

Review

# Research Progress on the Applications of Seashell Adsorption Behaviors in Cement-Based Materials

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**Abstract:** The use of seashells to replace traditional cement-based materials and study their adsorption capacity for pollutants can expand the functional engineering application range of cement-based materials. A large amount of seashell waste is produced in coastal areas every year. How to deal with and utilize this seashell waste is a common problem faced by coastal countries and regions. This paper first reviews the principles of adsorption kinetics and adsorption isotherms to demonstrate the adsorption mechanism of shell materials. Then the effects of pH, contact time, temperature, pollutant concentration and other factors on the adsorption of heavy metal ions and basic dyes to seashells are discussed. Finally, the relevant applications of seashells in the construction field are reviewed. The results showed that the optimal pH value in the process of seashell adsorption was 5–7, the active site on the surface of the seashell particles was limited, and that it would reach saturation at a certain concentration, but would not further increase with the increase of time. The active site area of the seashell would increase with the decrease of particle size, so the selection of seashell powder with small particle size was conducive to enhancing the absorption capacity and removal efficiency. The experimental use of seashells instead of cementitious materials or natural aggregates in cement-based materials showed good adsorption capacity and would have a wide range of application prospects in permeable concrete and architectural coatings. By analyzing the research progress on factors influencing seashell adsorption performance and the applications of seashell adsorption behaviors in cement-based materials, this paper could provide ideas and methods for the design of functional cement-based adsorption materials from multiple angles.

**Keywords:** architectural coatings; adsorption kinetics; cement-based materials; dyes; heavy metal ions; seashells



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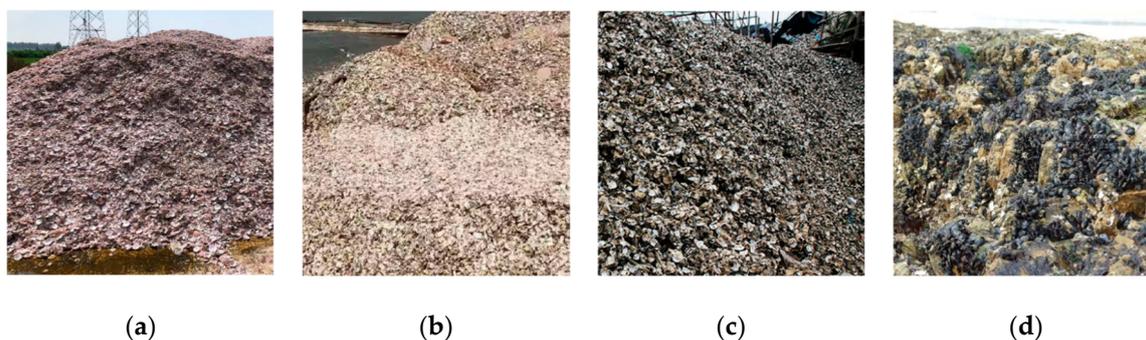
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## 1. Introduction

In many coastal areas, there is a severe problem of seashell waste accumulation. The output of seashells in China has always been the highest in the world, and about 15 million tons of discarded seashells are produced every year. A large amount of seashell waste is discarded, which not only occupies land resources but also pollutes the environment. There are many types of seashells, such as oysters, clams, scallops, mussels, etc. (Figure 1). Seashells are mainly composed of 95% CaCO<sub>3</sub>, along with about 5% organic matter and a small number of inorganic salts such as K, Na, Mg, Fe, Zn, Se and other elements [1,2]. As a natural material, a seashell is mainly composed of three parts: the outermost layer is protein, the middle layer is calcite, and the inner layer is calcium carbonate crystals. The seashell's structure is relatively loose, the pore diameter is relatively large, and the pore distribution is wide and uniform [3–5]. Seashell materials have broad application prospects in the fields of adsorption-type functional building materials.



**Figure 1.** Types of seashells: (a) Scallops; (b) Oysters; (c) Clam; (d) Mussel.

At present, the commonly-used adsorption materials in engineering include activated carbon, zeolite, bentonite, metal oxides and hydroxides, as well as some industrial and agricultural wastes, etc. [6]. Given the considerations of saving costs and natural resources, it is essential to find adsorbent materials that are economical and efficient, and that have strong adsorption capacity. The loose and porous seashell powder obtained by washing and grinding seashell waste has good adsorption, antibacterial properties and affinity with macromolecular substances [7]. Therefore, seashells and materials added with seashells can achieve the adsorption and removal of crude oil, heavy metals, sulfur, dyes, fungicides and other pollutants under certain conditions [8].

With the rapid development of cities, the demand for concrete is increasing. The annual consumption of aggregates in the world exceeds 40 billion tons, of which 64–75% are used to prepare concrete. Many alternative materials currently used to produce ‘green concrete’ are recycled from industrial waste and by-products, so finding sustainable alternatives to natural aggregates is imperative. Since the main component of seashells is calcium carbonate, which is similar to natural aggregate, it can also be divided into coarse aggregate and fine aggregate according to particle size [9]. The research efforts on cement-based materials used as adsorption materials focus on the mass concrete components, and are mainly in reference to pervious road concrete relative to rainwater adsorption, the solidification of cement kiln co-processing on heavy metal ions, and the processing of sludge containing heavy metal ions [10]. Incorporating adsorption materials such as rice husk ash, zeolite, activated carbon and graphene into cement-based materials can effectively improve the adsorption performances of cement-based materials relative to pollutants [11–13].

