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Adsorption of Pb(II) by Activated Pyrolytic Char from Used Tire

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Abstract. As a renewable resource, the pyrolytic char derived from used tire has promising adsorption capacities owing to its similar structure and properties with active carbon. The purification and activation of the pyrolytic char from used tire, as well as the application of this material in the adsorption of Pb(II) in water is conducted. The influences on the adsorption capacity by temperature and pH value are investigated and discussed; the adsorption thermodynamics and kinetics are also studied. The results show that the pyrolytic char from used tire has remarkable adsorption capacity for Pb(II), and the adsorption is an endothermic process complying with the Langmuir isotherm. The adsorption kinetics is a pseudo second-order reaction.

1. Introduction

Used tire can be a renewable resource by correct recycling though it is indeed a black pollution. There are many ways to recycle the used tire, among which pyrolysis is an environment-friendly method that can most completely process the used tire. The challenge of the economics of the pyrolysis is the application of the pyrolytic char that occupies more than 35% of the pyrolysis products. Researches have shown that the pyrolytic char has similar distribution of meso- and macropores with the commercial active carbon [1], and it can be used for adsorbing the pollutants in waste water for example heavy metal ions, hydroxybenzenes, pesticides, and dyes [2,3]. Metal ions will generate water pollution, many kinds of materials have been used for the adsorption of Pb^{2+} in water [4]. Carbon materials are often used as an adsorbent to remove pollutants in water [5-18]. Because of the particular surface and structure characters, the purified and modified pyrolytic char exhibits different adsorption behavior with the traditional carbon materials, which rarely been studied. The present paper is a systematic research on the adsorption capacity of the pyrolytic char for Pb(II) in water.

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2. Experimental

2.1Activation of the Pyrolytic Char from Used Tire

Activation of the pyrolytic char from used tire was carried out according to the literature method [2,3]. Purified pyrolytic char by removing the ash and residual oil was processed by steam under 800℃ for 3 hours. The activated pyrolytic char was analyzed by an isothermal nitrogen-adsorption instrument (Micromeritics Tristar 3000) for the porous structures and specific surface area. The morphology was observed by scanning electron microscopy (SEM).

2.2Adsorption of Pb(II)

1000 mg/L $Pb(NO_3)_2$ solution was prepared. The solution was diluted to a certain concentration referenced below and was processed by the prepared activated pyrolytic char for adsorption. After the adsorption process, the resulting homogeneous liquid was sampled for determining the Pb(II) concentration by ion-coupling plasma atomic emission spectroscopy (ICP-AES, ICP-9000(N+M) USA Thermo Jarrell-Ash Corp.).

3. Results and Discussion

3.1Characterization of the Activated Pyrolytic Char

The porous structures and specific surface area of the activated pyrolytic char were analyzed by the isothermal nitrogen-adsorption method. The results were shown in Table 1. It indicates carbon content and specific surface area are both obviously increased by removing the ash and residual oil species after the purification and activation treatments.

TABLE 1. PORE PROPERTIES OF THE ACTIVATED PYROLYTIC CHAR

	Pyrolytic char	Activated pyrolytic char
C, %	82.70	90.53
H, %	1.62	1.58
N, %	0.82	0.33
Specific surface area, m^2/g	30.6	720
Pore volume, cm^3/g	–	0.92
Pore diameter, nm	–	8.7

