Dynamic Adsorption and Re-adsorption Characteristics of Dissolved Organic Matter on Clinker

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Abstract: By using batch adsorption method, adsorption isotherms of dissolved organic matter (DOM) in landscape water on clinker was investigated and adsorption mass transfer process of DOM was also discussed by means of dynamic method. In addition，the re-absorption removal of DOM by clinker which without backwash-regeneration but natural air dry was researched in this paper. The study revealed that clinker as a low cost adsorbents performed well in adsorbing DOM in aqueous solutions. After adsorption balance, the maximum adsorption capacity of DOM in clinker was about 580 mg·kg^{-1}, and the maximum removal ratio by adsorption was about 88%. The kinetic and thermodynamic data indicated that the DOM adsorption of clinker was mainly physical adsorption and chemical adsorption played only a small part. The adsorption rate was controlled both by the adsorption rate on the surface as well as the particle diffusion.At the same time, the dynamic adsorption isotherm of the random material on the cement clinker was s-shaped, in line with the BDST dynamic adsorption model.With the increase of clinker feed height, absorption capacity increased, the penetration time was prolonged, but the apparent adsorption rate constant decreased. Moreover, no backwash regeneration,natural dry cement clinker and adsorption ability of cement, cement clinker in cement clinker accumulated adsorption capacity than the original adsorption capacity increased 20% to 30%．

1. Introduction

Dissolved Organic Matter (DOM) widely exists in various water bodies, which is the key link between life-form carbon and inorganic carbon[1], and has complex and complex environmental effects[2-3]. It is generally believed that removing DOM from natural water bodies has great ecological risks[4]. Therefore, researches on removing DOM from natural water bodies are rarely reported. However, removing DOM from urban landscape water has certain significance: 1. Reduce water turbidity and bacterial reproduction[5]; 2. Alleviate water eutrophication [6]; 3. The massive presence of 3.DOM poses a potential threat to human health[7-8]. As nearly 80% of DOM in landscape water is difficult to be degraded by microorganisms[9], the existing removal methods are mainly coagulation sedimentation[4], photocatalytic degradation[10], ultrafiltration[11], adsorption[12], etc. The adsorption method has the following advantages: small occupied area, simple process, quick effect, stable working conditions, etc. It is one of the more reasonable removal methods of DOM in landscape water. Its technical core is the screening of high-efficiency and low-cost adsorbents. At present, Such as zeolite, silicalite, goethite, vermiculite, sepiolite, wheat straw, and other adsorbents have been widely studied [13] . The slag is a kind of solid waste with high porosity and large specific surface area, which is easy to obtain and cheap. Taking the bottom slag of heating boiler as the research object, the adsorption and removal of DOM by slag was studied, and the re-adsorption of DOM by slag under non-regeneration condition was also investigated. In order to provide a theoretical basis for the utilization of slag in landscape water treatment field.

2. Materials and Methods

2.1. Experimental Materials

The slag used in the experiment was taken from the slag of a municipal coal-fired heating boiler in Xi' an. There was no residual ceramic, glass, masonry and other impurities. After sieving (particle size less than < 2 mm), the slag was cleaned and dried to a constant weight in an oven at $100\sim110℃$. The water samples were collected in Xingqing Park, Xi'an. Under the conditions of $4℃$, 4 000r·min^{-1}, centrifugation for 20 min and 0.45μm m glass fiber filter membrane, the filtrate was DOM solution. The filtrate was appropriately concentrated on RE-2003 vacuum rotary evaporator, and 1.5 mmol·L^{-1} NaN$_3$ solution was added. The filtrate was stored in refrigerator at $4℃$ for later use. DOM content of the solution is expressed by dissolved organic carbon (DOC). DOC is determined by IL500 total organic carbon analyzer, and the experimental water is ultrapure water.

2.2. Main Experimental Instruments

SHA-C Constant Temperature Oscillator (Guohua Enterprise), RE-2003 Vacuum Rotary Evaporator (Shanghai Kesheng Instrument), IL500 Total Organic Carbon Analyzer (US Hash Company), BT100-2J Precision Peristaltic Pump (Hebei Lange).

