Research Article

Adsorption Equilibrium and Kinetics of the Removal of Ammoniacal Nitrogen by Zeolite X/Activated Carbon Composite Synthesized from Elutrilithe

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Zeolite X/activated carbon composite material (X/AC) was prepared from elutrilithe, by a process consisting of carbonization, activation, and subsequent hydrothermal transformation of aluminosilicate in alkaline solution, which was used for the removal of ammoniacal nitrogen from aqueous solutions. Adsorption kinetics, equilibrium, and thermodynamic were studied and fitted by various models. The adsorption kinetics is best depicted by pseudosecond-order model, and the adsorption isotherm fits the Freundlich and Redlich-Peterson model. This explains the ammoniacal nitrogen adsorption onto X/AC which was chemical adsorption in nature. Thermodynamic properties such as ΔG , ΔH , and ΔS were determined for the ammoniacal nitrogen adsorption, and the positive enthalpy confirmed that the adsorption process was endothermic. It can be inferred that ammoniacal nitrogen removal by X/AC composite is attributed to the ion exchange ability of zeolite X. Further, as a novel sorbent, this material has the potential application in removing ammoniacal nitrogen coexisting with other organic compounds from industrial wastewater.

1. Introduction

Water pollution, such as heavy metals, dyes, organic, and inorganic pollutants, is a serious problem for the human being with the rapid urbanization, industrialization, and technological innovations in various disciplines. Many researchers have developed different methods and materials to remove the contaminants [1–7]. Among them, high concentration of ammonium ions is the a major pollutant and is harmful to animal and human health and also attacks the water plumbing systems [8]. The removal of ammoniacal nitrogen has attracted great attention in wastewater treatment.

For the water treatment, several methods such as chemical precipitation, biological processes, ion exchange, and adsorption have been taken and applied to the removal of ammoniacal nitrogen from wastewater [9–12]. Among

these technologies, biological processes as one of the most widely used technologies are effective for wastewater with low concentration ammonium ions but require complicated configurations and process routing. However, the biological processes are usually helpless in dealing with the solution containing high concentration ammonium ions. So, the drive to remove the ammoniacal nitrogen with high concentration has motivated a significant increase in research activities. Compared with the other methods, ion exchange is more attractive owing to the advantages of simple operation and high effectiveness [13, 14].

Due to the excellent ion exchange ability and high surface area, natural zeolites [15, 16] and synthetic zeolites [17, 18] are employed to remove the ammoniacal nitrogen from aqueous solution by the ion exchange method. Karadag et al. [19] and Huang et al. [20] demonstrated that both the natural Turkish clinoptilolite and Chinese zeolite had strong ability to remove

ammonium from aqueous solutions. In recent years, many researchers have investigated ammoniacal nitrogen removal from aqueous solutions by using eco-friendly material, such as the zeolites derived from agricultural waste, fly ash, or industrial waste. For example, Yusof et al. [21] reported that zeolite Y synthesized from rice husk ash waste was found to have higher adsorption capacity than mordenite for ammonium removal, and the equilibrium isotherm proved its monolayer adsorption. Mishra and Tiwari [22] found that zeolite 13X originated from Indian fly ash had a good sorption property for metal ions at acidic pH. However, the collection and processing of these raw materials are the major engineering problems to be solved in the case of commercializing those waste-originated zeolites.

Elutrilite, an unusable solid waste, is widely discharged and piled up outside the coal mines in China. Moreover, the number is a steady increase of about 130 million tons each year [23, 24]. So much solid waste not only occupies a large area of farmland but also causes ecological damage, such as air pollution and water pollution. However, elutrilite is a kaolinite-rich gangue containing aluminosilicate, according to the chemical composition of the raw material, and zeolites/activated carbon composites can be obtained, by a process consisting of carbonization, activation, and subsequent hydrothermal transformation of aluminosilicate in alkaline solution [25]. This composite material has the combination of the adsorptive properties of zeolite and activated carbon, and its applications have emerged in the wastewater treatment industries [26]. In our previous work, phenol adsorption on X/AC composite material has been studied, and this material showed an excellent adsorption capacity attributed to the existence of activated carbon [27]. However, the removal of ammoniacal nitrogen by this composite has not been reported.

