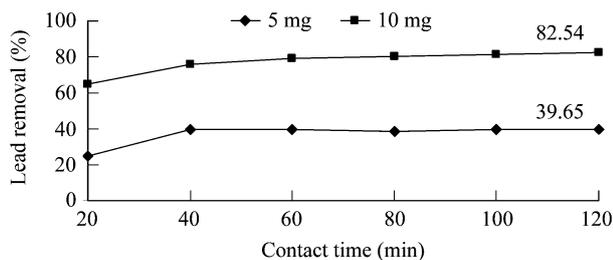
Fig. 6 Effect of contact time on the uptake of lead. Conditions: adsorbent 40 mg/L; pH 5; contact time 20 to 120 min.

Fig. 4 Effect of dosage on the uptake of lead. Conditions: adsorbent 20 and 40 mg/L; contact time 20–120 min.

Fig. 7 Pseudo second-order kinetics of Pb(II) using different dosage of CNTs.

2.4 Effect of contact time on the uptake of lead

The equilibrium time was measured from 20 to 120 min and the effect of contact time is determined by plotting the percentage uptake of Pb(II) against contact time (Fig. 6). It was observed that the removal rate was very fast for the first 40 min, but it gradually becomes slower until reached a maximum at 80 min. It was also detected that the percentage uptake of Pb(II) became saturated from 80 to 120 min.

2.5 Kinetics of adsorption

The kinetics were investigated using the information obtained from the effect of dosage (dry-weight basis) at 25°C at three different time intervals up to 100 min. The pseudo second-order equation (Fig. 7) was used in this study to investigate the mechanism of adsorption of lead by the CNTs and the potential rate-controlling steps, such as mass transport and chemical reactions (Ray *et al*., 2005).
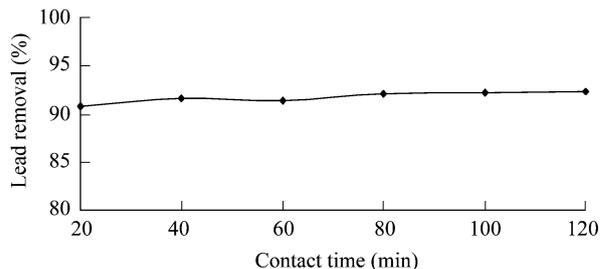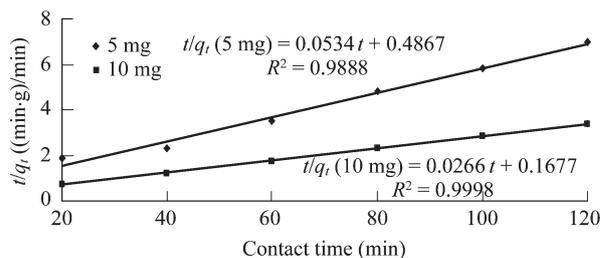
The values of pseudo second-order rate constant k^2, the

initial adsorption rate, h and the adsorption capacity (q_e) are presented in Table 1.

