Study on Adsorption Removal of Polycyclic Aromatic Hydrocarbons by Modified Mussel Shells

Jiaxing LIU[1,2], Muchen LANG[3], Mei LIU[1,2], Kecun MA[4,5], Qingguo CHEN[1,2]*

1. Zhejiang Provincial Key Laboratory of Petrochemical Pollution Control, Zhejiang Ocean University, Zhoushan 316022, China; 2. School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan 316022, China; 3. School of Marine Science & Technology, Zhejiang Ocean University, Zhoushan 316022, China; 4. ZPC (Zhejiang Pilot Free Trade Zone) Green Petrochemical Research Institute Co., Ltd., Zhoushan 316000, China; 5. Zhejiang Petroleum & Chemical Co., Ltd. (ZPC), Zhoushan 316000, China

Abstract Polycyclic aromatic hydrocarbons (PAHs) are typical persistent organic pollutants (POPs) that are commonly found in the environment. They are carcinogenic, teratogenic, mutagenic and biodegradable obviously. In this paper, the modified mussel shells were used to adsorb and remove anthracene. The results show that the adsorption removal rate of the mussel shells was higher after calcination at 600 ℃. 5% H_3PO_4 solution was more suitable for shell treatment than 3 mol/L $ZnCl_2$ solution. As the dosage of the modified shells was 0.5 g/L, the adsorption reached a stable state, and the removal rate of PAHs was about 69.44%; the adsorption efficiency rose with the increase of time. It can be seen that as a new and cheap biological adsorbent, the modified shells can be used to remove PAHs from wastewater.

Key words Mussel shells; Adsorption; Polycyclic aromatic hydrocarbons

DOI 10.19547/j.issn2152 - 3940.2024.01.015

Polycyclic aromatic hydrocarbons (PAHs), a kind of persistent organic pollutants (POPs), are highly carcinogenic, teratogenic and mutagenic, and do great harm to organisms and the environment[1]. Due to their special chemical properties in the environment, the concentration of pollutants in the atmosphere, soil and water increases along the food chain, and eventually leading to the decay and degradation of marine and coastal ecosystems[2]. Because of the development of industry and agriculture in recent years, the amount of PAHs discharged into the environment has increased rapidly, which has caused serious harm to human health and ecological environment. Therefore, it is of great practical significance to carry out in-depth research on the removal of PAHs in water environment to control marine pollution, and protect the safety of marine and biological resources[3]. China, one of countries suffering the most serious mussel pollution in the world, can produce 300 000 t of shell waste, and the environmental pollution caused by mussel waste has become an urgent problem to be solved. It is found that a mussel shell is composed of 95% calcium carbonate mineral and a small amount of shell mass[4]. The surface of a mussel shell is rough and porous, so the specific surface area is large. It has strong adsorbability and is an ideal adsorbent. Muslin shells have been used to study the adsorption and removal of heavy metals[5] and as soil amendments, functional materials, biological fillers and catalysts[6].

In this paper, mussel and anthracene, which are potentially harmful to the coastal ecology of China, were selected as the research objects. Based on the strong adsorption characteristics of mussel shell powder, the modified mussel shell powder was obtained by cleaning, soaking, calcination, crushing and adsorption to remove anthracene. This not only promotes the recycling of large amounts of local solid waste, but also degrades pollutants.

1 Materials and methods

1.1 Main experimental materials Mussel shells were provided by Shengsi Green Mussel Shell Ecological Development Co., Ltd.

1.2 Preparation of modified mussel shells Mussel shells brought back from the farm were washed with distilled water to remove impurities such as surface filaments and moss, and dried at 60 ℃. The mussel shells were immersed in 5% H_3PO_4 solution and 3 mol/L $ZnCl_2$ solution for 2 h, respectively, and then dried at 60 ℃. At 200 - 700 ℃, 100 ℃ was set as the temperature gradient, and the mussel shell were burned to form a loose and porous structure to modify them.

1.3 Adsorption of polycyclic aromatic hydrocarbons by modified mussel shells The same mass of modified mussel shells were added to 20 ml of 20 mg/L anthracene solution. After oscillation at 25 ℃ and 400 r/min, the samples were centrifuged by a high-speed centrifuge. After anthracene was extracted twice with dearomatized petroleum ether, the upper organic phase was placed in a 25 ml colorimetric tube, and the absorbance was measured at 357 nm to calculate the concentration of residual PAHs at adsorp-

Received: January 13, 2024 Accepted: February 19, 2024

Supported by the Technology Research Project (LGF22D060003); Zhoushan Municipal Science and Technology Cooperation (Active Design) Project (2023C13015).

* Corresponding author.

tion equilibrium.