So, this work aims to realize the value of zeolite X/activated carbon composite synthesized from solid waste on the removal of ammoniacal nitrogen from aqueous solutions. The optimal values of pH, temperature, and initial concentration were used for the batch experiments. In addition, the kinetic and equilibrium behaviors of the composite were investigated and several adsorption models such as Langmuir, Freundlich, and Redlich-Peterson were adopted to fit the adsorption isotherm. The adsorption kinetic rates were calculated to evaluate the possible adsorption mechanisms. The material has a significant potential in removing ammoniacal nitrogen coexisting with phenolic compounds from wastewater.

2. Materials and Methods

2.1. Preparation of Composite Materials. The preparation of zeolite X/activated carbon composite was based on the procedure reported by Ma et al. [25]. The following is a typical synthesis example: the mixture of elutrilite and 35 wt.% of pitch was used as starting material and extruded into cylinders (3.0 mm × 6.0 mm). The extrudate was carbonized by N₂ and then activated using CO₂ at 850°C for 24 h [27, 28]. After that, zeolite 13X was formed by hydrothermally treatment in NaOH solution at 65°C for 12 h, followed by 90°C for

24 h under stirring. Thus, the zeolite 13X/activated carbon composite was obtained and named as X/AC, in which the contents of SiO₂, Al₂O₃, and carbon were 29%, 20%, and 18%, respectively.

2.2. Characterization of Material. The X-ray diffraction (XRD) patterns of the material were recorded on Shimadzu XRD-6000 with Cu Kα radiation at the 2θ of 20°–70°, in steps of 8°. Nitrogen adsorption and desorption isotherms were measured at –196°C on a Quantachrome analyzer. Before the measurement, the samples were evacuated for 3 h at 300°C. The surface area was calculated by Brunauer-Emmett-Teller (BET) formula and the pore volume was estimated at the relative pressure of 0.98. The pore size distribution was derived from the adsorption branch of the isotherm, using the density functional theory (DFT) method. The morphology was analyzed by a Hitachi S-4800 scanning electron microscope.

2.3. Batch Adsorption Experiments. The adsorption isotherms of ammoniacal nitrogen were obtained by batch experiments at different temperatures (30, 35, and 40°C). For each experiment, 25 mL of ammoniacal nitrogen solution with different initial concentrations (C₀) and 6 g/L of X/AC adsorbent were mixed in a flask. The solution pH was adjusted to 6.5 by the addition of NaOH (0.1 mol/L) or HCl (0.1 mol/L). The mixture was shaken at 150 rpm for 20 h in a temperature-controlled shaker to ensure equilibrium. Finally, the adsorbent was filtered and the residual concentration of ammoniacal nitrogen was analyzed by Walter [29]. Adsorption kinetics was carried out with the same procedure at 25°C, the solution pH value was 6.5, and the initial ammoniacal nitrogen concentrations were 69, 122, 280, 460, and 500 mg/L. After different time intervals, the adsorbent was filtered and the residual concentrations were analyzed.

2.4. Adsorption Isotherm. The equilibrium adsorption amount of ammoniacal nitrogen, q_e (mg/g), was calculated by the following formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}, \quad (1)$$

where C₀ is the initial concentration of the solution; C_e is the concentration at equilibrium; m is the mass of adsorbent. The equilibrium adsorption data was fitted by Langmuir, Freundlich, and Redlich-Peterson models.

2.4.1. Langmuir Adsorption Isotherm. The Langmuir isotherm assumes that the adsorption takes place at specific homogeneous sites on the surface of the adsorbent and form a monomolecular adsorbed layer, which can be expressed as the following equation [30]:

$$q_e = \frac{q_m b C_e}{1 + b C_e}, \quad (2)$$

where q_m (mg/g) is the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir adsorption equilibrium constant.

2.4.2. Freundlich Adsorption Isotherm. The Freundlich isotherm provides an empirical isotherm, which assumes that nonideal adsorption takes place on a heterogeneous surface with different adsorption energy and characters [31]:

$$q_e = K_F C_e^{(1/n)}, \quad (3)$$

where K_F (mg/g)(L/mg) and n are Freundlich constants, related to adsorption capacity and adsorption intensity, respectively.