The plot of t/qt versus time as in Fig. 7 for both dosage of CNTs yields high correlation coefficients ($R^2 = 0.9888$ (5 mg) and $R^2 = 0.9998$ (10 mg)). The second order-rate constant obtained from this figure are 5.860×10^{-3} for CNTs dosage (5 mg) and 4.220×10^{-3} (g/(mg·min)) for CNTs dosage (10 mg). The second order rate constant indicates that higher dosage of adsorbent required less time to achieve initial adsorption of Pb(II) due to its greater surface area. The equilibrium adsorption capacity, q_e obtained from the graph also implies that the higher dosage of adsorbent ($q_e = 37.594$ mg/g) is capable to uptake more adsorbate compared to the lower dosage ($q_e = 18.727$ mg/g). This result indicates that the rate controlling steps in the adsorption process are chemisorptions, where interactions (chemical bonding) involved sharing or exchange of electrons between the adsorbate and the adsorbent (Ray *et al*., 2005). This proves that there are strong interactions between Pb and CNTs.
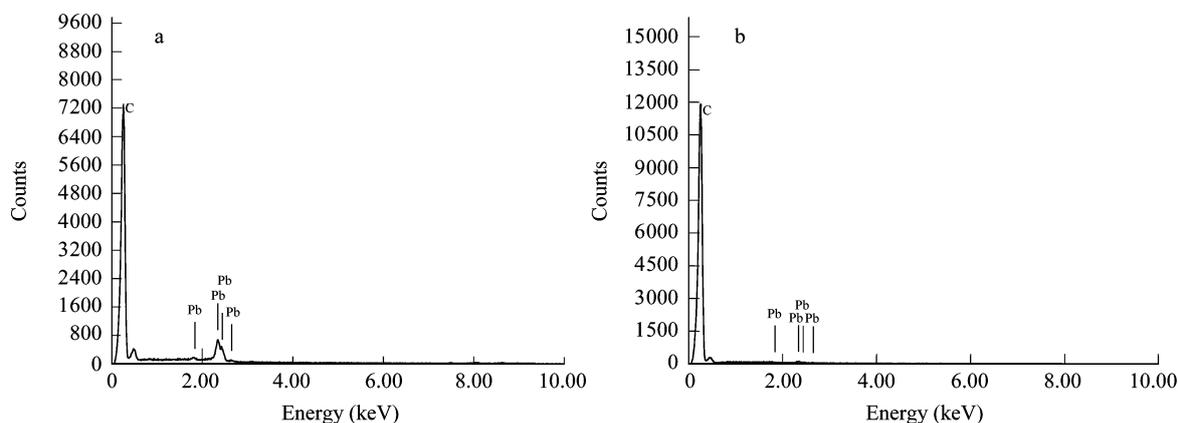
Fig. 5 EDX analysis of CNTs with different dosages. (a) 5 mg; (b) 10 mg.

Table 1   Kinetic parameters for pseudo second-order model

Adsorbent (mg)	q_e (mg/g)	h (m/ (g·min))	k^2 (g/(mg·min))	R^2
5	18.727	2.055	5.860×10^{-3}	0.9888
10	37.594	5.964	4.220×10^{-3}	0.9998

2.6 Adsorption isotherm

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Pb(II) by CNTs over the entire parameters range studied. The adsorption capacity for Langmuir (Xm) was 102.04 mg/g and for Freundlich (n) was 8.945 mg/g, determined from the slope as seen in equilibrium curve (Fig. 8).

Langmuir isotherm model shows better fitting (R^2 = 0.9966) with the experimental data compared to Freundlich isotherm (R^2 = 0.622). This indicates the applicability of monolayer coverage of Pb(II) on the homogeneous surface of the adsorbent. It is also due to the fact that, CNTs have greater surface area for metal adsorption (Karthikeyan *et al.*, 1996). The good correlation coefficient of Langmuir isotherm also indicates that Pb(II) is strongly adsorbed to the surface of CNTs. Therefore, it is verified that CNTs have great potential to be a good adsorbent for the removal of Pb(II) in water treatment. The usage of CNTs gives higher adsorption capacity (102.04 mg/g) compared to other adsorbents such as *Bacillus cereus* (70.423 mg/g) (Ray *et al.*, 2005), *M. spicatum* (46.69 mg/g) (Ahalya *et al.*, 2007), Oat (18.97 mg/g) (Rios *et al.*, 1999). This is due to the large surface area of CNTs that was oxidized at pH 5. At pH 5, the functional groups that were attached to the surface of CNTs were deprotonated, which contribute to an increase in the negative charges on CNTs surface. Therefore, this increased the ability of the adsorbent.