This article conducts dynamic and thermodynamic analysis on the adsorption process of different types of seashells, lists the matching situations between seashells and adsorption models, analyzes the effects of factors such as pH value, contact time, temperature, adsorbent dosage and pollutant concentration on the adsorption process of seashells, and explores the influences of replacing cementitious materials and natural aggregates with seashells on the adsorption performances of cementitious materials, providing references for the preparation of cement-based adsorption materials.

## 2. Seashell Adsorption Theory

### 2.1. Isothermal Adsorption Theory

Adsorption isotherms describe the retention (or release) or migration of substances from aqueous porous media or aquatic environments to the solid phase at a constant temperature and pH value [14,15]. Adsorption equilibrium is established when the adsorbate is in contact with the adsorbent for a long enough time. The adsorbate concentration in the bulk solution is in dynamic equilibrium with the interface concentration. This constitutes a mathematical connection that plays important roles in the modeling analysis, operation design and application practice of the adsorption system. Graphics are usually used to describe the relationship between the solid phase and the residual concentration of the adsorbate, and its physicochemical parameters describe the surface characteristics, adsorp-

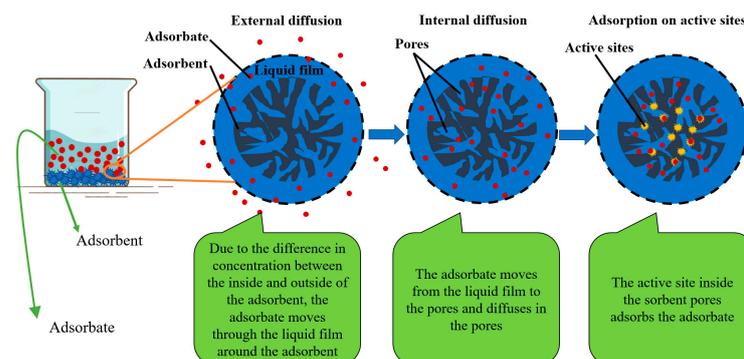
tion mechanism and other characteristics [16–18]. The common isotherm models based on the Langmuir and Freundlich isotherm model are summarized in Table 1.

**Table 1.** Adsorption isotherm models.

Isotherm	Linear Formula	Parameter	Reference
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m K_L} + \frac{1}{q_m}$	$q_e$ : equilibrium concentration on the adsorbent, $\text{mg L}^{-1}$ ; $C_e$ : equilibrium concentration in solution, $\text{mg L}^{-1}$ ; $q_m$ : maximum adsorption capacity, $\text{mg L}^{-1}$ ; $K_L$ : adsorption equilibrium constant.	[19]
Freundlich	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$	$K_F$ : adsorption capacity correlation constant; $n$ : non-uniformity factor.	[20]
Dubinin–Radushkevich	$\ln q_e = \ln q_m - \beta \varepsilon^2$	$\beta$ : D-R isotherm constant; $\varepsilon$ : D-R isotherm constant.	[21]
Temkin	$q_e = \frac{R_T}{b_T} \ln A_T + \frac{R_T}{b_T} \ln C_e$	$R_T$ : gas constant 8.314; $b_T$ : Temkin isotherm constant; $A_T$ : Temkin isotherm equilibrium constant.	[22]
Flory–Huggins	$\log \frac{\theta}{C_0} = \log K_{FH} + n_{FH} \log(1 - \theta)$	$C_0$ : initial concentration in solution, $\text{mg L}^{-1}$ ; $K_{FH}$ : Flory–Huggins isotherm constant; $n_{FH}$ : Flory–Huggins isotherm index; $\theta$ : surface coverage.	[23]
Hill	$\log(1 - \theta) \log\left(\frac{q_e}{q_{sH} - q_e}\right) = n_H \log C_e - \log K_D$	$n_H$ : Hill binding interaction synergy coefficient; $K_D$ : Hill isotherm constant; $q_{sH}$ : Hill isotherm maximum uptake saturation, $\text{mg L}^{-1}$ .	[24]
Redlich–Peterson	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln a_R$	$K_R$ : Redlich–Peterson isotherm constant; $a_R$ : Redlich–Peterson isotherm constant.	[25]
Sips	$\beta_s \ln C_e = \ln a_s - \ln \frac{K_s}{q_e}$	$\beta_s$ : Sips isotherm model index; $a_s$ : Sips isotherm constant; $K_s$ : Sips isotherm constant.	[26]
Toth	$\ln \frac{q_e}{K_T} = \ln C_e - \frac{1}{i} \ln(a_T + C_e)$	$a_T$ : Toth isotherm constant.	[27]

## 2.2. Theory of Adsorption Kinetics

The study of adsorption kinetics provides information on the adsorption rate, the properties of the adsorbent used, and the mass transfer mechanism; it consists of three steps (Figure 2). The first step is external diffusion, where the adsorbate is transferred through the liquid film surrounding the adsorbent. The concentration difference between its bulk solution and the surface of the adsorbent is the driving force for external diffusion. The second step is internal diffusion, which describes the adsorbate's diffusion in the adsorbent's pores. The third step is the adsorption of the adsorbate on the active sites of the adsorbent [28]. The commonly used kinetic models are listed in Table 2.