2.4.3. Redlich-Peterson (R-P) Adsorption Isotherm. R-P isotherm proposed by Redlich and Peterson [32] is a combined form of Langmuir and Freundlich expressions. It can be used for predicting homogenous and heterogeneous adsorption systems. The equation is as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}, \quad (4)$$

where K_R (L/g) and a_R (L/mg) $^\beta$ are the adsorption R-P constants and β is the exponent and ranges between 0 and 1. When $\beta = 0$, the R-P equation reduces to Henry's equation which is a linear isotherm and to the Langmuir isotherm for $\beta = 1$. For high adsorbate concentration, the R-P equation reduces to the Freundlich isotherm.

2.5. Adsorption Thermodynamics. The thermodynamic parameters, including change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), were determined by using following equations and represented as

$$\begin{aligned} \Delta G^0 &= -RT \ln K_D, \\ K_D &= \frac{q_e}{C_e}, \\ \ln K_D &= \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \end{aligned} \quad (5)$$

where K_D is the adsorption equilibrium constant, ΔG^0 was given from the classical Van't Hoff equation, and ΔH^0 and ΔS^0 were calculated from the slope and of $\ln K_D$ against $1/T$. R is the universal gas constant (8.314 J/mol) and T is the adsorption temperature (K).

2.6. Adsorption Kinetics

2.6.1. Pseudofirst-Order Model. The pseudofirst-order model is depicted as follows [33]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t). \quad (6)$$

When integrated under the boundary conditions $t = 0$, $q = 0$, and $t = t$, $q = q_t$, the equation becomes

$$\ln (q_e - q_t) = \ln q_e - k_1 t, \quad (7)$$

where k_1 is the pseudofirst-order rate constant and q_e and q_t are the adsorption capacity of the adsorbent at equilibrium and at time t , respectively.

FIGURE 1: XRD patterns of the composite material.

2.6.2. Pseudosecond-Order Model. The pseudosecond-order model can be expressed as follows [34]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2. \quad (8)$$

The linearized-integrated form of the equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (9)$$

where k_2 is the pseudosecond-order rate constant.

3. Results and Discussion

3.1. Adsorbent Characterization. The XRD patterns of the samples are demonstrated in Figure 1. A well-crystallized X-ray diffraction pattern of typical zeolite X is found in the composite X/AC, which is in agreement with [35]. It is indicated that the zeolite X/activated carbon composite is successfully prepared from the waste raw materials.

N_2 adsorption-desorption isotherms of the composite are shown in Figure 2. As seen from Figure 2, the N_2 adsorption-desorption isotherms of X/AC composite exhibit both type I and IV isotherms, corresponding to hierarchical porosity ranging from micropore, mesopore, to macropore. The specific BET surface area and the total pore volume are 888 m²/g and 0.63 cm³/g, respectively. This result is much higher than the untreated elutrilite, attributing to the formation of zeolite 13X from the aluminosilicate in the raw material by the hydrothermal crystallization.

The scanning electron microscopy (SEM) images of the samples are given in Figure 3. As demonstrated from Figure 3, the prepared X/AC material has the features of 13X and activated carbon. From the magnifying image of Figure 3(b), octahedral structure of 13X and rough structure of activated carbon coexisted, which confirms the 13X zeolite has been successfully prepared, and the crystal aggregates have been

FIGURE 2: N_2 adsorption-desorption isotherms of the composite material.

covered by activated carbon. Furthermore, the surface of activated carbon in X/AC is looser and more porous compared with the raw material.

3.2. Effect of the Solution pH. The adsorption capacities of ammoniacal nitrogen in the pH range of 3.2–8.5 were performed and given in Figure 4. The maximum adsorption amount of ammoniacal nitrogen was achieved when the experiment was operated at pH 6.5. The pH has an important effect on ammoniacal nitrogen removal since it can impact the character of ammonium ion. When the pH value is higher than 7, the adsorption capacities of ammoniacal nitrogen decrease, because the ammonium ion is transformed to nonionized forms of ammonia gas, which is unfavorable for adsorption on X/AC composite [36–38]. When the pH is lower, ammonium ions compete with hydrogen ions on the adsorption sites. Hence, in this study, the pH of 6.5 is selected as the optimum pH on ammoniacal nitrogen adsorption.