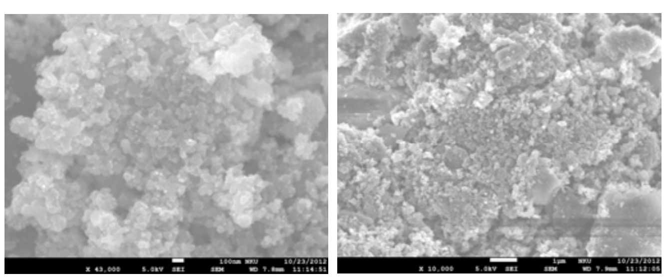

Fig. 1 SEM images of the pyrolytic char from used tire

The SEM images show the activated pyrolytic char are composed by aggregates of 20 – 50 nm particles. Pyrolytic char is porous with certain specific surface area. However, the obtained pyrolytic char exhibits relatively low specific surface area before activation, resulting from the adsorption of tar and some other hydrocarbons generated by pyrolysis. Upon purification of the pyrolytic char, the adsorbates were removed, leading to the micropores opened and the crystallite surface exposed. When further activating the pyrolytic char by steam, the microcrystalline on crystallite surface was ablated. In general, carbon atoms in the basic microcrystalline corner or the position with lattice defects are easy to react with the activation agent steam. Such nonuniform ablation endows the pyrolytic char with new pores. During the course of the gradual activation, carbon of the microcrystalline was continuously consumed, resulting in the formation of larger pores. Consequently, the specific surface area and pore volume of the pyrolytic char are improved dramatically upon activation, and then the activated pyrolytic char can serve as one kind of satisfied adsorbing materials.

3.2Adsorption Capacity for Pb(II) of the Activated Pyrolytic Char

The maximum adsorption capacity of the activated pyrolytic char for Pb(II), which is about 24 mg/g, was tested in high concentration Pb(II)-containing solution after 10 hours adsorption.

The adsorption ratios for Pb(II) by the activated pyrolytic char under different pH values are shown in Fig. 2, which shows a maximum adsorption degree in the $Pb(NO_3)_2$ solution with intrinsic pH = 6. Decreasing the pH value, the adsorption degree for Pb(II) was sharply decreased. Previous researches reveal that the isoelectric point of activated pyrolytic char is 6.7. When pH is below this point, the activated pyrolytic char is positively charged and the positive charges are enriched with gradually decreasing pH. The positive charges lead to the electrostatic repulsion between the activated pyrolytic char and Pb(II). Moreover, H^+ would competitively occupy on the surface of activated pyrolytic char too, which is unfavorable for the absorption of Pb(II). This is the other reason why the adsorption ratio obviously decreases at lower pH value level. A minor recovery of adsorption degree was observed when pH value is below 5, which is probably due to the increase of ionic strength.

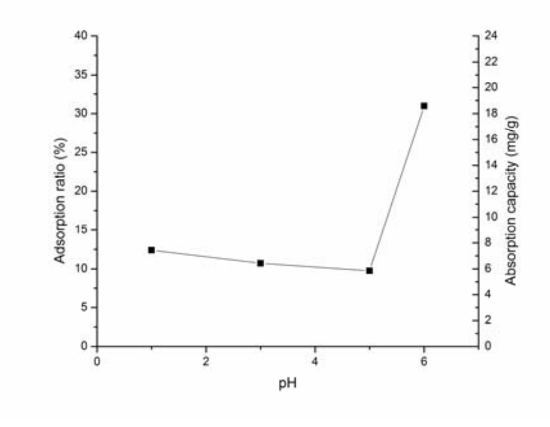

Fig.2 Adsorption ratio under different pH values

In the adsorption, solid and liquid phases interact thoroughly with each other, and a dynamic absorption/desorption equilibrium would be achieved. The equilibrium adsorption amount is defined as the amount of adsorbate on the unit weight of adsorbent. The equilibrium adsorption amount is a function of the solution concentration and temperature. The higher the equilibrium adsorption amount is, the larger amount of solution per unit weight of adsorbent can process. The isotherms are received by plotting the equilibrium adsorption amount with the respective equilibrium concentration, which is necessary to investigate the absorbing mechanism. The adsorption capacity is a significant factor to evaluate the performance of the absorbent, which can be calculated via the absorption isotherms. Generally, the Langmuir isothermal equation is used to fit these parameters:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}$$

where C_e and q_e are the equilibrium liquid-phase and solid-phase of concentration, respectively; Q_0 (in unit of mg/g) is the single layer adsorption amount of the adsorbant, b (L/mg) is the Langmuir Constant that is related to the adsorption energy.

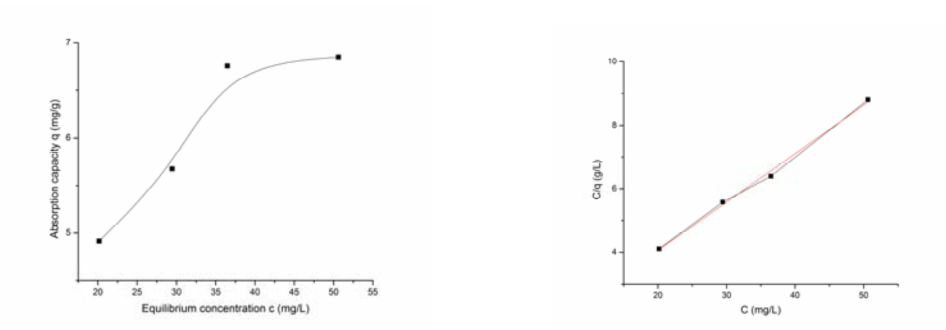

Fig. 3 The absorption isotherm and linear Langmuir isotherm fitting

Fig. 3 shows the absorption isotherm and linear Langmuir isotherm fit, and the linear equation is as follows with a $R^2 = 0.995$.