1.4 Optimization of adsorption conditions

1.4.1 Adsorbent dosage. Based on the optimization of modification temperature, the effect of adsorbent dosage on the adsorption effect was investigated. The mass of mussel shell powder samples with the same particle size was set to be 0, 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 g, respectively. They were added to a conical flask containing 20 ml of 20 mg/L anthracene solution, and shaken at 25 ℃ and 400 r/min for 3 h. The samples were centrifuged with a high-speed centrifuge. The remaining anthracene in the samples was extracted twice with 30 ml of dearomatized petroleum ether. 10 ml of the upper liquid was taken in a 25 ml colorimetric tube, and diluted with dearomatized petroleum ether to determine its absorbance at 357 nm.

1.4.2 Adsorption time. On the basis of the optimization of modification temperature, the effect of adsorption time on the adsorption effect was discussed. Firstly, 0.50 g of mussel shell powder with the same particle size was added to a conical flask containing 20 ml of 50 mg/L anthracene solution, and shaken at 25 ℃ and 400 r/min for 0, 1, 2, 3, 4 and 5 h. Secondly, the remaining anthracene in the samples was extracted twice with 30 ml of dearomatized petroleum ether, and 10 ml of the upper liquid was taken in a 25 ml colorimetric tube. The absorbance was measured at 357 nm. The absorbance was used as the ordinate, and the concentration was used as the abscissa to draw the curve.

1.4.3 Salinity. Based on the optimization of modification temperature, the effect of salinity on the adsorption effect was analyzed. 0.5 g of mussel shell powder with the same particle size was weighed and added to a conical flask containing 20 ml of 20 mg/L anthracene solution. The salinity was 0‰, 5‰, 10‰, 20‰, 30‰, 40‰, and 50‰, respectively (the salinity content can be adjusted by NaCl). The samples were shaken at 25 ℃ and 400 r/min for 3 h. After the samples were centrifuged with a high-speed centrifuge, the remaining anthracene in the samples was extracted twice with 30 ml of dearomatized petroleum ether. 10 ml of the upper liquid was taken in a 25 ml colorimetric tube and diluted with dearomatized petroleum ether. The absorbance was measured at 357 nm.

1.4.4 Removal rate of polycyclic aromatic hydrocarbons. The removal rate of PAHs can be calculated by the following formula:

$$\eta = \frac{C_0 - C_e}{C_0} \quad (1)$$

where C_0 represents the initial adsorption concentration (mg/L); C_e is the adsorption concentration at adsorption equilibrium (mg/L).

1.4.5 Adsorption capacity. The adsorption capacity of PAHs can be calculated by the following formula:

$$Q = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 represents the initial adsorption concentration (mg/L); C_e is the adsorption concentration at adsorption equilibrium (mg/L); V is the volume of the solution (ml); M is the mass of the mussel shells added (g).

2 Results and analysis

2.1 Modification technology of mussel shells In Fig. 1, with the rise of temperature, the combustion loss rate of mussel also increased gradually. At 200 – 600 ℃, the internal water and organic matter of mussel shells were oxidized and decomposed at high temperatures, and the porosity increased. At 700 – 800 ℃, organic matter was completely decomposed to form calcium carbonate. In Fig. 2, with the increase of temperature, the adsorption performance showed an increasing trend. When mussel shells were immersed in 5% H_3PO_4 at 600 ℃, the highest removal rate (71.88%) was higher than that at 300 ℃ and 3 mol/L $ZnCl_2$ (68.12%). The mussel shell powder calcined at 600 ℃ and treated with 5% H_3PO_4 was selected to study the following conditions.

