Research of Adsorption on PCBs: Isotherm Modeling and Influencing Factors

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Abstract. PCBs are a group of persistent organic pollutants (POPs) in the environment. Adsorption behavior of PCBs has obtained great attention affecting the degradation, mobility activities. In this paper, adsorption process was studied systematically to figure out the model of adsorption, adsorption mechanism and the influencing factors, which will provides the theoretical basis for further research.

1 Introduction

The properties of PCBs (PCBs) are stable, which have carcinogenicity-mutagenicity teratogenicity effects. PCBs became a research hotspot for its serious environmental pollutions[1,2].PCBs were widely used for transformers, fire retardant agent, battery, fuel dispersant, heat carrier , pesticide delay effect agent and so on. At present, there are still 2.1×10^3t PCBs in surface soil [3, 4]. Adsorption behaviors of PCBs influences its migration, transformation, distribution, biodegradability and biological availability[5,6,7].So exploring the PCBs' adsorption behaviors deeply has a great significance in researching the PCBs' migrating rules in environmental behaviors.

2 Progress in the Study of Adsorption of PCBs

The sources of adsorbents which have adsorption effects on PCBs are abundant. Different adsorption materials have different effects on the adsorption property of PCBs[8-23]. PCBs' adsorption kinetics most belong to first-order kinetics model and second-order kinetics model .From the analysis of the different adsorption materials' adsorption isotherm models, we can conclude that PCBs' adsorptions conform to Langmuir and Freundlich adsorption isotherm models.

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3 Mechanism and Influence Factors of Adsorption of PCBs

3.1 Adsorption mechanism analysis

3.1.1Conjugate reaction

4, 4'-DCB was able to form hydrogen bonds and electron donor acceptance potentials with the functional groups of Chitosan on the surface of the attapulgite. 4, 4'-DCB can be conjugated with hydroxyl and amino groups on the chitosan chains and then enhanced adsorption efficiency of 4, 4'-DCB by modified attapulgite. The isothermal adsorption line can be approximated as a straight line [8].

3.1.2 Physical and chemical adsorption

Dominant mechanism is surface adsorption of organic compounds by soil. There are two types of absorption. 0ne is the physical absorption which is mainly functioned van der waals force, another is chemical adsorptions which are functioned by dipole bond, hydrogen bond and coordination bond [8].

3.1.3 Freundlich adsorption

The behavior of adsorption of PCBs can be well described. The multi molecular layer, complex and heterogeneous adsorption model are the main forms. Exponential values of equation of n are less than one. The whole adsorption process is nonlinear [9, 10, 29].

3.1.4 Langmuir adsorption

It is essentially monolayer adsorption. The adsorption processes include fast adsorption and slow adsorption [8, 11, 15, 17, 29]. When the organic carbon content increase, Langumuir adsorption is the main method [12]. The Langumuir adsorption is characterized by solid layer surface [21].

The adsorption process of organic matter is mainly surface adsorption. The adsorption process of PCB28 by PC and TG showed the distribution of PCB28 to 2 kinds of lipids and the surface adsorption of lipid substances. The distributional effect is occupied the dominant position in the adsorption process [16].

3.1.5 Bio adsorption

The removal mechanism of PCBs by the inactivated bacteria is biological adsorption. Biodegradation remains stable in 24h. The removal rate of sterilization is consistent with the adsorption rate of bacteria. It illustrates that the biological adsorption is the only way to do. With the treatment of live bacteria, biological adsorption and biodegradation of live bacteria exist at the same time [12, 30].

3.1.6 Reversible adsorption and irreversible adsorption

The adsorption is divided into two parts. One part is linear reversible adsorption, the other part is the irreversible adsorption of Langmuir adsorption isotherm. It comprehensively reflects the internal connection between the various factors of the

adsorption equilibrium. When organic carbon content is low in soils, the adsorption is linear. Along with the increase of organic carbon content, the isotherm gradually shows nonlinear. So either single equation of Langmuir or Freundlich could not explain the adsorption behaviors of PCBs well [29].

