High performance adsorption of Orange II dye onto modified mussel shell powder

Fang Zhu[a], Lingli Ji[a], Qinqin Sun[a], Jianfeng Ma[a,*], Sridhar Komarneni[b,*]

[a]School of Environmental and Safety Engineering, Changzhou University, Jiangsu 213164, China, emails: jma@zju.edu.cn (J. Ma), 635835458@qq.com (F. Zhu), 1215047959@qq.com (L. Ji), 1509145978@qq.com (Q. Sun)
[b]Department of Ecosystem Science and Management and Materials Research Institute, 204 Energy and Environment Laboratory, The Pennsylvania State University, University Park, PA 16802, USA, email: komarneni@psu.edu

ABSTRACT

A low-cost and high-efficiency adsorbent was synthesized to remove Orange II dye from wastewater by modifying waste mussel shells with formic acid. The modified mussel shell powder was characterized by X-ray powder diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, Brunauer–Emmett–Teller surface area determination, and X-ray photoelectron spectroscopy. The effects of solution pH, contact time and temperature on the adsorption of Orange II dye by modified mussel shell powder were investigated. The adsorption capacity of modified mussel powder to Orange II decreased with the pH value increased from 3 to 11. The adsorption capacity gradually increased with contact time, and reached the maximum in about 18 min. The pseudo-first-order kinetic model can fit the adsorption behavior well. Thermodynamic results show that the adsorption process is spontaneous and endothermic. The maximum adsorption capacity of modified mussel shell for Orange II dye was determined to be 65.43 mg/g, which is much higher than the previously reported results. The results showed that modified mussel shell powder had a potential application prospect as an adsorbent for the removal of Orange II from waste water.

Keywords: Mussel shells; Adsorbent; Kinetics; Adsorption isotherm

1. Introduction

Industrialization and urbanization are the inevitable trends of societal development, which tends to aggravate environmental pollution with dyes. Dye wastewater is produced in papermaking, printing, plastic processing, leather, coating, pharmaceutical industries, etc. [1–3]. Many dyes used in the textile industry show stability under light and oxidation conditions and are resistant to aerobic degradation, so they are difficult to remove [4]. Therefore, dye removal is an important and challenging area in wastewater treatment. Many studies have been carried out using physical and chemical methods to remove dyes, including flocculation, chemical oxidation, electrochemical method, biological treatment method, etc. [5,6]. Among various methods, adsorption method occupies a very important position. Adsorption method is better than other methods in terms of low cost, simple design and operation method and insensitivity to toxic substances [7], so it is favored in practical application. Activated carbon is the most widely used adsorbent. Due to its large specific surface area, high porosity and various functional groups on the surface, it is the most effective and popular adsorbent for the removal of organic and inorganic pollutants [8]. However, the wide application

* Corresponding authors.

of activated carbon is limited due to its limited adsorption capacity, selective adsorption, complex regeneration process and high-cost [9]. Therefore, the research and development of adsorbents with wide application range, high adsorption efficiency, easy regeneration, stable performance and low treatment cost has become the popular research direction of many researchers. It is reported that many natural, renewable, eco-friendly adsorbents can adsorb dyes in water, including agricultural waste (soybean shell, rice husk, peanut shell, banana, eucalyptus leaves, coconut coir, etc.) [10–14], biological adsorbent (chitosan, biomass), and other materials such as starch, cotton, etc. [15,16]. However, the search for more efficient, environmentally friendly, cheap and readily available adsorbents continues.

With the development of aquaculture, mussels became a popular food. However, the disposal of the waste of mussel shells has become a major issue. If discarded shells are not properly disposed of, large quantities of shells will result in environmental pollution [17]. In order to prevent environmental pollution and reduce environmental impact, it is urgent to recycle waste shells. In recent years, shells, as a renewable and low-cost biomass material, has attracted much attention for its potential application in many fields [18,19]. It can be used as an environment-friendly adsorbent to adsorb heavy metals, dyes, fluorine, phosphate and sulfur compounds in wastewater [20–27]. Orange II [28,29] is a kind of anionic dye, which is widely used in textile, paper, food, wig and leather dyeing industries whose water solubility is up to 116 g/L. This dye is not biodegradable in nature and has been found to be harmful by inducing changes in animal cells. It also has a high mobility and permeability as it can penetrate into the soil and has the potential to pollute groundwater [30]. Many studies have found that structural modification of some adsorbents can improve the original adsorption capacity. For example, coating eggshell powder with manganese oxide can improve the adsorption of arsenic ions in aqueous solution [31]. Modified mussel shell with $Fe(OH)_3$ can be used as a low-cost adsorbent to remove phosphorus from wastewater [32]. Our research group has also carried out some research work on adsorbing dyes with phosphoric acid modified clam shell powder [33].