2.3. Experimental Methods

2.3.1. Adsorption Kinetics of DOM on Slag.

Using the method of static oscillation balance, 1.0 g slag and 20 mL DOM solution of 30 mg·L^{-1} were added into 50 mL triangle bottle with plug, and 0.01 mol·L^{-1}CaCl$_2$ was added as electrolyte 1.5 mol·L^{-1} NaN$_3$was used as microbial inhibitor to plug the bottle tightly. Under the conditions of temperature of 25 ± 1 ℃, pH of 6.8±0.5 and vibration frequency of 150 r·min^{-1}, the vibration frequency is 0.5, 1.0, 1.4, 2.4, 4.8, 6.4, 12.4, 18.6 and 24 hours respectively. After shaking, the supernatant was centrifuged at 4000 r·min^{-1} for 15min, and passed through a 0.45μm glass fiber filter membrane to determine DOM concentration in the filtrate. Blank samples and 3 parallel samples were set in the experiment.

2.3.2. Dynamic Adsorption Experiment of DOM on Slag.

The dynamic adsorption column method is adopted, and the adsorption column is made of glass with a diameter of 25mm. The bottom of the column is stuffed with absorbent cotton, and then the washed and dried slag is loaded into the adsorption column. During the filling process, the adsorption column was continuously vibrated to ensure uniform slag distribution. Before the experiment, the slag was soaked with ultra-pure water for 12 h to make the filling more uniform. DOM solution with a concentration of 100 mg·L^{-1} was prepared. 0.01 mol·L^{-1} CaCl$_2$ was added as electrolyte and 1.5 mmol L-1 NaN3 solution as microbial inhibitor. Finally, the DOM solution was uniformly added to the adsorption column from top to bottom by peristaltic pump at a flow rate of 40mL/min. At different time periods, a certain volume of effluent was taken to measure DOM concentration.

2.4. Data Processing and Analysis

2.4.1. Kinetics Model of DOM Adsorption by Slag.

Four kinetic equations were used to fit the kinetic curves of DOM adsorption by slag, and the kinetic equations were as follows [14]:

Pseudo-first-order equation:

$$q_s = q_e \left(1 - e^{-k_1 t}\right) \quad (1)$$

Pseudo-second-order equation:

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

Elovich equation:

$$q_s = A + B \ln t \quad (3)$$

Intra-praticle diffusion equation:

$$q_s = K_{di} t^{1/2} + C_i \quad (4)$$

In the formulae (1) to (4), q_s is the adsorption amount of DOM at time t, mg·kg^{-1}; q_e is the saturated adsorption amount of DOM at adsorption equilibrium, mg·kg^{-1}; k_1、 k_2 are adsorption reaction rate constants, h^{-1}kg·(mg·h)$^{-1}$; A and B are constants of the kinetic equation and are dimensionless. K_{di} is the diffusion rate constant in particles, mg·kg^{-1}·h$^{-1/2}$; C_i is related to the thickness of the diffusion layer.

2.4.2. Dynamic Adsorption Model of DOM on Slag.

BDST (bed depth service time) model is one of the most common simplified models in the dynamic adsorption model of adsorption column method. This model can predict the adsorption operation time under different packing heights, injection flow rates and other operation conditions, as shown in the following [15].

$$t = \frac{N_0}{c_0 v} z - \frac{1}{K c_0} \ln(\frac{c_0}{c} - 1) \quad (5)$$

In formula (5), it is the initial concentration of DOM in the influent, mg·L^{-1}; For DOM concentration in effluent, mg·L^{-1}; Is the adsorption rate constant, L·(mg·h)$^{-1}$; Is the maximum adsorption capacity of DOM, mg·L^{-1}; For the height of the filled slag layer, cm; For adsorption time, h; For the inlet line flow rate, m·h^{-1}. From the time point = 0 to the penetration end point, the final cumulative adsorption amount of DOM by slag, mg·kg^{-1}, can be calculated by the integral area enclosed by the straight line between the penetration curve and the initial concentration, and the calculation formula is shown in formula (6).

$$q_{ad} = \frac{Q}{1000m} \int_0^{t_e} (c_0 - c_e) dt \quad (6)$$

In formula (6), m for the amount of slag, kg ; t_e for penetration time, h; Q for inflow, L·h^{-1}.