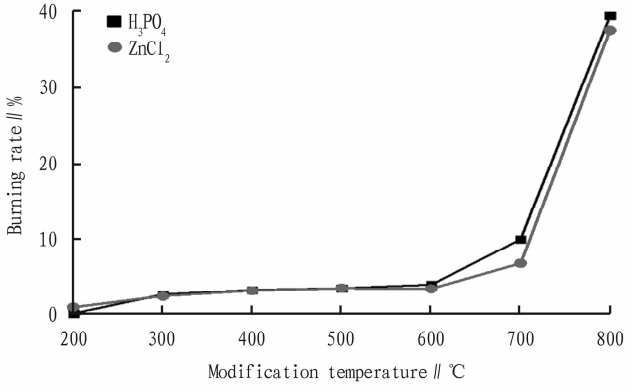


Fig. 1 Burning rate of mussel shells

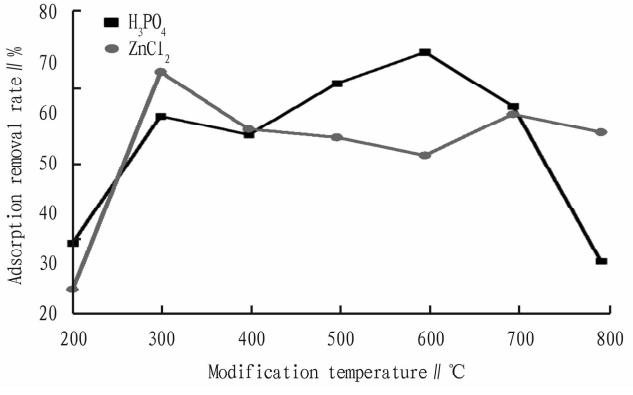
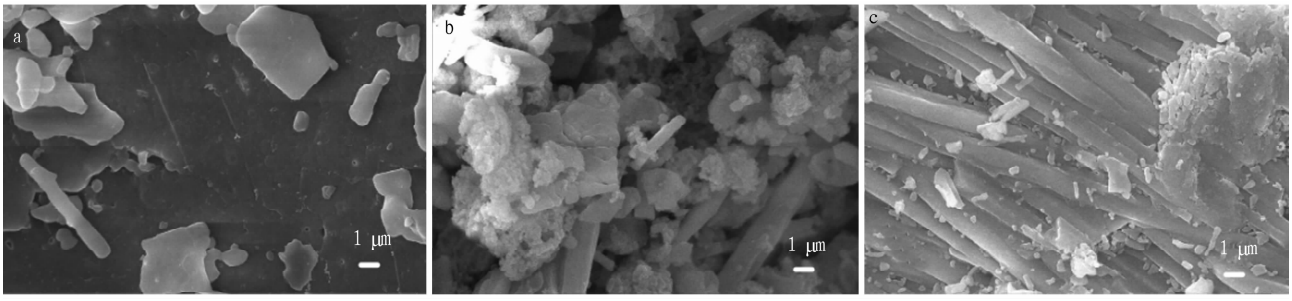


Fig. 2 Adsorption removal rate of mussel shells

2.2 Characterization of materials Mussel shells are mainly composed of a pearl layer, a prism layer and a cuticle[7]. The outermost layer is a cuticle composed of hard protein; the middle layer is a prismatic layer composed of calcite or aragonite crystals, mainly providing hardness and corrosion resistance for shells. The innermost layer is the nacre layer, mainly providing hardness and toughness for shells. It is relatively thin, and there is a small amount of organic matter between the layers[8].

In Fig. 3a, the surface of the mussel sample before calcination was smooth and flaky. After high-temperature calcination, a large number of nano-sized pores appeared on the surface of the

shell, and the surface became loose and porous. The specific surface area increased, thereby improving the adsorption performance. After soaking (Fig. 3b and Fig. 3c), the mussel surface became porous. After soaking in H_3PO_4, the mussel showed a block structure, and the specific surface area increased. After soaking in $ZnCl_2$, the mussel showed a rod-shaped structure. By comparison, after soaking in 5% H_3PO_4, more adsorption sites were found.



Note: a. Natural mussel shell (×5 000); b. Mussel shell treated with H_3PO_4 (×5 000); c. Mussel shell treated with $ZnCl_2$ (×5 000).

Fig. 3 SEM diagram of the mussel shell powder (×5 000)

2.3 Effect of environmental factors on adsorption From Fig. 4a, it is seen that with the increase of adsorbent dosage, the adsorption capacity also rose gradually. The shell powder has certain holes and high specific surface area, so the adsorption removal rate of PAHs was high in the initial stage. Obviously, the modified mussel shells had a certain adsorption capacity for PAHs, and the initial concentration had a great effect on the adsorption removal rate. However, when the mussel shells absorbed PAHs to a certain extent, the adsorption capacity increased and slowed down. In the actual use of the process, attention should be paid to the adsorption capacity to prevent the waste of adsorption materials.

As shown in Fig. 4b, within a certain range, the adsorption capacity increased with the extension of the adsorption time. With the continuous increase of time, the adsorption rate and capacity rose slowly. The rapid adsorption was basically completed at about 3 h, and the adsorption equilibrium was reached at 4 h[9]. The adsorption removal rate remained unchanged after 4 h, up to 85.29%. The adsorption capacity of the shells tended to be saturated after 4 h.

Salinity had a great influence on the adsorption effect of modified mussel shells (Fig. 4c). With the increase of salinity, the solubility of hydrophobic PAHs decreased, and the tendency to escape from the water phase increased, namely salting-out effect[10], so the adsorption performance was rapidly improved. The total solubility of organic matter in seawater increases with the decrease of ionic strength. Secondly, due to the decrease of ionic strength, the humus in the sediment releases PAHs into the water, resulting in a decrease in adsorption capacity and then distribution coefficient. The change of ionic strength not only affects the solubility of PAHs adsorbed by mussel shells, but also changes the interaction between PAHs and particulate matter. Organic pollutants such as PAHs carry negative charges themselves, and the increase of salinity will weaken the electrostatic repulsion force of PAHs and the shells with negative charges, so the adsorption capacity will be enhanced[11]. The mechanism behind this particular phenomenon remains to be studied.