Therefore, this paper aims to develop a cheap and easily available modified shell powder adsorbent to adsorb Orange II dye in wastewater, so as to treat waste with the waste. First, shells were made into a soft sponge [34], and then manganese oxides were coated on its surface to study the feasibility of this new modification method to improve the adsorption performance of dyes by the modified shells. The optimum adsorption conditions of Orange II in solution were studied by the adsorption parameters such as pH, contact time and temperature.

2. Materials and methods

2.1. Materials

Orange II dye ($C_{16}H_{11}N_2NaO_4S\cdot5H_2O$, molecular weight of 350.32) and ethanol (EtOH) were purchased from the Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Formic acid (CH_2O_2) was purchased from the Chinasun

Specialty Products Co., Ltd., (Jiangsu, China) and used without further purification.

2.2. Pretreatment of mussel shells

The mussel shells were obtained from Lianyungang City, Jiangsu Province. First the surface sediment was washed off and the inside contents were washed off with tap water, leaving only the shell, which was then boiled in hot water for 10 min. After boiling, the shell was taken out and washed with ultrapure water for 3 times, and dried at 120°C for 3 h. After drying, the shell was broken into small pieces with a hammer, and then the small pieces were crushed with a pulverizer into a powder of less than 20 mesh.

2.3. Preparation of modified adsorbent

The modification process of shell powder includes the following steps: (1) A known amount of mussel shell powder was put into formic acid solution (3%) with a solid to liquid ratio of 1:20, (2) the mixture was soaked and reacted while stirring with a magnetic stirrer for 6 h, (3) after soaking, the suspension was filtered with suction filter to separate solid from solution, rinsed with ethanol (95%) for three times, and then rinsed with deionized water for several times to ensure the removal of formic acid, (4) an appropriate amount of shell powder was weighed and it was soaked in 50 g/L manganese chloride solution for 48 h. The treated shell powder was centrifuged and filtered and then calcined in a tube furnace at 400°C for 2 h. The modified mussel shell powder was stored in glass bottles before characterization and adsorption studies.

2.4. Adsorption experiments

The modified mussel shell powder was used as an adsorbent for the removal of dye from wastewater. Adsorption experiment was carried out in a 200 mL beaker containing 100 mL Orange II (50 mg/L) while stirring with a magnetic stirrer (500 rpm). The adsorption reactions were initiated by adding 300 mg of modified mussel shell powder. 1.5~2 mL solution was taken out every 2 min with a syringe, and the liquid was separated through a 0.22 μm filter. The absorbance values of the Orange II dye at its maximum wavelength of 484 nm were recorded by UV-visible spectrophotometer (UV-2450, Shimadzu, Japan). When the adsorption equilibrium was reached, the following formula was used to calculate the adsorption amount:

$$q = \frac{V(C_0 - C)}{W} \tag{1}$$

where q is the adsorption amount (mg/g), C_0 and C in (mg/L) are the liquid-phase concentrations of dye at initial and at equilibrium, respectively, V is the volume of solution (L), and W is the mass of adsorbent in (g).

2.5. Characterization of materials

The structure and phase compositions of modified mussel shell powder were monitored by powder X-ray

diffraction (XRD) analysis using an X-ray diffractometer (Rigaku D/Max-2500 PC) with Cu Kα (λ = 1.54056 Å) radiation (40 kV, 300 mA) of 0.154 nm wavelength. The functional groups of modified mussel shell powder were analyzed by Fourier-transform infrared spectroscopy (FTIR). The surface morphology of modified mussel shell powder was observed and analyzed by the JSM-6360LA scanning electron microscope (SEM, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was used to analyze chemical components by a Thermo Scientific K-Alpha electron spectrometer. The specific surface area of the modified mussel shell powder samples was determined by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms on a surface area analyzer (Micromeritics, ASAP 2010C, USA).

3. Results and discussion

3.1. Characterization analysis of materials

3.1.1. XRD analysis

The XRD patterns of the raw shell powder and the modified shell powder are shown in Fig. 1a, revealing that there are significant differences between the two samples. The modified shell powder has fewer peaks than the raw shell powder, because the chemicals in the shell reacted with formic acid and led to this result. The modified shell powder has a main peak at 2θ = 29.396°, and the peak intensity is obviously higher than that of the same peak of unmodified shell powder. The peaks at 2θ of 35.967°, 39.444°, 43.210°, 47.533°, 48.526°, 57.403°, 60.677° and 64.677° are consistent with the X-ray diffraction pattern of calcite (Fig. 1a), which is consistent with the literature report [34]. The XRD pattern also confirmed the absence of aragonite. However, no Mn crystallites were detected in the XRD patterns of modified powder, which may be due to the low amount and poor crystallinity of Mn adsorbed on the surface of mussel shell powder. Mn phase was not detected because the high crystallinity of calcium carbonate crystals could have masked the diffraction peaks of other crystals [35]. In addition, no other peaks were found, indicating that no other phases could be detected in the modified shell powder.