**Figure 2.** Adsorption and mass transfer diagram.

**Table 2.** Adsorption kinetic models.

Kinetic Equations	Differential Equation	Significance	Reference
<b>Pseudo-first order model PFO</b>	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	Describes the rate at which active sites in the initial phase of an adsorbent adsorb solutes under conditions of high initial concentration.	[29]
<b>Pseudo-second order model PSO</b>	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	Describes the process of adsorbate diffusion from the surface of the adsorbent to the interior. Due to the difference in mass transport at the beginning and end of adsorption, this model is more suitable for describing the diffusion process of substances in particles.	[30]
<b>Intra-particle diffusion IPD</b>	$q_t = k_1 t^{1/2} + C$	Describes the equilibrium rate at which an adsorbent adsorbs a solute, assuming that the adsorption rate is governed by a chemisorption mechanism.	[31]
<b>Hybrid model MO</b>	$\frac{dq_t}{dt} = k_1(q_e - q_t) + k_2(q_e - q_t)^2$	Based on the nonlinear model of PFO and PSO, the adsorption process at any stage is described.	[32]
<b>Ritchie equation</b>	$\frac{d\theta}{dt} = \partial(1 - \theta)^n$	Describe the adsorption process of gases on solids where active sites dominate the adsorption.	[33]
<b>Pseudo n-order model PNO</b>	$\frac{dq_t}{dt} = k_n(q_e - q_t)^n$	The PNO model is an empirical equation, which describes the adsorption process with a series factor greater than 2, and it has no specific physical meaning	[34]

### 3. Seashell Adsorption

#### 3.1. Study on Adsorption of Seashells to Heavy Metal Ions

With the rapid development of industrialization and urbanization, the heavy metal contents of urban and rural rivers and lakes have exceeded the standard limits. In particular, toxic heavy metal ions are widely dispersed in aqueous solutions, which not only have strong toxicity and non-degradable physical and chemical properties but also have serious impacts on human health and environmental ecosystems. The treatment method currently commonly used to reduce or remove heavy metals is chemical precipitation [35]. Although this method is more economical, it has some disadvantages, including slow reaction times, the need to control pH during processing [36], low metal solubility at near-neutral pH, and reliance on polyelectrolytes or other chemicals as coagulant aids in the coagulation and flocculation steps to facilitate rapid settling. Using seashells as a substitute for sedimentation can replace or reduce the current reliance on the large amounts of corrosive chemicals required by conventional sedimentation treatment methods, avoiding secondary pollution. Compared with conventional chemical precipitation, the separation and dehydration steps of physical coagulation of seashell residues are simpler and more manageable [37]. Thus, no coagulants or coagulants are required to facilitate flocculation and rapid settling. The two primary crystalline forms of seashells are calcite and aragonite. Earlier studies showed that minerals in the crystalline forms of calcite and aragonite have the ability to adsorb metal ions. For example, manganese ions are adsorbed by calcium carbonate, and  $Mn^{2+}$  is replaced by  $Ca^{2+}$  on the surface of calcite [38]. The factors affecting the adsorption of heavy metals by seashell materials (Table 3) include pH value, initial concentration of pollutants, contact time, amount of adsorbent, etc.

**Table 3.** Factors affecting the adsorption of heavy metals.

Influencing Factors	The Effects on the Adsorption of Heavy Metals	Reference
pH value	The initial pH value of the solution changes the charge on the adsorbent surface and the ionization degree of the adsorbed species. As the pH value increases, the competition and repulsion between protons and heavy metal ions becomes weakened, and the adsorption rate also increases.	[37,39]
Contact time and Temperature	Temperature and time will affect the adsorption process equilibrium and reaction rate. Due to the electrostatic reaction between the adsorbent and metal ions at high temperatures, the adsorption capacity and removal efficiency generally decrease with the increasing temperature and reach saturation with time.	[40,41]
Adsorbent dosage	The amount of adsorbent determines the adsorption capacity of the adsorbent at a certain concentration of the adsorbed substance. Usually, due to the increase in the active sites of the adsorbent and the easy penetration of metal ions into the adsorption sites, when the amount of adsorbent increases, the adsorption efficiency will improve. When the amount of adsorbent is too much, it will lead to partial coverage of adsorbent particles, a decrease in concentration gradient and a decrease in the effective surface area of adsorption.	[41–43]
Initial concentration of pollutants	When the concentration of heavy metals in the aqueous solution is different, the separation speed is also different. As the initial concentration of metal increases, the ratio of the number of active sites on the adsorbent surface to the number of moles of metal ions at low concentrations is high. At the same time, as the initial concentration of pollutants increased, the adsorption rate decreased instead.	[43–46]

In the experiment of Masukume et al. [47], the washed and dried seashells were crushed and sieved, and the seashells with a particle size below 0.15 mm were weighed and mixed with acid mine wastewater (mainly containing  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ). It is common to seal the container and place it in a shaker at a constant temperature of 25 °C for 24 h, and then to filter the sample with filter paper to detect the concentration of residual iron, manganese and sulfate solution. The experimental results showed that the removal of metal ions increased with the increasing seashell mass, and the metal removal performance followed the following trend:  $\text{Al}^{3+} > \text{Fe}^{3+} > \text{Mn}^{2+}$  [48]. Meanwhile, the experiment measured the influence of different pH values on the adsorption performance. With the increase in pH value,  $\text{H}^+$  gradually decreases, and more metal ions occupy the adsorption sites. The metal adsorption rate increases with the increasing pH value of the initial solution.