3. Results and discussions

3.1. Adsorption Kinetics of DOM on Slag

As can be seen from fig. 1, the adsorption of DOM by slag experienced two stages with the increase of time. The first stage (0~5 h) is the fast adsorption stage, and the second stage (5 h later) is the adsorption equilibrium stage. The maximum adsorption capacity is 580 mg·kg^{-1} and the maximum adsorption removal efficiency is about 88%. The adsorption of pollutants by slag includes both physical and chemical effects of surface and pore diffusion[15], and the adsorption mechanism includes coordination exchange, van der Waals force, electrostatic attraction, hydrophobic effect, ion exchange[16]. The kinetic equations (1) to (3) are used to fit the adsorption kinetic curve. the fitting results are shown in fig. 1 and table 1. The Pseudo-first-order model is based on the assumption that adsorption is controlled by diffusion steps, the Pseudo-second-order model is based on the assumption that adsorption rate is controlled by chemisorption mechanism, and the Elovich adsorption model is commonly used to describe the chemisorption process on solid surfaces [17].As can be seen from figure 1 and Table 1, the order of the correlation coefficients of these three equations is Pseudo-first-order (R20.979) > Pseudo-second-order (R20.914) > Elovich

(R20.881) , which shows that the Pseudo-first-order model can describe the kinetics of Dom adsorption on slag The adsorption of DOM by slag is mainly controlled by external mass transfer, and chemical adsorption is not the main control step. A large number of studies show that [1] there are mainly two types of physical adsorption between DOM and minerals. One is direct Electron donor-accepter, EDA) interaction between molecules (ligand exchange, complexation, hydrogen bond, ion bridge, cation-π bond, n-π electron, etc.), which is relatively strong. The second is electrostatic action and van der Waals force, which are relatively weak.

It is considered that [18] there are two kinds of adsorption process controlled by external mass transfer. One is internal diffusion control, I. E. The diffusion process of adsorbate from the surface of the particle to the internal adsorption point. The other is surface diffusion control, i.e. diffusion process of adsorbate to particle surface. For this reason, the absorption kinetic curve is fitted by using the Intra-praticle diffusion equation. the fitting results are shown in fig. 2 and table 1. As can be seen from figure 2 and Table 1, in the two stages of adsorption, q_t and $t^{1/2}$ have a non-complete linear relationship, the correlation coefficients are 0.865 and 0.864 respectively It is shown that the diffusion of DOM on slag particles is not the only step to control the adsorption process, but is controlled by both surface diffusion adsorption and particle diffusion adsorption [19]. In the first stage of adsorption, DOM rapidly diffuses to the surface and inside of slag, and K_{d1} value is relatively large. In the second stage, DOM adsorption sites in slag particles are occupied. The adsorption reaches equilibrium state and the straight line approaches the level. The K_{d2} value is small at this time. Therefore, the second stage is adsorption speed control stage.
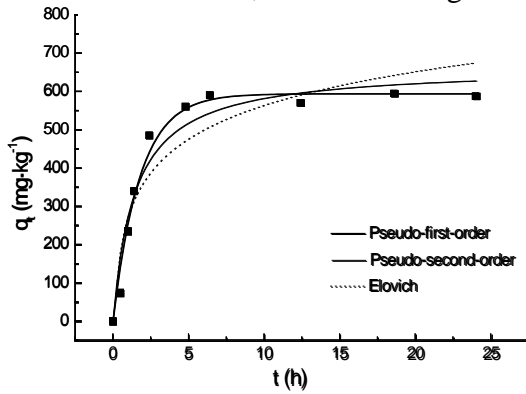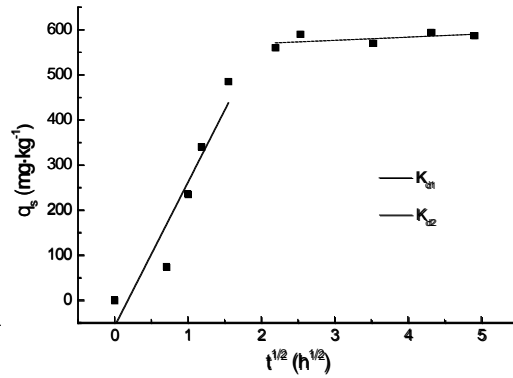

Fig.1 Adsorption kinetic data for clinker onto DOM   Fig.2 Kinetic plots of intra-particle diffusion equation

Table 1 Adsorption kinetic parameters for DOM onto clinker (Initial concentration C_0=30 mg·L^{-1})

Pseudo-first -order equation	q_e	k_1	R^2
	593±16.4	0.567±0.0573	0.979
Pseudo-second -order equation	q_e	k_2	R^2
	664±38.1	$1.05×10^{-3}±2.96×10^{-4}$	0.914
Elovich equation	A	B	R^2
	271±48.6	126±25.7	0.881
Intra-praticle diffusion equation	K_{d1}	C_1	R^2
	319±61.8	-56.9±63.7	0.865
	K_{d2}	C_2	R^2
	7.10±6.05	555±22.0	0.864