3.1.2. Infrared analysis

The surface functional groups of modified mussel shells were characterized by FTIR. The dried modified shell powder (2 mg) was compacted with 100~150 mg potassium bromide under pressure, and the infrared (IR) spectra were collected in the spectral range of 400~4,000 cm^{-1} [36]. The infrared spectrum was obtained after the modified mussel powder sample was evenly mixed with potassium bromide and then pressed into pellets (Fig. 1b). As can be seen from Fig. 1b, a wide peak at 3,448.74 cm^{-1} is –OH stretching vibration peak, which refers to the hydroxyl groups (moisture content) from water. The two small peaks near 2,900 and 2,500 cm^{-1} are attributed to the C–H bond stretching of the protein and the –OH of HCO^{2-} [37]. The existence of $CaCO_3$ polyphase can be recognized by an obvious peak at 1,428.94 cm^{-1} while calcium carbonate deformation peak occurred at 1,637.03 cm^{-1} and out-of-plane bending vibration of CO_3^{2-} ion occurred at 873.91 cm^{-1} [33]. In addition, the peak at 1,794.47 cm^{-1} can be attributed to C=O in carbonate ion while the peak at 712.84 cm^{-1} is attributed to the in-plane bending vibration of CO_3^{2-} ion. Thus, the FTIR results show that the main component of the modified shell powder is calcite calcium carbonate [38].

3.1.3. SEM analysis

The raw mussel shell powders and modified mussel shell powders were characterized by SEM and the results are shown in Fig. 2. It can be seen from Fig. 2b that the modified mussel shell powders are mainly in the nest-like morphology formed by prismatic columns or needles of crystals [34], which may be caused by erosion after formic acid treatment. The BET specific surface area of modified mussel shell powder was determined to be 7.68 m^2/g.

3.1.4. XPS analysis

In order to further understand the chemical composition and adsorption mechanism of modified mussel shell powder, the valence states of elements in the materials were determined by XPS [39]. Fig. 3a shows the XPS spectrum of modified mussel shell powder. It can be seen
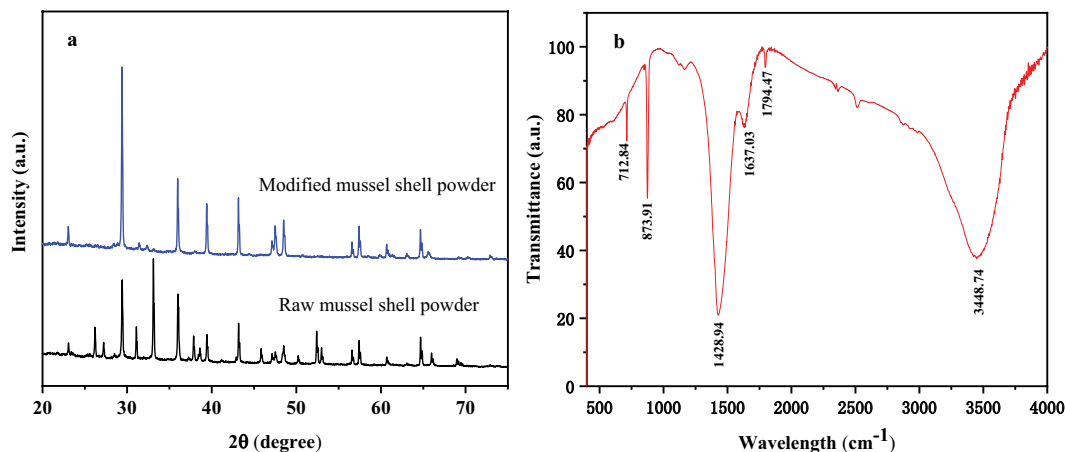