Helen et al. [49] chose clams and oysters as research objects, and the experimental treatment method was similar to that of Mike Masukume et al. [47]. The seashell powders with a particle size range of 0.125–0.25 mm were mixed with the metal salt, and stirred evenly at room temperature. The adsorption experiment was conducted on the metal solution containing  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ . The experimental results showed that the adsorption performance of seashell is better than that of limestone in the initial adsorption stage. It has the potential for continuous adsorption capacity and rapid removal of high-concentration metal ions. In the experiment of Mahendra et al. [50], firstly, the seashells were cleaned and dried, and then the seashell powders with a particle size of 0.1 mm were ground and screened for research; secondly, the metal solution (containing  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ ) was mixed with the seashell powders and placed in a shaker for 3 h; finally, the analysis was carried out using adsorption kinetics and adsorption isotherms. According to the analysis of the experimental results, heavy metal accumulation on bivalve mollusks results from ion exchange. At the same time, the adsorption process conforms to the

Langmuir isotherm and the pseudo-second-order kinetic models. The experimental results also showed that the optimal pH range for the seashell to adsorb heavy metals was 5–7, and the equilibrium adsorption amounts of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  were  $588.23 \text{ mg g}^{-1}$ ,  $476.19 \text{ mg g}^{-1}$  and  $357.14 \text{ mg g}^{-1}$ , respectively. Wang et al. [51] soaked the cleaned clam shell in the 0.5% dilute hydrochloric acid for 30 min, and then cleaned and dried them. Clam shell powders with a particle size below 0.1 mm were screened out and calcined at  $1000 \text{ }^\circ\text{C}$  for 3 h in a muffle furnace for experimental analysis. After high-temperature calcination, almost all calcium carbonate is converted into calcium oxide and adsorbs  $\text{Pb}^{2+}$ . The experimental results showed that the adsorption process conformed to the Freundlich isotherm and pseudo-second-order kinetic models. The calcined clam shell powder had good adsorption performance on  $\text{Pb}^{2+}$ , and the adsorption capacity reached  $102.04 \text{ mg g}^{-1}$ .

The effects of pH value, contact time, temperature, pollutant concentration and other factors on the adsorption of heavy metals by seashells are shown in Table 4. A small amount of organic matter inside the seashell has little effect on the adsorption capacity, and the main adsorption work is undertaken by  $\text{Ca}^{2+}$  ions and  $-\text{CO}_3$  groups [36]. The optimum pH value in the seashell adsorption process is 5–7, and when the pH value is less than 4, the  $-\text{CO}_3$  group will be protonated. When the pH is 6–10,  $-\text{CO}_3$  groups react electrostatically with metal ions, which is more conducive to exchanging  $\text{Ca}^{2+}$  with metal ions. When the pH value is  $>10$ , it will increase the deposition of  $\text{OH}^-$  ions, thereby reducing the adsorption capacity [50]. At high temperatures, the binding ability of the active sites of seashells relative to heavy metals becomes weaker, the solution is more inclined to the liquid phase, and the seashells have a stronger ability to capture solid-phase pollutants, resulting in a decrease in adsorption capacity. Since the active sites on the surface of seashell particles are limited, they will reach saturation at a certain concentration, so they will not increase further with time. However, the active sites of seashells will increase with the decrease of particle size, so choosing seashell powders with small particle sizes is beneficial for enhancing the absorption capacity and removal efficiency.

**Table 4.** The strongest influencing factors for seashell adsorption of heavy metals.

Adsorbent	Pollutants	pH	Contact Time h	Temp $^\circ\text{C}$	Concentration of Pollutants $\text{mg L}^{-1}$	Maximum Adsorption Capacity %	Isotherm Model	Kinetic Model	Ref
Oyster shell powders	$\text{Cu}^{2+}$	5.5	24	25	10	99.9	Freundlich	—	[52]
Oyster shell powders	$\text{Ni}^{2+}$	2	24	60	200	47.2	Langmuir	PSO	[53]
Oyster shell powders	$\text{Cu}^{2+}$	2	24	60	200	80.7	Langmuir	PSO	[53]
Oyster shell powder.	$\text{Cd}^{2+}$	10	1	—	5	99.7	—	—	[54]
Calcined oyster shell powders	$\text{Hg}^{2+}$	6	1.3	25	10	95.72	—	—	[55]
Calcined oyster shell powders	$\text{As}^{2+}$	7	1.3	25	10	96.88	—	—	[55]
Oyster shell powders	$\text{Cd}^{2+}$	5	0.8	25	80	39.5	Langmuir	PSO	[56]
Scallop shell powders	$\text{Cd}^{2+}$	5	0.8	25	80	33.3	Langmuir	PSO	[56]
Clam shell powders	$\text{Pb}^{2+}$	6	10	35	160	80.1	Langmuir	PSO	[57]
Clam shell powders	$\text{Pb}^{2+}$	6	24	35	20	85	Langmuir	PFO	[58]
Mussel shell powders	$\text{Cu}^{2+}$	—	—	—	50	100	—	—	[59]
Mussel shell powders	$\text{Cr}^{6+}$	—	—	—	50	100	—	—	[59]
Mussel shell powders	$\text{Cd}^{2+}$	—	—	—	50	100	—	—	[59]

### 3.2. Study on Adsorption of Seashells to Dyes

There are many studies on removing dyes from sewage systems using natural materials, industrial waste or industrial by-products [60]. Shamik Chowdhury et al. [3] investigated the feasibility of removing the cationic dye Basic Green 4 (malachite green,

BG4) from aqueous solutions with seashell powders. The washed and dried seashells were crushed and sieved in the experiment into three particle sizes larger than 0.5 mm, 0.25–0.5 mm and smaller than 0.25 mm. Using Fourier transform infrared spectroscopy (FTIR) for observation and analysis, it was found that the negatively-charged functional groups on the surface of seashell powders interacted with BG-4 at the peak point and reached the maximum adsorption amount at pH = 8. The adsorption isotherm of BG-4 on seashell powders best fit the Langmuir isotherm equation, which indicated that the binding energy of the seashell adsorbent was uniform across the surface. According to the parameters of the Dubinin–Radushkevich isotherm, it can be inferred that the adsorption property of BG-4 on seashell powders is physical adsorption.