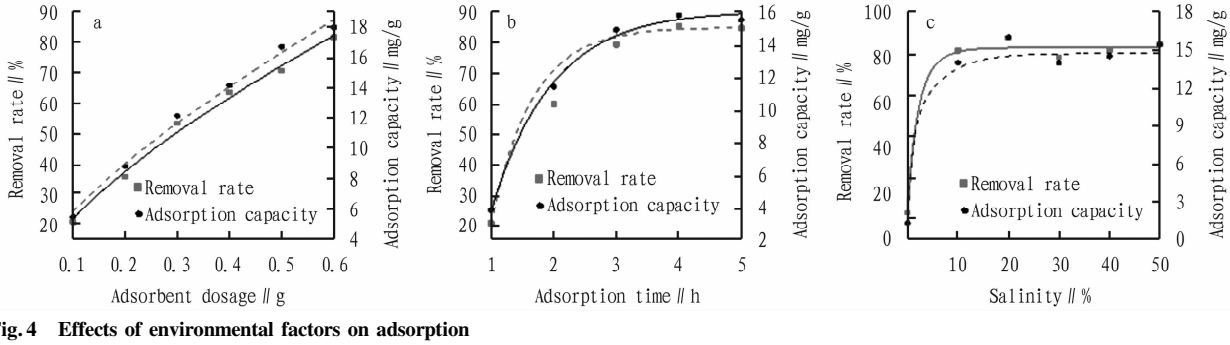


Fig. 4 Effects of environmental factors on adsorption

3 Conclusions

(1) The calcined mussel shells are an excellent biosorption material, with low cost, high efficiency and broad development potential.

(2) After soaking in H_3PO_4 and $ZnCl_2$, the surface pore size of mussel shells increased, and the specific surface area rose, so the adsorption performance was improved.

(3) The modified mussel shells were affected by adsorption temperature, adsorption time, adsorption capacity and solution salinity, and the best adsorption effect was achieved in different states.

References

[1] BOOSE BL, LAMBERSON JO, SWARTZ RC, *et al.* Photoinduced toxic-

ity of PAHs and alkylated PAHs to a marine infaunal amphipod[J]. Archives of Environmental Contamination and Toxicology, 1998, 34(3): 235 – 240.
[2] SYAKTI AD, OURSEL B, GARNIER C. *et al.* Characterisation of the dynamics of organic contaminants (n-alkanes, PAHs and PCBs) in a coastal area[J]. Marine Pollution Bulletin, 2017, 117: 184 – 196.
[3] GARCIA BI, GARCIAC U, PACHECO N, *et al.* Optimization of the biodegradation of aliphatic, aromatic, and ucm hydrocarbons from light crude oil in marine sediment using response surface methodology (RSM)[J]. Bulletin of Environmental Contamination and Toxicology, 2022, 108: 107 – 113.
[4] WANG K, LARKIN T, SINGHAL N, *et al.* Amendment of municipal sewage sludge with lime and mussel shell: Effects on fate of organic matter and pharmaceutically active compounds[J]. Waste Management, 2019, 85: 272 – 282.
[5] GRANADOS ML, POVES Z, ALONSO DM, *et al.* Biodiesel from sunflower oil by using activated calcium oxide[J]. Applied Catalysis B Environmental, 2007, 73(3): 317 – 326.
[6] AHMAD M, SOO LS, YANG JE, *et al.* Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil[J]. Ecotoxicology and Environmental Safety, 2012, 79(4): 225 – 231.
[7] CHAKRBORTY, ANUPAM P, SAIDA C, *et al.* An insight into the structure, composition and hardness of a biological material: The shell of freshwater mussels[J]. RSC Advances, 2020, 49(30): 29543 – 29554.
[8] KUMAR, GOVINDAN S, EASWARADAS K, *et al.* One step method to synthesize flower-like hydroxyapatite architecture using mussel shell biowaste as a calcium source[J]. Ceramics International, 2017, 3(47): 3457 – 3461.
[9] ZHOU D, ZHANG D, ZHANG M, *et al.* Efficient treatment of PAH-contaminated water using magnetic-modified *Myriophyllum aquaticum* waste biomass[J]. Water Air & Soil Pollution, 2023, 234(7): 459.
[10] SCHWARZENBACH RP, GSCHWEND PM, IMBODEN DM. Environmental organic chemistry (2nd edition)[J]. Journal of Contaminant Hydrology, 2005, 23(4): 361 – 362.
[11] FLORES C, CARLOS E, CHAZARO R, *et al.* Biosorption removal of benzene and toluene by three dried macroalgae at different ionic strength and temperatures: Algae biochemical composition and kinetics[J]. Journal of Environmental Management, 2017, 193: 126 – 135.

Copyright Authorization Statement