Fig. 1. (a) XRD patterns of raw shell and modified shell powders and (b) IR spectrum of modified mussel shells.
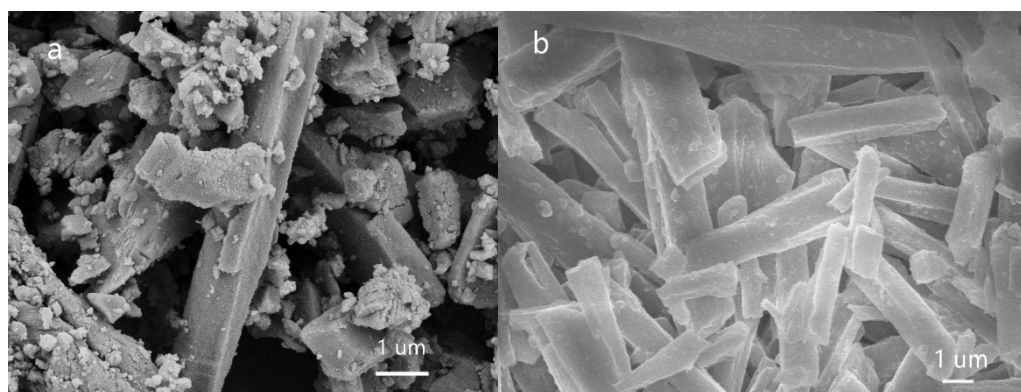
Fig. 2. SEM images of (a) raw mussel shell powder and (b) modified mussel shell powder.
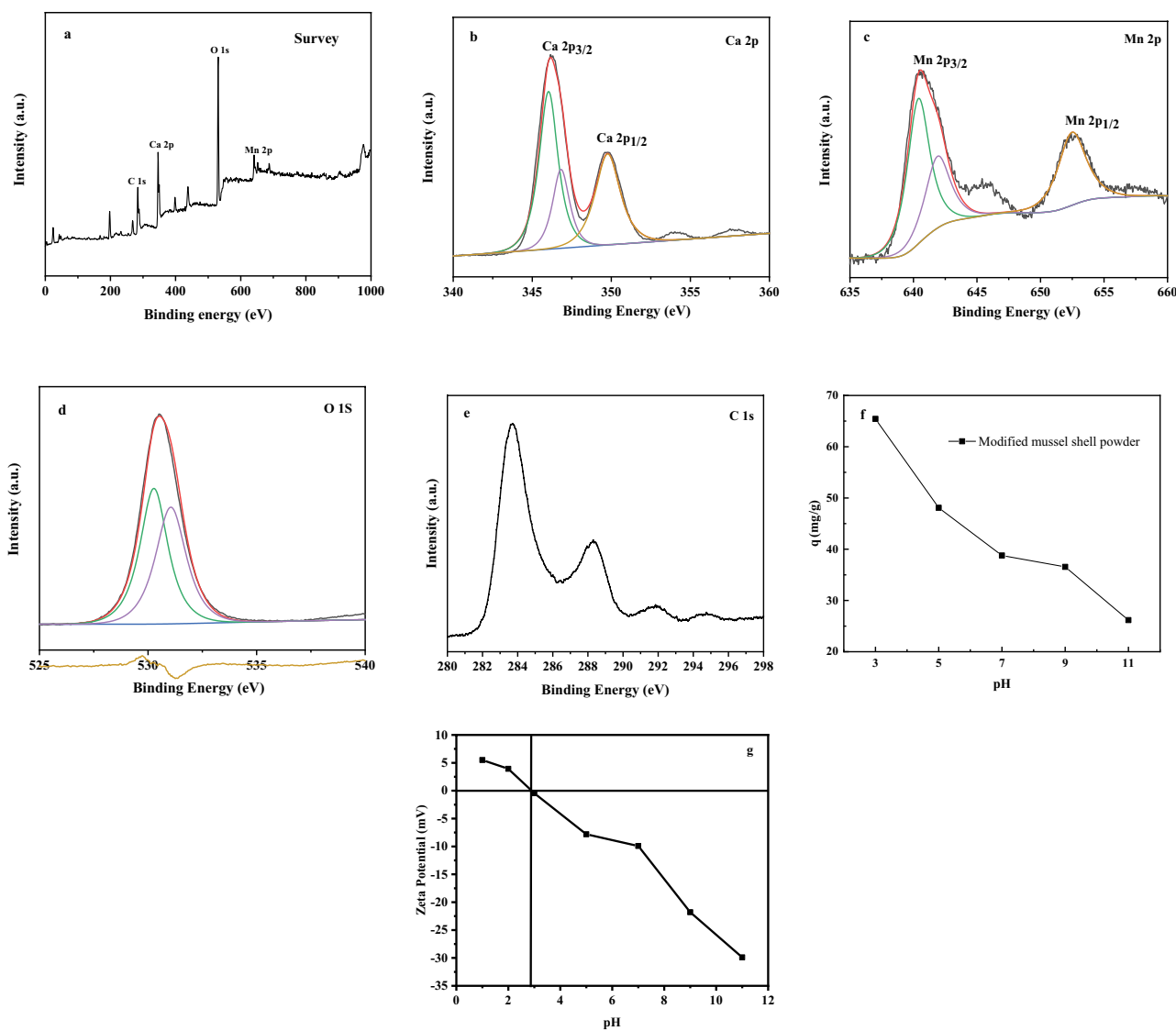