3.1.7 Fast adsorption and slow adsorption

The fast adsorption stage is related to the properties of the PCBs and the number of surface active sites of the adsorbent. The slow adsorption is mainly related to the arrangement of the internal active sites of PCBs in the adsorbent. At the initial stage of adsorption, the surface active sites of the adsorbent are more active, and the solute concentration around the active site is also higher. The driving force of the solute is also relatively large. At the same time, the biphenyl ortho carbon hydrogen was not replaced by chlorine atoms. It reduces the steric hindrance of the combination of the binding of the binding agent with the adsorbent, and they are more likely to form Van der Waals force. Hydrophobic molecules are more likely to be assigned to the adsorbent molecules, so the adsorption rate is relatively fast. Accompany the adsorption, the active sites of the adsorbent surface are gradually saturated, and the arrangements of the surface of the adsorbent are gradually stable. The adsorption reaction of biphenyl is diffusion adsorption in the interior of the adsorbed molecules. Compared with the initial stage, the velocity and intensity of surface adsorption both decrease, and it change into enter the slow adsorption stage [26, 27, 28].

3.2 Influencing factors

3.2.1 The pH value

The adsorption rate decreases with the increase of pH value, and then gradually shows stable. The optimal pH value is 6, and at this time the adsorption rate is 56.17%. Because pH may be one of the important factors that affect the biological adsorption. The pH value influences the adsorption mainly via the change of the adsorption adsorbent and the surface electrical property, which affects the electrostatic interaction between them [12, 27].

The change of pH in the aqueous phase can affect the configuration of the sediment particles and the existing forms of PCBs, which affects the interaction between PCBs and sediment. When the pH value is relatively low, small molecule organic matter combines into larger aggregates due to the role of organic matter and mineral surface oxygen bond. So the adsorption of PCBs enhanced. With increase of pH value, the organic polymer is destroyed, hydrophobic sites disappear, and the affinity of PCBs in sediment release to the aqueous phase, making adsorption capacity decrease [23].

In the presence of HA (humic acid), the adsorption capacity of the PCBs by bological carbon is greatly enhanced. With the increase of HA concentration, the solubility of PCBs also increase. The mechanism of the adsorption is mainly due to the change the electrical property between the surface of the PCB and the adsorbent, resulting in the effect of the electrostatic interaction between them [27]. The wheat straw biochar has stronger adsorption force than pine biochar. The causes of the above phenomena are some kinetic and equilibrium adsorption characteristics induced by the chemical heterogeneity of HA.)The adsorption of HA or PCBs by biochars may be due to hydrophobic or Van der Waals' interactions [31]. These results are consistent with previous studies [32, 33]. The presence of HA reduced the pH value of the solution, and the HA is absent after the adsorption equilibrium of PCBs. This may be due to the intrinsic acidity and the buffering capacity of

HA [34].

3.2.2 Ash

The value of looks increased with the increase of ash content in soil.
The ash content increased the adsorption capacity of PCBs.

3.2.3 Organic Matter Content

The adsorption capacity of PCBs positively correlated with the amount of organic matter in the soil [10, 20, 8, 23, 28]. And higher the organic matter content, faster the adsorption rate. When the content of organic matter in soil is more than 0.1%, the adsorption process of organic matter is mainly influenced by the content of organic matter in soil. When the content of organic carbon is high, the distribution mechanism plays a major role. When the content of organic carbon is relatively low, the microstructure of the particles plays a major role [35].

3.2.4 Molecular Size of PCBs

The molecular size of PCBs is the main reason for the adsorption of PCBs by clay minerals. When the number of chlorine atoms increases, its molecular volume increases and the potential changes of the top and the side surface of the molecules will be caused, which will affect the adsorption [11]. As the number of chlorine atoms of PCBs increases, its molecular volume increases, induce the potential changes of the molecules of the top and the side surface, and then affect the adsorption. The HA solubilization effect of high chlorinated PCBs was more obvious. The hydrophobicity of PCBs is mainly related to the number of chlorine atoms connected to PCBs. The more chlorine atoms are connected, the more hydrophobic the water is, Thus the trend of combining with organic and will be more obvious [27].The more the connected chlorine atoms, the more hydrophobic the PCBs. Thus the trend of combining with organic phase will be more obvious [27].