3.3. Adsorption Isotherms. The composite was made into particles with the size of 20–60 mesh as adsorbent for ammonium. In a 100 mL beaker, the composite was added to 25 mL NH_4Cl solution with a ration of 6 g/L. The pH value of the solution was adjusted to 6.5, and the time for adsorption is 12 h. The thermodynamics and kinetics of the adsorption were studied by evaluating the effect of adsorption time and initial concentration.

Adsorption temperature and initial concentration affected the adsorption significantly. The concentration at equilibrium point and the rate of adsorption were affected by the initial concentration and temperature. The adsorption isotherms at the temperatures of 30, 35, and 40°C were shown in Figure 5. With the same initial concentration, the adsorption increased when the temperature was increased. At the concentration of 151.73 mg/L, the uptake of ammonium was 15.55, 17.44, and 19.02 mg/g, respectively, when the temperature was 30, 35, and 40°C. The removal of ammonium from solution by the composite of X/AC originated from the ion exchange by zeolite. The effectiveness and

efficiency of this material are close to the fly ash and 13X reported by Zheng et al. [7] and Zhang et al. [18]. This result demonstrates that ammoniacal nitrogen removal by this new composite synthesized from elutriate is feasible. Moreover, the process of ion exchange [39] is endothermic, which explains the result that the adsorption of ammoniacal nitrogen increased as the temperature increased. At the same temperature, the uptake increased when the concentration rose. With the same adsorption time, the solution with higher concentration could result in bigger difference of concentration between that in the solution and that in the adsorbent, which offered higher driving force for the ion exchange, and increased the efficiency of adsorption.

Three different models (Langmuir, Freundlich, and Redlich-Peterson (R-P)) were applied to fit the adsorption isotherms. The isotherm parameters, the values of the correlation coefficient R^2 , and the statistical error RSME are summarized in Table 1. The values of R^2 of Langmuir model in the range of 0.9221–0.9571 are relatively low, which cannot describe the experimental data accurately. Moreover, the composite of X/AC does not have homogeneous surface, and the adsorption of ammonium is not in a monolayer. So Langmuir model does not apply in this case. The values of R^2 are higher for Freundlich and R-P model than that of Langmuir model, indicating that Freundlich and R-P model give the better fitting in the adsorption of ammoniacal nitrogen on X/AC. The Freundlich constant K increased with the increasing of the temperature, implying that adsorption of ammoniacal nitrogen is endothermic, Freundlich constant n was less than 1 revealing that the surface of X/AC is heterogeneous. Also, R-P model works in the situation of a wide range of concentration, explaining solid surface adsorption is heterogeneous. Further, the calculation of statistical error RMSE was also performed. The RMSE results indicate that the fitted data of Freundlich and Redlich-Peterson model are close to the actual value, it is superior to the Langmuir model, and the results are in a good agreement with the result of R^2 .

3.4. Adsorption Thermodynamics. The adsorption equilibrium isotherms of ammoniacal nitrogen can be described better by R-P model. The values of K_D are obtained from R-P adsorption isotherm, according to literature [27]. In a study of the adsorption process in environmental engineering, Gibbs free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) are normally evaluated to judge whether an adsorption of an adsorbate on an adsorbent can happen spontaneously or not. These parameters can be calculated from the graph of $\ln K_D$ versus $1/T$, which are listed in Figure 6 and Table 2. The free energy changes (ΔG^0) obtained were –36.81, –37.41, and –38.02 kJ/mol at 30, 35, and 40°C, respectively. When the value of ΔG^0 is negative, adsorption can happen by itself. On the other hand, when the value of ΔG^0 is positive, adsorption cannot happen spontaneously. The negative values of ΔG^0 indicate the spontaneous nature of ammonium uptake by the X/AC composite. The enthalpy change (ΔH^0) of adsorption was obtained as 24.44 kJ/mol. The positive value of ΔH^0 means the adsorption process is an endothermic nature [26]. This is in agreement with the expected higher

FIGURE 3: SEM images of the composite material.