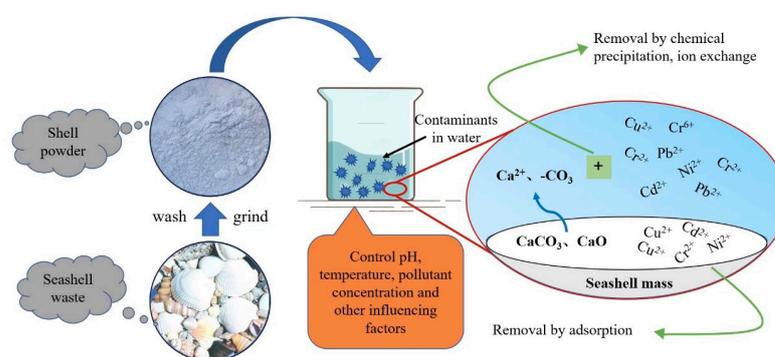
Suteu et al. [61] used seashells to conduct adsorption experiments on Brilliant Red (HE-3B) dye at different temperatures. First, the cleaned and dried seashells were ground and screened to obtain a particle size of 0.06–0.11 mm; then, the seashells were used to conduct adsorption experiments on Brilliant Red with different initial concentrations of 50–300 mg L<sup>-1</sup>. The results showed that the experiment was more in line with the Langmuir isotherm equation, and the adsorption capacities of the monolayer at 20 °C and 60 °C were 109.89 mg g<sup>-1</sup> and 294.118 mg g<sup>-1</sup>, respectively. Based on the Dubinin–Radushkevich isotherm parameters, it can be inferred that this is a combined mechanism of physical adsorption and electrostatic interactions. Mehdi et al. [62,63] used calcined scallop seashells with azo dye Reactive Black 5 (RB-5), anionic dye Reactive Blue 19 (RB-19) and Acid Cyanine-5R (AC-5R) for adsorption tests. The adsorption experiments of RB-5 on scallop shells showed that the adsorption efficiency of scallop shells increased with the increasing amounts of adsorbent. When the dye concentration increased from 100 mg L<sup>-1</sup> to 300 mg L<sup>-1</sup>, the removal efficiency decreased from 94.78% to 59.51%. Adsorptions of RB-19 and AC-5R were carried out using the same scallop seashells used for the adsorption of Reactive Black 5 dye. The results showed that the adsorption efficiency of scallop seashells increased with the amount of adsorbent, and the maximum dye adsorption amounts for RB-19 and AC-5R were 12.36 mg g<sup>-1</sup> and 12.47 mg g<sup>-1</sup>, respectively.

The effects of pH value, contact time, temperature, pollutant concentration and other factors on the adsorption of dyes by seashells are shown in Table 5. It can be seen that the positive charge density on the adsorbent increased in neutral or slightly acidic environments. As the pH value further increased, the H<sup>+</sup> on the particles' surface gradually lost its activity, which had a certain impact on the adsorption performance. The surface smoothness of uncalcined seashells conformed to the monolayer adsorption characteristics, and its isotherm adsorption model conformed to the Langmuir adsorption isotherm. However, after calcined seashells, its isotherm adsorption model became more in line with the Freundlich adsorption isotherm. Since the surface of calcined seashells was rougher, and more pores were generated inside, it would be more in line with the multi-layer heterogeneous adsorption characteristics, further improving adsorption performances [61–63]. Since the number of active sites on the surface of the seashell increases with the decrease of particle size, the storage capacity and removal efficiency are improved, so the smaller the particle size of the seashells, the stronger the adsorption capacity.

Firstly, the adsorption properties of seashells relative to heavy metals and dyes were reviewed; secondly, the effects of pH value, contact time, temperature, pollutant concentration and other factors on seashell adsorption were analyzed; finally, the adsorption mechanism of seashells was judged by the isothermal adsorption model and the adsorption kinetics model. It can be seen from the results that the seashell structure is relatively loose, the pore size is large, and the pore distribution is wide and uniform. While the seashell adsorbs pollutants, its Ca<sup>2+</sup> can ion-exchange with metals and dyes, and the CO<sub>3</sub> group captures pollutants, as shown in Figure 3. Seashell has certain advantages in both physical and chemical adsorptions, and its adsorption rate and effect are also pronounced, proving that it has the potential as an adsorbent.

**Table 5.** The strongest influencing factors for seashell adsorption dyes.

Adsorbent	Dye	pH	Contact Time h	Temp °C	Concentration of Pollutants mg L <sup>-1</sup>	Maximum Adsorption Capacity %	Isotherm Model	Kinetic Model	Ref
Sea shell powders	Malachite green	8	2	30	50	84.6	Langmuir	PSO	[3]
Seashells	Reactive brilliant red	1.2	24	60	300	98.1	Langmuir	PSO	[61]
Calcined scallop shell powders	Reactive Black 5	6	3	—	100	96.7	Langmuir	PSO	[62]
Calcined scallop shell powders	Reactive Blue 19	6	2	—	100	99.9	Freundlich	PSO	[63]
Calcined scallop shell powders	Acid Cyanine 5 R	6	2	—	100	99.9	Freundlich	PSO	[63]
Mussel shell powders	Methyl blue	—	—	—	100	59.8	—	—	[59]
Mussel shell powders	Methyl red	—	—	—	100	99.9	—	—	[59]