3.2. Dynamic Adsorption of DOM by Slag

Under the conditions of initial DOM concentration c_0 of mg·L^{-1}, flow rate of 0.136 cm·h^{-1}, packing height of H1=30 cm, H2=60 cm and H3=90 cm, the dynamic adsorption column method is adopted. Refer to fig. 3 for the adsorption penetration curve of slag on DOM. According to the

formula (5), the software OriginPro 8.5 was used for the fitting. The fitting results are shown in Table 2. As can be seen from figure 3 and Table 2. As the contact time between DOM and slag increases, the penetrating curve presents a typical "s" shape, which increases slowly, then rapidly and then slowly. The higher the filler height is, the larger the maximum adsorption capacity N_0 is. The later the penetration time t_e is delayed and the greater the final cumulative adsorption capacity is. The values of H1, H2 and H3 are 54.1mg·L^{-1},68.5mg·L^{-1} and 83.1mg·L^{-1}, respectively. The values of t_e are 2.07 h, 5.10h and 9.17h, respectively. The values of q_{ad} are 30 .3mg·kg^{-1},39.1 mg·kg^{-1} and 40.1mg·kg^{-1} respectively. This is because as the height of slag filler increases, the residence time and adsorption sites also increase, DOM solution is fully contacted with slag, and the longer the adsorption saturation time is, the better the adsorption effect is [31]. At the same time, with the increase of filler height, the adsorption capacity N_0 and penetration time t_e also increase, but the adsorption rate constant decreases, which is consistent with the research results of many dynamic adsorption column methods for wastewater treatment[16,20]. In addition, for different slag filler layer heights, the shape of the penetration curve does not change much, because the dynamic adsorption equilibrium and the mass transfer diffusion rate do not change with the filler height [20].
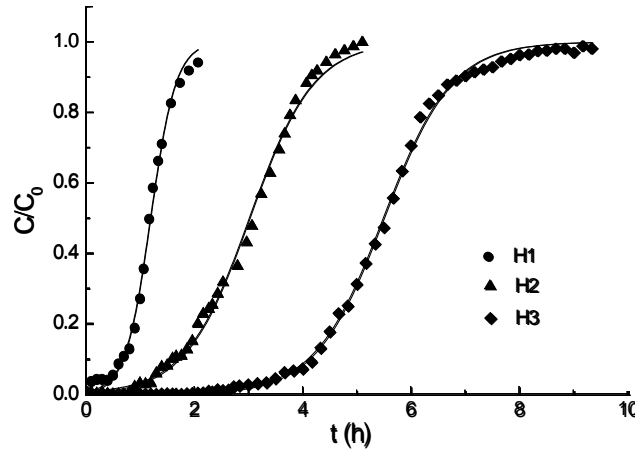

Fig 3 The breakthrough curves of dynamic adsorption

Table 2 Dynamic adsorption parameters for DOM onto clinker

adsorption column number	z / cm	N_0 / mg·L^{-1}	K / L·(mg·h)$^{-1}$	R^2	t_e / h	q_{ad}/ mg·kg^{-1}
H1	30	54.1±0.418	0.0179±1.69×10^{-3}	0.995	2.07	30.3
H2	60	68.5±0.349	0.0169±3.65×10^{-4}	0.996	5.10	39.1
H3	90	83.1±0.164	0.0159±2.40×10^{-4}	0.998	9.17	40.1
D1	30	16.5±0.710	0.0289±1.86×10^{-3}	0.978	0.910	6.22
D2	60	28.1±0.376	0.0261±1.03×10^{-3}	0.995	2.10	9.04
D3	90	41.1±0.112	0.0212±2.97×10^{-4}	0.999	4.23	13.7

3.3. Re-dynamic Adsorption of DOM by Slag under Non-regeneration Conditions

Kleber and his colleagues [21] proposed the concept of "organic layer on mineral surface" based on the idea that the organic molecular layer formed on mineral surface creates potential adsorption sites for adsorbing DOM. Mayes and his colleagues [22] have also proved that the number of adsorbent points available for DOM selection on the mineral surface is proportional to the organic matter content on the mineral surface. The higher the content of organic matter, the easier it is to "enter" the layered "mineral-organic matter" complex on the mineral surface, and the greater the adsorption capacity. Based on the above findings, this study made a bold assumption that slag, as a solid mineral, adsorbed DOM and saturated. Does it also have the ability to reabsorb Dom?