Fig. 3. (a) XPS survey, (b) Ca 2p, (c) Mn 2p, (d) O 1s and (e) C1s XPS spectra of modified mussel shell powder. (f) Influence of pH on adsorption performance of modified mussel shells. (g) Zeta potential of modified mussel shells with different pH. Adsorption conditions: Orange II 50 mg/L, adsorbent 1 g/L and adsorption temperature was 298 K, adsorption time was 18 min.

from Fig. 3a that the appearance of Mn 2p peak indicates that Mn element has been successfully introduced into this material. The peaks of O 1s and C 1s are at 532.3 and 284.6 eV [40–42] respectively. The Mn 2p spectrum in Fig. 3b shows two peaks at 653.5 and 641.5 eV. Due to spin orbital splitting, Ca $2p_{3/2}$ and Ca $2p_{1/2}$ are clearly visible around ~345.5 and ~349 eV, respectively.

3.2. Effect of pH on adsorption properties

In the adsorption process, the initial pH of the solution is an important parameter because pH has a great influence on chemisorption, which can affect not only the surface charge of the adsorbent, but also the surface charge of the adsorbate in the adsorption process [43]. The influence of pH on the adsorption process of modified shell powder was investigated by changing the initial pH of Orange II dye solution. The initial pH of the orange dye solution was set as 3, 5, 7, 9, 11, and the time required for adsorption to reach equilibrium at each pH value was measured. When pH increased from 3 to 11, the adsorption capacity of modified mussel shell powder on Orange II dye decreased from 65.43 to 25.03 mg/g (Fig. 3b). When pH was equal to 3, the adsorption effect on orange dye was the best. Adsorption decreased with increasing pH of the solution because of the existence of more OH⁻ species at higher pH, which would compete with anionic Orange II dye for adsorption sites on the modified mussel shell powder. In addition, the reduction in the adsorption quantity may also be associated with the reversal of the adsorbent surface charge due to treatment of mussel shell powder with manganese chloride, which led to a layer of manganese oxide coating after calcination. After manganese oxide coating, the surface may have become positively charged and therefore adsorbed negatively charged Orange II dye in large quantities under acidic conditions. However, with the increase of pH, charge repulsion occurred between the adsorbent and dye, resulting in the decrease of adsorption capacity of modified mussel shell powder [36,44]. In addition, zero point of charge (PZC) value represents the zero charge of the catalyst, which is a necessary research object in the study of dye adsorption. When (pH_{PZC}) catalyst < pH (solution), cationic dye molecules will be adsorbed, while when (pH_{PZC}) catalyst > pH (solution), anionic dye molecules will be adsorbed [45,46]. As the pH_{PZC} value of the modified mussel shell powder is 2.9 (Fig. 3g). When the pH of the solution is lower than 2.9, the number of positive charges on the catalyst surface will increase, so more anionic Orange II dyes can be adsorbed in this case.

3.3. Influence of contact time on adsorption properties

Fig. 4 shows the effect of contact time on the amount of dye adsorption. It can be seen from Fig. 4 that with the increase of contact time between modified mussel shell powder and Orange II dye, the adsorption capacity gradually increased, and reached the maximum value of 30.56 mg/g at about 18 min. Compared with other adsorbents, the adsorption rate of modified mussel shell powder on orange dye was faster [33]. This is because the adsorption sites of mussel shell powder increased after

modification by formic acid erosion and manganese chloride addition followed by calcination. The diffusion rate to the surface and interior of the modified mussel shell powder was faster, and the removal rate and adsorption capacity increased significantly for the negatively charged orange dye. With the increase of adsorption time, the adsorption amount decreased after 18 min, which may be because the adsorption sites of the adsorbent reached saturation, that is, total adsorption occurred. Therefore, any further extension of contact time had no significant effect on the adsorption amount of Orange II. Therefore, in subsequent experiments, the adsorption time of 18 min was used.

3.4. Adsorption isotherms

Adsorption isotherms are important for understanding adsorption systems. Langmuir and Freundlich adsorption isotherm models were used to analyze the adsorption data of Orange II dye on modified mussel shell powder under different temperatures (273, 298, and 323 K). Langmuir adsorption isotherm is characterized by adsorption occurring as a monolayer at specific sites, which are distributed on the uniform surface of adsorbent, and its formula can be expressed as [47,48]:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{2}$$

where C_e is the concentration of dye in the solution when the adsorption reaches equilibrium (mg/L), q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), q_m is the adsorption capacity of the adsorbent (mg/g), and b is the Langmuir model constant (L/mg).