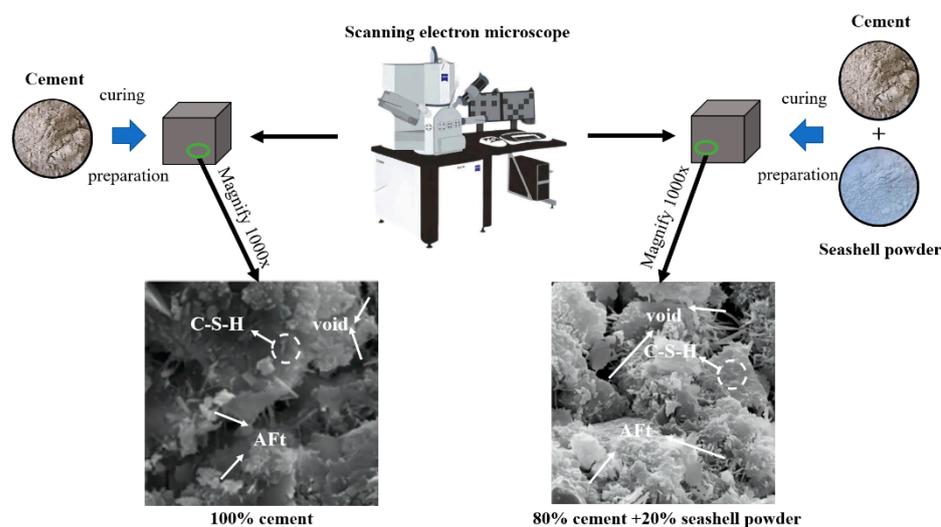
**Figure 3.** Schematic diagram of the seashell adsorption process.

#### 4. Application of Seashell Adsorption Behaviors in Cement-Based Materials

In past studies, the application of seashell materials in cement-based materials has been well-tested mechanically [64,65]. The current processing methods for seashell materials are mainly rinsing, drying or calcination, grinding, and sieving to obtain the required particle sizes [66–68]. The results show that adding seashell materials will reduce the strength of concrete, and when the replacement rate of concrete is below 20%, the concrete strength attenuation will be relatively weak [69–72].

##### 4.1. Application of Seashell Adsorption Behavior in Cement Mortar

Finding alternatives to cement is especially important, because cement emits large amounts of greenhouse gases during production. Currently, materials commonly used to partially replace cement include seashells, blast furnace slag, coal fly ash, etc. The organic matter contained in seashells has different effects on the performance of cement mortar, and the organic matter contained in it can be used as a retarder in cement mortar. The organic matter in the seashells acts in a manner similar to an air-entraining agent on the cement mixtures, introducing air into the cement slurry [73,74]. These alternative materials can improve the durability and mechanical properties of concrete, helping to achieve high acid resistance and water absorption [75]. The process of changing the hydration products of different dosages of seashells instead of cement was observed by scanning electron microscopy, as shown in Figure 4. It can be seen that, in addition to calcium silicate hydrate (C-S-H), more ettringite (AFt) and calcium carbonaluminat phases appeared in the hydration products with the increase of seashell powders in the cement mixture [76]. Lertwattanakul et al. [77] found that some ettringite, especially calcium carbon-aluminat, formed near or on seashell powders. The addition of seashell powders not only enriched the hydration cement matrix, but also promoted the precipitation of hydration products.



**Figure 4.** Scanning electron microscope images of the cement mixtures with different contents of seashell powders.

In the experiments by Carolina et al. [78], heat-treated mussel shells were ground and screened for fine aggregates in the particle size ranges of 0–1 mm and 0–4 mm to replace fine aggregates in cement base coatings and surface coatings for water absorption performance testing. Experimental results showed that mussel mortars had higher water absorption than did the benchmark mortars, and the use of high displacement rates (50% and 75%) significantly affected this property. The main reason is that the addition of flaky seashells would reduce the bonding ability with cement, thereby producing large pores and improving water absorption performance.

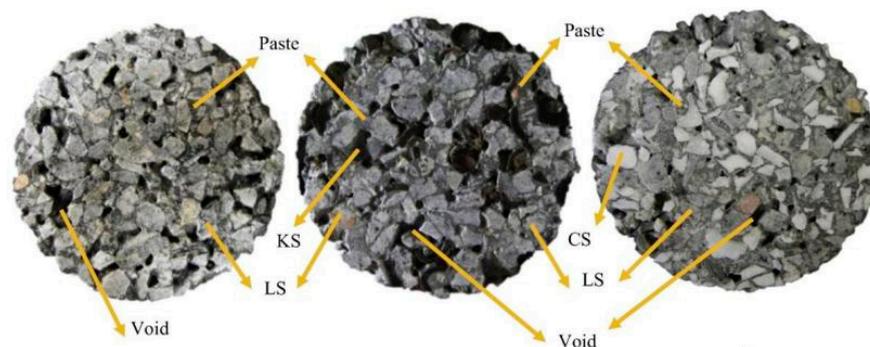
In the experiment by Chen et al. [79], firstly, fly ash and slag were used to replace cement; secondly, the fine aggregate was made of an oyster shell with a 30% substitution rate (particle size below 5mm) to prepare the mortar test block; finally, the water absorption experiment was carried out after curing for 28 days and 90 days, respectively. The results showed that adding fly ash and slag based on oyster seashell waste would effectively increase the water absorption capacity of seashell mortar. After 90 days of curing, the water absorption performance of the seashell mortar decreased, and the water absorption capacity of the test block was significantly reduced due to the influence of curing time. Qasem et al. [80] chose seashell powders (with a particle size below 0.3 mm) to replace cement. The experimental results found that the water absorption performance of cement mortar was improved with the addition of seashell powders.