Therefore, through the dynamic adsorption column method, the re-adsorption ability of slag packing column to DOM after adsorption and penetration was studied. In the experiment, the solution of the penetrating 3 packed columns was drained, not rinsed for regeneration, and air dried naturally for 24 hours (referred to herein as " non-regeneration conditions"). Then, DOM stock solution was introduced again to analyze the dynamic adsorption process of slag on DOM. The three packed columns are denoted by D1, D2 and D3 respectively and the experimental results are shown in fig. 4. As can be seen from fig. 4, with the increase of contact time, the penetration curves of D1, D2 and D3 also show a typical " s" shape. The initial effluent concentrations of D1, D2 and D3 are 20%, 2.5% and 0.0% of the influent concentration respectively. The penetration times t_e were 0.8h, 2.5h and 4.3h respectively. Fit the curve according to equation (5). The fitting results are shown in Table 2. Table 2 shows that the fitting result is very good. The correlation coefficient is between 0.978 and 0.999, which is the same as H1, H2 and H3. With the increase of filler height, the adsorption rate constant K decreases while the adsorption capacity N_0 and penetration time t_e increase. The cumulative adsorption capacities of D1, D2 and D3 were 6.22 mg·kg^{-1}, 9.04 mg·kg^{-1} and 13.7 mg·kg^{-1}, respectively. On the basis of the original accumulated DOM adsorption capacity, the slag filler column increased by 20.5%, 23.1% and 34.2%. Moreover, the higher the packing column height, the greater the increase. Therefore, when the slag adsorption column method is used to treat DOM in water, intermittent operation can be adopted to improve the removal efficiency. That is, when the effluent concentration reaches the specified limit, do not backwash and regenerate immediately. It's an interval. After natural drying, adsorption treatment is carried out again. And so on. Back flushing regeneration will be carried out until the slag finally fails. Of course, how much impact this intermittent operation will have on backwash regeneration remains to be further studied. In addition, if other mineral adsorption materials are used to adsorb DOM in water, such as zeolite, kaolin, bentonite, quartz sand, etc., such phenomena may also exist.
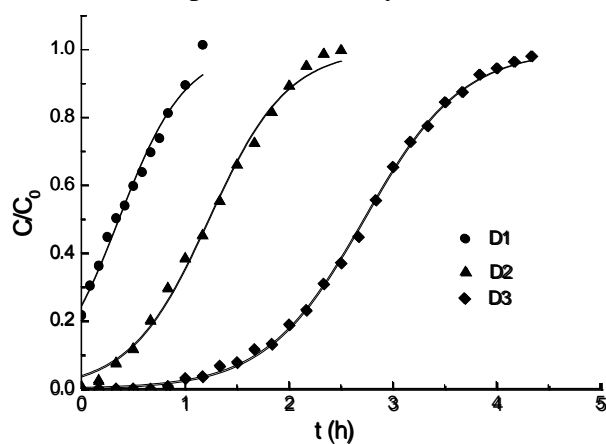
Fig 4 The breakthrough curves of dynamic adsorption

4. Conclusion

(1) As a low-cost adsorbent, slag has good adsorption capacity for DOM in landscape water. When the adsorption equilibrium is reached, the maximum adsorption amount is 580 mg·kg^{-1} and the maximum adsorption removal efficiency is about 88%. The adsorption of DOM by slag is mainly physical adsorption and chemical adsorption is very small. The adsorption force may be mainly direct electron donor-acceptor interaction, electrostatic interaction and van der Waals force interaction among molecules. The adsorption rate is jointly controlled by the surface adsorption rate and intraparticle diffusion.

(2) BDST dynamic adsorption model can well describe the process of DOM treatment in water by adsorption column method. The penetration curve presents a typical " S" shape. The higher the slag filler height, the greater the adsorption capacity. The later the penetration time is delayed, the final cumulative adsorption quantity increases and the adsorption rate constant decreases. However,

the shape of the penetration curve has not changed much.

(3) After absorbing and penetrating DOM, the slag filler column has the capability of dynamic adsorption of DOM again under non-regeneration conditions, which can increase the cumulative adsorption of DOM by 20% to 30%. Therefore, when the slag adsorption column method is used to treat DOM in water, intermittent operation can be adopted to improve the removal capacity.

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