Freundlich isotherm model is a commonly used model to describe adsorption on non-uniform surfaces. The formula is expressed as [44]:
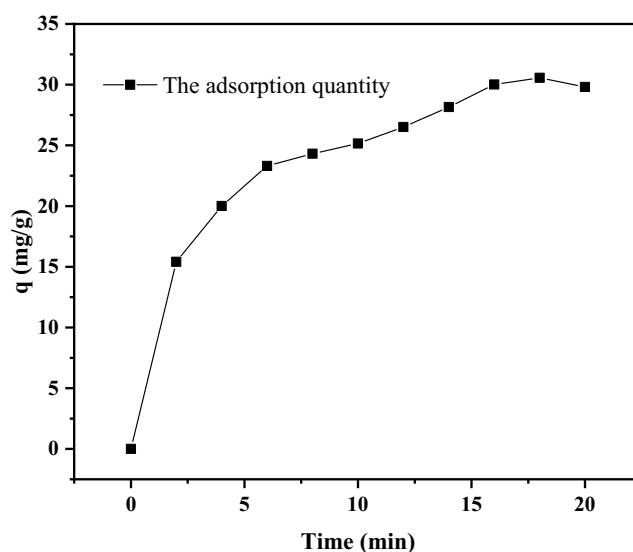

Fig. 4. Influence of contact time on adsorption performance of modified mussel shells. Adsorption conditions: Orange II 50 mg/L, adsorbent 1 g/L and adsorption temperature was 298 K, initial solution pH = 5.86 ± 0.20.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{3}$$

where n and K_F are Freundlich constants, representing adsorption strength and adsorption capacity respectively, and $1/n$ is the factor of non-uniformity. When $n > 1$, it indicates that the adsorption process is favorable.

As can be seen from Fig. 5, the adsorption effect of modified mussel shell powder on Orange II dye was significantly improved compared with the original powder, indicating that the physical and chemical properties of manganese modified mussel shell powder were enhanced and the adsorption performance was improved.

Fig. 6 shows the adsorption isotherms of two different models based on experimental data. Table 1 is the value of adsorption isotherm parameters. For modified mussel shell powder, there was a linear relationship between $\ln C_e$ and

lnq_e and between $1/C_e$ and $1/q_e$ at all temperatures, so both Langmuir and Freundlich models could well fit the experimental data of adsorption of Orange II dye by modified mussel shell powder at different temperatures. The detailed analysis of the regression coefficients showed that Langmuir R^2 (0.96206~0.97687) was higher, so the Langmuir isothermal model was more suitable, indicating that the adsorption of Orange II dyes by modified mussel shells was uniform, and the adsorption mainly occurred as a monolayer. In addition, the linear form of Langmuir adsorption isotherm fits the data better than the nonlinear form.

It can be seen from Table 1 that the adsorption order of modified mussel shells at different temperatures is as follows: 323 > 298 > 273 K, indicating that within a certain range, the higher the temperature is more conducive for the adsorption of dye. The increased adsorption capacity with the increase of temperature indicates that the adsorption process is endothermic. It was previously reported that the increase in volumetric adsorption capacity might be due to an increase in the diffusion rate within the adsorbate particles, since diffusion is an endothermic process [49].

3.5. Adsorption kinetics

The quasi-first order kinetic model, the quasi-second-order kinetic model and the intraparticle diffusion equation were used to describe the adsorption process of Orange II dye by modified shell powder.
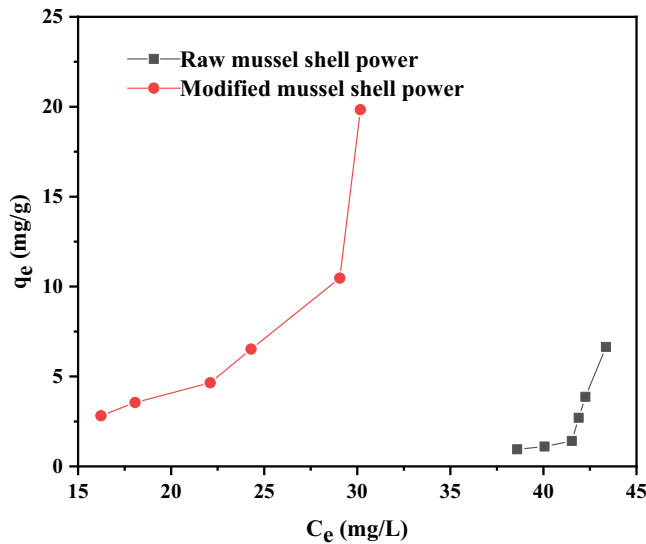

Fig. 5. Comparison of adsorption of Orange II on raw mussel shell powder and modified mussel shell powder. Adsorption conditions: Orange II 50 mg/L, adsorbent 1 g/L and adsorption temperature was 298 K, initial solution pH = 5.86 ± 0.20.