FIGURE 4: Effect of initial pH on ammoniacal nitrogen adsorption on X/AC composite at 298 K.

FIGURE 6: Plot of $\ln K_D$ versus $1/T$ for ammoniacal nitrogen adsorption on X/AC for thermodynamic parameters.

FIGURE 5: Adsorption isotherms of ammoniacal nitrogen on X/AC composite.

negative values of ΔG^0 at higher temperatures for endothermic adsorption. The entropy change (ΔS^0) was calculated as 0.1215 kJ/(mol·K). The positive value of ΔS^0 indicates the randomness at the solid/solution interface is related to the degree of freedom [19].

Generally, the values of ΔH^0 are 0~–20 KJ/mol and –80~–400 KJ/mol related to physical adsorption and chemical adsorption, respectively. The result in this work showed that the adsorption of ammoniacal nitrogen on the X/AC composite includes some chemisorption. The adsorption of ammoniacal nitrogen on the composite is attributed to ion exchange process. The values of ΔH^0 are 2.1~20.9 kJ/mol and 80~200 kJ/mol indicating physical adsorption and chemical adsorption. The value of ΔH^0 in Table 3 is higher than 20.9, indicating that adsorption of ammoniacal nitrogen on the composite is chemical adsorption. This result was in well agreement with ΔG^0 .

3.5. Adsorption Kinetics. In a typical adsorption experiment, 0.15 g of the composite was added in 25 mL ammonium

TABLE 1: Isotherm parameters of ammoniacal nitrogen adsorption on X/AC at different temperatures.

Isotherm model	Isotherm constants	Ammonium		
		30°C	35°C	40°C
Langmuir	q_m (mg/g)	35.04	35.50	35.91
	b_1 (L/mg)	0.013	0.018	0.026
	R^2	0.9221	0.9571	0.9512
	RMSE	1.76	1.96	2.29
Freundlich	$K_F ((\text{mg/g}) (\text{L/mg})^{1/n})$	3.23	3.56	4.69
	n	0.38	0.37	0.34
	R^2	0.9936	0.9805	0.9681
	RMSE	0.17	1.11	1.34
R-P	K_R (L/g)	$2.85 * 10^5$	1.83	$1.21 * 10^4$
	α_R (L/mg) $^\beta$	$8.84 * 10^4$	0.28	$2.6 * 10^3$
	β	0.62	0.73	0.67
	R^2	0.9936	0.9867	0.9681
	RMSE	0.19	0.91	1.64

TABLE 2: Thermodynamic parameters of ammoniacal nitrogen adsorption on X/AC.

Temperature/°C	Ammoniacal nitrogen		
	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/(mol·K))
30	-36.81		
35	-37.41	24.44	121.55
40	-38.02		

solution in 100 mL beaker, at the temperature of 25°C. After adsorption, the solution was separated from the adsorbent by centrifugation, and the concentration was analyzed. The figure of adsorption versus time is shown in Figure 7.

As shown in Figure 7, within 30 min, the adsorption speed increased while the concentration of ammonium increased. The higher the concentration of ammonium is, the bigger the difference is between the concentration in solution and that in the adsorbent, which offers high driving force for ion exchange in the composite and speeds up the adsorption of ammonium. The adsorption speed slowed down until getting equilibrium from 30 to 120 min. Figure 7 showed the uptakes of ammonium increased from 7.74 to 34.27 mg/g when the initial concentration of ammonium increased from 69 mg/L to 500 mg/L. The adsorption got equilibrium because ion exchange reached equilibrium, at which point ammonium could not be removed anymore. The kinetic results are fitted by pseudofirst-order kinetic model and pseudosecond-order kinetic model, as shown in Figures 7(b) and 7(c) and Table 3.