2.7 Modeling by statistical analysis

The factors in the adsorption study were examined using the graphical analysis, the best two levels for each factor
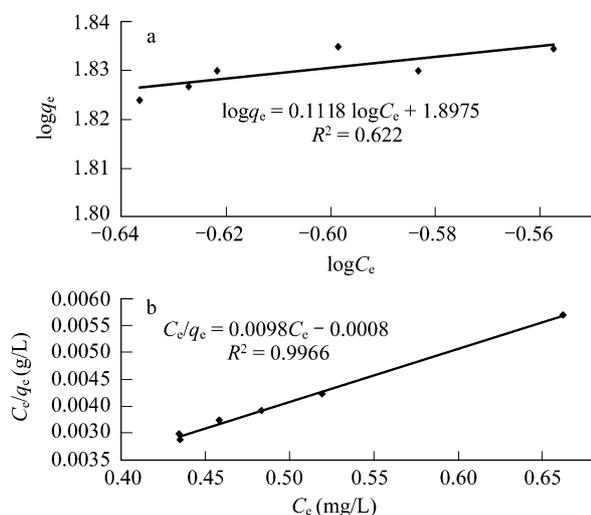

Fig. 8   Adsorption isotherms model for Langmuir kinetic model (a) and Freundlich kinetic model (b).

was chosen for the development of regression analysis using the MINITAB analysis to determine the maximum removal of Pb(II) by CNT. The design characteristics which have been used to develop an optimization equation are as follows: full factorial, 2 replicates, 4 factors, 2 levels, 1 centre point.

2.8 Modeling for the removal of lead using CNTs

For lead removal, five factors, namely, pH (A), agitation speed (B), CNTs dosage (C) and contact time (D) were selected to optimize the lead removal R_{Pb}.

$$
\begin{aligned}
R_{Pb} = &(528 - 72.7A - 5.07B + 18.5C - 2.24D + \\
& 0.722\,A \times B - 4.00A \times C + 0.385A \times D - \\
& 0.419B \times C + 0.0294\,B \times D + 0.0581C \times D + \\
& 0.0843A \times B \times C - 0.00603\,A \times B \times D) \times 100\%
\end{aligned}
$$
$$(2)$$

In order to search the optimum lead removal, experiments were designed based on central composite design. The second-order regression model relates to the lead removal with the independent variables of A, B, C, and D. The value of the adjusted determination of coefficient was also very high (95.09%) to indicate a high significance of the model (Akhnazaroza and Kefarov, 1982; Khuri and Cornell, 1987). The ANOVA of quadratic regression model demonstrated the model was highly significant, as an evident from the Fisher's F-test with a very low probability

Table 2   Analysis of variance (ANOVA) for the second-order regression model

Source	Degree of freedom	Sum of squares	Mean squares	F	$P > F$
Regression	12	33484.7	2790.4	89.96	0.000
Residual error	19	589.3	31.0		
Total	31	34074.0			

Table 3   Statistical analysis for evaluating the linear, quadratic, and interaction effects

Predicator	Coefficient	Standard error coefficient	t-Value	P-value
Constant	528.49	83.02	6.37	0.000
pH (A)	−72.74	13.57	−5.36	0.000**
Agitation speed (B)	−5.068	1.044	−4.85	0.000**
CNTs dosage (C)	18.512	7.667	2.41	0.026*
Contact time (D)	−2.2405	0.9583	−2.34	0.030*
$A \times B$	0.7216	0.1717	4.20	0.000**
$A \times C$	−3.995	1.245	−3.21	0.005**
$A \times D$	0.3854	0.1557	2.48	0.023*
$B \times C$	0.41927	0.09582	−4.38	0.000**
$B \times D$	0.02935	0.01198	2.45	0.024*
$C \times D$	0.05813	0.01969	2.95	0.008**
$A \times B \times C$	0.08425	0.01575	5.35	0.000**
$A \times B \times D$	0.006029	0.001969	−3.06	0.006**
Analysis of variance				
Source	DF	SS	MS	F	P
Regression	12	33484.7	2790.4	89.96	0.000
Residual error	19	589.3	31.0		
Total	31	34074.0			

R-Sq: R^2 obtained from the adsorption study (R-Sq = 98.3%); R-Sq(adj): adjusted R^2 variation in the adsorption capacity (R-Sq(adj) = 97.2%). * $P < 0.05$; ** $P < 0.01$.