$$\frac{C_e}{q_e} = 1.006 + 0.153C_e$$

This implies the adsorption of Pb(II) on the activated pyrolytic char complies with the Langmuir isotherm model. According to the fitted linear equation it is reasonable to know $Q_0 = 6.535$ mg/g, and b = 0.153L/g (25 °C).

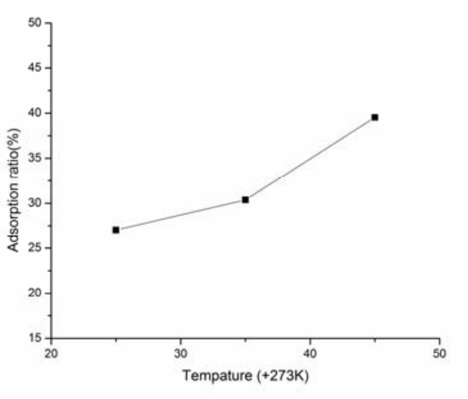

Fig. 4 Adsorption ratio for Pb(II) under different temperatures

Fig. 4 shows the adsorption ratio for Pb(II) under different temperatures, showing that increasing temperature is favorable for the adsorption for Pb(II). The temperature-improved absorption ratio indicates that adsorption on the activated pyrolytic char should be an endothermic process.

Adsorption kinetics reveals the relationship between the structure and adsorption property of the material. The adsorption process and the adsorption structure can be predicted according to the adsorption kinetics model. Several models have been assumed to express the absorption rate, where Lagergren's pseudo first-order and second-order rating equations were commonly employed. In the pseudo first-order reaction, k_1 (min^{-1}) is the adsorption rate constant. First-order reaction is favored if $\ln(Q_e-Q_t)$ is linearly vaired with t.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

In the pseudo second-order reaction, k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is the adsorption rate constant. Second-order reaction is favored then if t/Q_t is linearly varied with t.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

The present absorption kinetics data were both fitted by these two models. As shown in Fig. 5, the absorption process for Pb (II) on the activated pyrolytic char could be well linearly fitted by the pseudo second-order kinetics model, but not the first-order one. As a result, the present absorption process exhibits a pseudo second-order kinetics with k_2 = 1.575×10^3 $g \cdot mg^{-1} \cdot min^{-1}$.

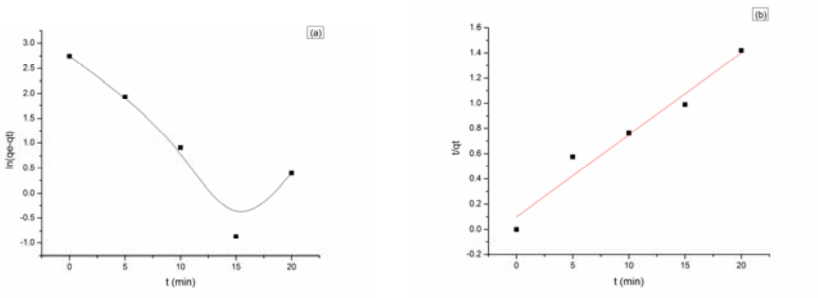

Fig. 5 Adsorption data fitting results according to (a) pseudo first-order and (b) pseudo second-order reaction

4. Conclusion

Activated pyrolytic char shows the desired adsorption capacities for Pb(II). For lower concentration Pb(II) solution, a dosage of 5 g/L of the adsorbant will generate a adsorption degree of 99%. The absorption depends mainly on pH. When the pH value is below 6, the adsorption capacity of the activated pyrolytic char will decrease. The adsorption of Pb(II) on the activated pyrolytic char complies with the Langmuir isotherm and is an endothermic process. The kinetics results show that the absorption is a pseudo second-order reaction.

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