A curve of $\ln(q_e - q_t)$ versus t was fitted by the pseudofirst-order kinetic model and was shown in Figure 7(b). A curve of t/q_t and t was fitted by the pseudosecond-order kinetic model and was shown in Figure 7(c). The correlation coefficients (R^2) are used to describe the applicability of the adsorption kinetics model. The R^2 values for the pseudofirst-order model are the lowest among the used models. The R^2 values are 0.8405, 0.9517, 0.6940, 0.7841, and 0.6982, respectively. Moreover, the value of $q_{e(\text{exp})}$ differs significantly from that of $q_{e(\text{cal})}$, which indicates the pseudofirst-order model does not work

for the adsorption of ammonium by the X/AC model. It has been reported that the pseudofirst-order model fits better the adsorption in the early stage, but not the whole adsorption process.

However, the R^2 values for the pseudosecond-order kinetic model are higher than 0.999 for five different initial concentrations, and the values of $q_e(\text{exp})$ are very close to that of $q_e(\text{cal})$, which indicates the pseudosecond-order kinetic model fit better the adsorption of ammonium by X/AC than the pseudofirst order. On the other hand, the $q_e(\text{cal.})$ value for the pseudofirst-order model is lower than the experimental adsorption capacity of ammoniacal nitrogen ($q_e(\text{exp.})$), but the $q_e(\text{cal.})$ value for the pseudosecond-order model is in agreement with $q_e(\text{exp.})$ values. Generally, the pseudosecond-order model is proper to the adsorption kinetics.

In a water bath the temperatures were controlled at 298, 303, and 308 K; the adsorbent was added to the ammonium solution with a concentration of 65.50 mg/L and adsorbent to solution ratio of 6 g/L. The result is shown in Figure 8(a). The value of K was calculated from the pseudosecond-order kinetic model. From Arrhenius equation, $\ln K = -E_a/RT + \ln A$. The curve of $\ln K$ versus $1/T$ is shown in Figure 8(b). From the slope of the linear fitting, the active energy of adsorption E_a was calculated to be 47.74 KJ/mol. The activation energy of adsorption E_a for physical adsorption is 5~40 KJ/mol, while the activation energy of adsorption E_a for chemical adsorption is 40~800 KJ/mol. Thus, the adsorption of ammoniacal nitrogen on the composite is chemical adsorption.

4. Conclusions

In this work, it is demonstrated that the zeolite X/activated carbon composite originated from elutrilithe is an effective adsorbent for the removal of ammoniacal nitrogen. The adsorption equilibrium, thermodynamic, and kinetics parameters for the adsorption process have been investigated. Compared with Langmuir adsorption isotherm, the equilibrium adsorption data were better described by Freundlich

TABLE 3: Kinetics parameters for ammoniacal nitrogen adsorption on X/AC.

C_0 (mg/L)	$q_{e(\text{exp})}$ (mg/g)	Pseudofirst order			Pseudosecond order		
		$q_{e(\text{cal})}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e(\text{cal})}$ mg/g	K_2 (min^{-1})	R^2
69	7.52	1.45	2.2×10^{-2}	0.8405	7.78	6.55×10^{-2}	0.9997
122	14.45	1.98	3.6×10^{-2}	0.9517	14.56	6.56×10^{-2}	0.9999
280	30.59	1.35	6.1×10^{-3}	0.6940	30.81	4.41×10^{-2}	0.9999
460	32.96	1.47	2.0×10^{-2}	0.7841	32.95	7.23×10^{-2}	0.9999
500	34.43	1.64	2.0×10^{-2}	0.6982	34.36	5.76×10^{-2}	0.9999

FIGURE 7: Adsorption kinetics of ammonium from aqueous solution: (a) effect of contact time on ammonium adsorption, (b) pseudofirst-order kinetic model, and (c) pseudosecond-order kinetic model.

FIGURE 8: The activation energy of ammonia adsorption on X/AC (a) and plot of $\ln k$ versus $1/T$ (b).

models and the Redlich-Peterson. The thermodynamic properties of ammoniacal nitrogen adsorption concluded that the process was spontaneous and endothermic process by the adsorption of X/AC. The adsorption kinetics is best depicted by the pseudosecond-order model, indicating the adsorption process is chemisorption. This material has a significant potential in removing ammoniacal nitrogen coexisting with other organic compounds from industrial wastewater.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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