Table 1
Freundlich adsorption model and Langmuir adsorption model constants

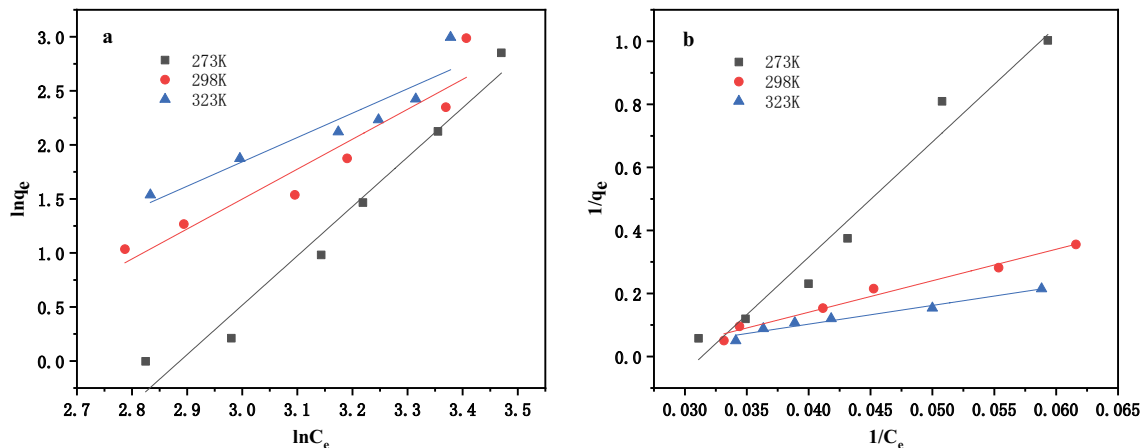|	T (K)	273	298	323
Langmuir	q_m	10.17461	13.33815	20.47314
	b	4.99495	11.40386	15.64209
	R^2	0.96635	0.97687	0.96206
Freundlich	K_F	0.000187	0.001103	0.007319
	n	1.218925	1.361105	1.443766
	R^2	0.96732	0.90355	0.87464

Fig. 6. (a) Freundlich and (b) Langmuir adsorption model.

The quasi-first-order kinetic model is based on the assumption that the occupancy rate of adsorbed sites is proportional to the number of unoccupied sites, and the equation form is [50]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

where k_1 is a quasi-first-order rate constant (min^{-1}), and q_t (mg/g) is the adsorption capacity of dye at time t (min).

The quasi-second-order kinetic model assumes that the occupancy rate of adsorption sites is proportional to the square of the number of unoccupied sites and the equation is written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where k_2 is a quasi-second-order rate constant (g/min·mg).

The intraparticle diffusion equation is [39]:

$$q = k_{int} t^{1/2} + b \qquad (6)$$

where k_{int} is the internal diffusion rate constant (mg/g·min$^{1/2}$), t is the adsorption contact time (min), and b is a constant (mg/g).

Fig. 7 shows the experimental results of adsorption kinetics of Orange II dye on modified mussel shell powder at 273, 298 and 323 K. As can be seen from Fig. 7, when the temperature is 273, 298 and 323 K, the adsorption process of modified mussel shell on Orange II dye progresses rapidly in about 2 min, and then gradually decreases into a slow adsorption stage until the maximum adsorption amount is reached. In the early stage of adsorption, the reason why the mussel shell powder modified by the calcination of manganese chloride adsorbed faster was that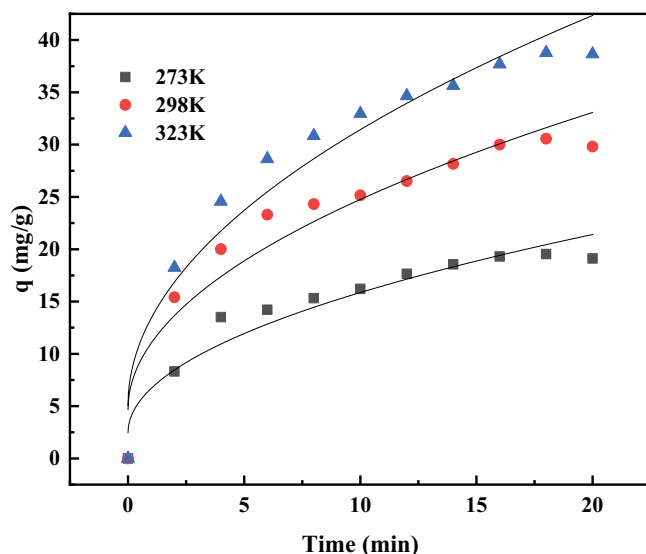 there were many adsorption sites and the dye concentration was high, resulting in surface adsorption. As the adsorption site of the adsorbent is gradually filled, the Orange II dye would further diffuse into the adsorbent. During the process of adsorption, the concentration of Orange II dye decreased gradually, the mass transfer force weakened, the adsorption amount increased slowly, and the adsorption entered the equilibrium stage.