3.2.5 Adsorbent (Carbon Chain Length、Pore Size、Oxygen Functional Groups、Particle Size)

The isothermal adsorption of PC and TG on PCB28 was expressed as the distribution process of PCB28 in 2 lipids. The adsorption capacity of PC to PCB28 was stronger than TG. The length of fatty acid carbon chain may be the main reason for the influence of the adsorption mechanism of lipid substances [16].

The rate of four kinds of activated carbon adsorption of PCBs is similar to their average pore size and the size of the functional groups of activated carbon, which shows that the adsorption effect is closely related to the oxygen functional groups, pore volume and surface area of the adsorbent. PCBs are mainly in the microspore of adsorbent and suffer multiple physical adsorption of the wall of the hole.

The smaller the particle size, the stronger the adsorption capacity of PCBs .The greater the particle size, the weaker the adsorption capacity of PCBs. Probably because the larger the particle size, the higher the content of organic carbon [28, 36, 37].

3.2.6 Ratio of solid to liquid

With the increase of the ratio of solid to liquid, the adsorption capacity of two kinds of paddy soil on PCBs decreased. The main reason is that the contact area between the adsorbent and the PCB reduced, which leads to the decrease of unit adsorption capacity.

3.2.7 Temperature

The effects of temperature on the adsorption process include two processes. One is that the temperature changes the dispersion coefficient, which affects the degree of adsorption. The other is that the temperature has a direct relationship to the diffusion of solute in solution and pore water [38].

When the temperature changes, the surface adsorption activity and water solubility of PCBs will change, and affect the adsorption performance of PCBs. The adsorption capacity decreases slightly with the increase of temperature. The reason may be that the increase of the temperature leads to the raise of water soluble of PCBs [39-44], while reducing the PCBs adsorption partition coefficient in soil. It can be deduced that the adsorption of PCBs on paddy soil is likely to be an exothermic process. Akkaya G showed that the adsorption rate increased with the increase of temperature. The reason may be that the adsorption is endothermic process temperature range in this temperature range. The temperature raise is more favorable for the adsorption reaction [45-52].

3.2.8 Ion Concentration

When the ionic strength of the solution increased, the adsorption capacity of PCBs decreased. The reasons are as follows:

The phenomenon of salting out exists in electrolyte solution, that is ion concentration increasing, dissolved organic matter content decreasing, adsorption competition between dissolved organic matter and cation will reduce the adsorption of particulate matter to organic matter. The ion can occupy some adsorption sites on the particles, then competes with PCBs on adsorption; The ionic strength increasing will compress the double layer and weakens the electrostatic interaction between the PCB and the adsorbent, which is not conducive to the adsorption of PCBs. With the increase of cation concentration, organic matter exists in the "closed" structure, which weakens the affinity of PCBs [16, 23].

3.2.9 The Content of Clay

If the clay content higher, soil particle size is smaller and the soil adsorption capacity of PCBs is stronger.

4 Conclusions

By studying the adsorption mechanism and the influencing factors of PCBs, it is helpful to study the environmental chemical behavior of PCBs, and to better understand the migration and transformation law of PCBs. It is of great significance to provide theoretical basis for the establishment of PCBs migration and transformation model, which is of great significance for the management and control of environmental pollution, and thus provides a reliable scientific basis for the management of persistent organic pollutants in China.

5 Outlook

4.1 Getting more types of adsorbents and adsorption data of soil to PCBs is necessary.

4.2The adsorption and desorption process are actually carried out at the same time. Therefore, it is needed to further study on the desorption behavior of PCBs.

4.3 Quantifying different influence factors on the adsorption of PCBs.

4.4 Strengthening dynamic, field, composite research. The researches on the multi components are lesser; The experimental will focus on the complex field situation.

4.5 Going deep into studying on organic matter and having a quantitative description of the effects of organic matter on Adsorption Behavior.

4.6 The researchers put forward a number of relevant theories and models, but these theories and models are not universally applicable. We need to further study the adsorption behavior of PCBs in mechanism.

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