#### 4.2. Application of Seashell Adsorption Behavior in Concrete

Currently, three main uses of seashells in concrete have been proposed: coarse aggregate substitute, fine aggregate substitute and high-temperature calcination as an activator in concrete [81]. The porous nature of seashells makes them better at absorbing water, but seashells with flakes or elongated shapes have large surface areas, which is not conducive to bonding with cement mortar. The seashells produce many pores in the concrete matrix, reducing the density of the concrete.

Ettu et al. [66] used periwinkle to replace coarse aggregate in concrete, and the replacement rates were 25%, 50% and 75%, respectively. Compared with the control group, after 28 days of curing, the density dropped by 33%, 36% and 41%, respectively. Martínez-García et al. [67] alternately replaced coarse and fine aggregates in concrete with mussel seashells. The results showed that replacing coarse aggregate with mussel seashells had no significant effect on the density of the concrete, which dropped by only about 1% after 28 days of curing. The specimen density with mussel seashells instead of fine aggregate decreased by about 10% after 28 days of curing. After 28 days, the density of concrete specimens with a

20% scallop replacement rate was basically the same as that of the control group. Nguyen et al. [82] found that the density of concrete specimens with a 40% scallop replacement rate and a 60% scallop replacement rate dropped by 4% and 7%, respectively. Khankhaje et al. [83] used seashells (CS) and palm kernel seashells (KS) with replacement rates of 25%, 50%, and 75% to replace coarse aggregate (LS) in the preparation of pervious concrete, as shown in Figure 5. After 28 days of curing, the density of the pervious concrete specimens had a slight change of about 3%. It can be seen that scallops had little effect on the density of pervious concrete, which meets the requirements for pores and can be applied to pervious concrete with low mechanical performance requirements [84].

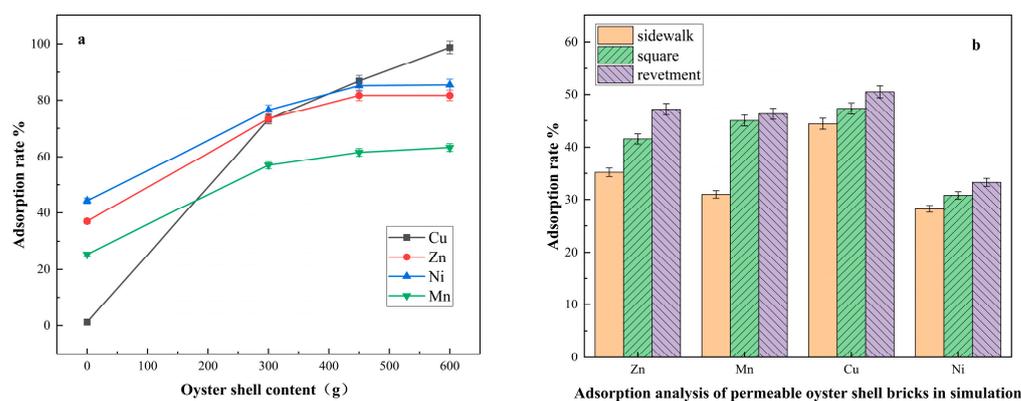


**Figure 5.** Structural diagrams of permeable concrete with different aggregates, from left to right are natural aggregates, palm shells and shells.

Randrianarimanana et al. [85] used scallop materials with a 2–6 mm particle size to replace 40% of the coarse aggregate in an experiment to prepare pervious concrete. In this experiment, a square column composed of the pervious concrete surface, geotextile, cushion and subbase was designed to simulate the rainfall experiment. The results showed that the initial vertical saturated permeability coefficient of the whole permeable pavement system was  $0.25 \text{ cm s}^{-1}$ . In the hydraulic test, the hydraulic function was affected by the value of the inlet flow rate and the duration of the test, and the total moisture loss, including evaporation, was between 9% and 20%. The results showed that the pollutant removal efficiency of the whole system was about 80%, and that of the pervious concrete was 27.4%. It can be seen from this experiment that adding seashells to replace part of the coarse aggregate in pervious concrete could enhance its water permeability and adsorption capacity with respect to pollutants to a certain extent. In the experiment by Nguyen et al. [82], the coarse aggregate in the pervious concrete was replaced by scallop seashells with a particle size of 2–4 mm and replacement rates of 20%, 40%, and 60%. Experimental tests explored the adsorption degrees and permeability coefficients. The results showed that both the porosity and the permeability coefficient increased after the replacement ratio increased, mainly because the seashell materials were more porous than the natural aggregate, and that the combination of the two different materials would produce more pores. Similar trends were also found in other articles [86,87]: after increasing the replacement ratio of seashells, the strength of pervious concrete would decrease, and the water absorption, porosity and water permeability would increase.

Xia et al. [88] used oysters, ordinary Portland cement, natural gravel, standard sand, diatomaceous earth, etc., to make permeable oyster shell bricks. After the washed oysters were dried, they were subjected to controlled heat at  $500 \text{ }^\circ\text{C}$  for 1 h for pulverization, and two types of particle sizes, 2–2.5 mm and 2.5–5 mm, were screened out. They put the experimental materials together, stirred them into a paste, put them into a breathable brick mold and vibrated them, and finally compacted them with a metal plate. After compaction, the experimental materials were calcined in a muffle furnace at  $800 \text{ }^\circ\text{C}$  for 10 min and tested after 7 days of curing. The results of adsorption tests and the simulated permeable adsorptions of copper, zinc, nickel and manganese at different oyster seashell contents (Figure 6) showed that the adsorption capacity of permeable oyster seashell bricks

increased with the increase of oyster seashells. The main reason is that the seashell material itself has a good adsorption capacity for heavy metals, so the adsorption performance of the test block shows a parabolic upward trend. The permeable oyster seashell bricks have a continuous adsorption effect and have many applications in daily life, with great potential in wastewater treatment. It also shows that the seashell material is a feasible concrete additive material, one which can effectively improve the adsorption performance of permeable concrete.