Table 4   Comparison of various adsorbents and its percentage uptake of Pb(II)

Adsorbent	Condition				Removal (%)	Reference
	pH	Initial contact time (min)	Agitation speed (r/min)	Dosage (mg/L)		
Maize leaf	3	30		10000	96	Adesola *et al.*, 2006
Mountain laurel	5	30	300	10000	95.9	Adeyiga *et al.*, 2006
Common persimmon					95.9	
Eastern redbud					91.8	
Southern magnolia					92.9	
Activated carbon					93.9	
Clinoptilolite	4	45	200	20000	55	Inglezakias *et al.*, 2007
Bentonite	3	45	100		100	
Bacillus cereus M16	6	30	5500	1800	96	Ray *et al.*, 2005
CNTs	5	40		500	87.8	Li *et al.*, 2002
CNTs	5	40	50	40	96.03	This study

value ($P_{model} > F = 0.000$) (Table 2).

The coefficient of determination, R^2 that was obtained from this study is 0.983, which means 98.3% of the variation in adsorption capacity can be explained by the pH, CNTs dosage, and agitation speed and contact time. It was also noted that the adjusted R^2 obtained from this study is 97.2% of the variation in the adsorption capacity (Table 3). This adjusted R^2 is necessary when comparing two or more regression models that predict the same dependent variable but have different number of explanatory variables (Levine *et al.*, 2001). By this adjusted R^2, the best model can be identified. It can be concluded from this study that the most influential factors that contribute to the highest percentage removal of lead are pH, CNTs dosage and agitation speed in which the interactions of these factors contribute to the highest *t*-value and lowest *p*-value. Therefore, interactive effects are important for optimization of lead removal rather than the single factor for a time method (Kumar and Satyanarayana, 2007).

2.9 Optimum conditions for the removal of Pb(II) using CNTs

The highest predictive percentage removal is 96.03%. The parameters that contribute to these optimal conditions are pH 5, 10 mg dosage of CNTs in 250 mL Pb(II) solution, agitation speed at 50 r/min and contact time of 80 min. The control of carbon surface chemistry through the exclusive introduction of a certain surface group is a natural goal for the lead removal using carbon structures. It is highly challenging, as most methods give a surface covered with a mixture of acidic and basic groups. Moreover, the properties of each group are again dependent on its neighbors (Schlogl, 1999). Therefore, the deposition of metal particles is usually achieved through multistep and time-consuming procedures.

2.10 Comparative analysis of various adsorbents

In comparison with the adsorption kinetics of the various adsorbents, it was concluded that most of the removal process occurred very fast within the first 40 min. It can be concluded that the adsorption capability of the adsorbent is highly dependent on many factors such as surface functional groups, the specific surface area and the solution components (Table 4).

3 Conclusions

The optimum pH is 5 in which gave 85% removal of Pb(II) from aqueous solution. The percentage uptake decreased with an increase in agitation speed from 50 to 150 r/min, in which 50 r/min gave 37.76% removal. The percent removal of Pb(II) was observed to be optimal for higher dosage of CNTs, in which 10 mg contribute to 82.54% removal of Pb(II). The Langmuir model fitted best, in which the highest adsorption capacity is 102.04 mg/g. The effect of contact time experiment indicated that higher fraction of the Pb(II) migrates from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent. The overall adsorption rate demonstrated that the kinetics of the adsorption of Pb(II) on the CNTs was best described by pseudo second-order model. The results obtained from these analyses proved that this method of adsorption of Pb(II) using CNTs are promising for further development of water and wastewater treatment.

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