**Figure 6.** The effects of oyster shell content on the adsorption capacity of heavy metals and the simulated permeable adsorption analysis: (a) the effect of oyster shell content on adsorption; and (b) the simulated permeable adsorption analysis [88].

#### 4.3. Study on Adsorption of Seashell Materials Used in Architectural Coatings

With the enhancement of people's health and environmental protection concepts and the continuous innovation of coating technology, solvent-based coatings that release toxic gases are gradually replaced by powders and water-based coatings [89]. Seashells are made into water-based paints through special processes such as grinding and high-temperature calcination, which can absorb and decompose harmful gases [90]. Mollusk seashells have a porous and fibrous double helix structure after modification and calcination. Therefore, the seashell coating has a wide range of applications in the aspects of alkali resistance, crack resistance, humidity regulation and adsorption of harmful gases. For example, using seashell waste as a calcium source, hydroxyapatite is prepared and coated on the coating substrate, and the prepared coating exhibits excellent corrosion resistance and low roughness [91].

The formaldehyde purification rate of water-based coatings prepared from seashell powders increases linearly with the addition of seashell powders [92]. Wang [93] et al. prepared water-based seashell powder coatings with different amounts of seashell powders and calculated the effect of seashell powder admixture on the adsorption of formaldehyde in water-based coatings. The results showed that with the addition of seashell powders increased from 100 g to 200 g, the formaldehyde purification rate increased from 39.2% to 68.3%. Seashell powders contain many micropores, and the adsorption performance increases gradually with the increase in seashell powder content.

The moisture absorption and desorption performances of coatings means that when the indoor humidity is too high or too low, the coatings rely on their characteristics to adjust the relative humidity in the space and keep the air at a certain humidity [94]. The porous structure of seashell powder gives it an excellent moisture absorption capacity. Studies have shown that 1 kg of seashell powders can absorb 3.244 g of water in a standard indoor environment [95]. Liquid interior wall coatings containing diatomaceous earth and seashell powders as functional fillers have excellent humidity regulation functions [96]. Wang et al. [93] studied the moisture absorption and desorption of seashell powders, calcined seashell powders and calcined mature seashell powders, and found that all of these three seashell powders could reach saturation within 36 h. The order of moisture absorption

rate is calcined seashell powders > calcined mature seashell powders > uncalcined seashell powders. The main reason is that calcium carbonate is converted into calcium oxide after seashell powders are calcined, which then reacts with moisture in the air to form calcium hydroxide. Therefore, even though the specific surface area of calcined and cured seashell powders is higher, their moisture absorption rate is higher than that of uncalcined seashell powders, but still lower than that of calcined seashell powders. The order of dehumidification speed is calcined mature seashell powders > calcined seashell powders > uncalcined seashell powders. Calcined seashell powders will react with part of the moisture during the moisture absorption process, and it is irreversible, so the moisture cannot be completely released.

## 5. Conclusions

This paper analyzed the adsorption properties of seashells and some applications of seashells in the field of architecture. First, the influences of the physical and chemical properties of seashell materials on the adsorption process were analyzed, and the matching of different types of seashells with the adsorption model was listed. Secondly, the effects of pH value, contact time, temperature, adsorbent dosage, pollutant concentration and other factors on the seashell adsorption process were analyzed. The results showed that the seashells had good adsorption performances. The adsorption performance with respect to pollutants was better in a neutral or slightly acidic environment, and its adsorption performance was further enhanced with the increase of temperature. According to the performance analysis of shells in cement-based materials, given the physical and chemical characteristics of shells themselves and their adsorption performance, the addition of shells below 20% would not seriously impact the mechanical properties of cement-based materials. Meanwhile, grinding seashells into pieces and adding them to cement-based materials can effectively enhance the adsorption performance of cement-based materials and thus filter pollutants. In terms of non-structural aspects, cement-based materials are used as aggregate substitutes to provide a reference for the design of functional cement-based materials.

New adsorption materials have become a research hotspot, and the research on the applications of cement-based materials in the adsorption field is gradually increasing. However, there is relatively little research on adsorption performance and pollutant treatment when adding seashells to cement-based materials.

- (1) At present, seashells are mostly used for the adsorption of metal ions, and there are few studies on the adsorption properties of seashell materials relative to oil pollution. Seashell materials are porous, and their pore structure has a great influence on the adsorption performances of oil-absorbing materials.
- (2) After calcining, the main components of the seashell change from calcium carbonate to calcium oxide and calcium hydroxide, and its interior presents a more complex pore structure. To a certain extent, the physical adsorption of seashells is improved, but this will also decrease the abilities of shell groups to capture pollutants. Therefore, the comparison of the adsorption performance of seashells before and after calcination needs further study.
- (3) At present, research on adding seashells to cement-based materials has shown that seashells offer a certain improvement in the adsorption performance of cement-based materials, although their strength is lower than that of traditional cement-based materials. Further research is needed to ensure their adsorption performance while improving their strength.

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