In order to better understand the adsorption of Orange II dye by modified mussel shell powder, different kinetic models were used to fit the adsorption kinetic data of orange dye on modified mussel shell powder at different temperatures, and the fitting data are shown in Table 2. As can be seen from Table 2, the correlation coefficient R^2 (69.365–85.262) of the quasi-second-order adsorption kinetic equation is lower than that of the quasi-first-order adsorption kinetic equation (78.567–97.755), indicating that the entire adsorption process was more in line with the quasi-first-order adsorption kinetic model. The occupation rate of adsorption sites in the adsorption process between modified caustic shell powder and Orange II dye was proportional to the number of unused sites. It can be inferred that the adsorption of Orange II dye by modified mussel shell is not only physical adsorption, but also chemical adsorption.

Table 3 represents the fitting results of the particle diffusion model for the adsorption of Orange II dye by modified mussel shell powder at different temperatures. As can be seen from Table 3, in the rapid adsorption stage, the regression coefficient R_2^2 is high and can be well fitted, while in the slow adsorption stage, the regression coefficient is low. The fitting degree was good for the whole process of adsorption, which indicated that the adsorption of Orange II dye by modified mussel shell powder had an internal diffusion mechanism, and the internal diffusion process could be divided into two stages. In the rapid adsorption stage, the internal diffusion rate constant K_{int2} is larger, while in the slow adsorption stage, the internal diffusion rate K_{int3} is smaller. This may be because the Orange II dye diffuses from the outer surface of the modified mussel shell powder to the internal process, the resistance increases, resulting in a lower adsorption rate and a slower adsorption. In the whole process, $K_{int3} < K_{int1} < K_{int2}$, and the internal diffusion rate in the slow stage is the minimum, so the speed of the adsorption rate in the slow stage determines the speed of the whole adsorption process. Moreover, with the increase of temperature, the internal diffusion rate of each stage gradually increases with the increase of temperature, indicating that the internal diffusion rate of Orange II dye on modified mussel shell powder can be increased by increasing

Fig. 7. Adsorption kinetics of Orange II dye on modified mussel shells at different temperatures.

Table 2
Fitting parameters of adsorption kinetics model at different temperatures

	T (K)	273	298	323
Quasi-first-order	k_1 (×10^{-2})	23.218	4.891	11.456
kinetic parameters	R^2	97.755	81.718	78.567
Quasi-second-order	k_2 (×10^{-2})	0.2473	0.6047	1.3045
kinetic parameters	R^2	69.365	80.778	85.262

the temperature in a certain range. The intercept b indicates whether the boundary effect exists, that is, when $b = 0$, intraparticle diffusion is the only rate control step, but $b \neq 0$ as shown in Table 3. Therefore, the existence of the boundary layer effect can be inferred, indicating that there are surface phenomena such as mass transfer or liquid film diffusion in the process of adsorption of Orange II dye by modified mussel shell powder [38]. This may be caused by the erosion of mussel shell powder by formic acid.

3.6. Adsorption thermodynamics

Thermodynamic analysis is of great significance for the study of adsorption mechanism, which guides practical production and application [35]. In any adsorption process, energy and entropy are needed to determine whether the adsorption process is spontaneous or not. Thermodynamic parameters are calculated as follows [51]:

$$K_d = \frac{q_e}{C_e} \tag{7}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

where K_d is the solid–liquid partition coefficient (L/g), R is the standard gas constant (8.314 J/(mol·K)), T is the absolute temperature (K), ΔG is the Gibbs free energy changes (kJ/mol), ΔH is the standard enthalpy changes (kJ/mol), ΔS is the standard entropy changes (kJ/(mol·K)).

In order to better understand the influence of temperature on the adsorption of Orange II dye by modified mussel shell powder, the thermodynamic parameter equation was used to fit the obtained data. The results are shown in Fig. 8 and Table 4.

As can be seen from Table 4, ΔG gradually decreases with the increase of temperature, and a negative value appears at 323 K, indicating that the increase of temperature is more conducive to the spontaneous adsorption reaction. $\Delta H = 14.128$, which is >0, indicating that the adsorption process of modified mussel shell powder for Orange II dye is an endothermic adsorption process, which is the same as that obtained by isothermal adsorption model. The heat generated during physical adsorption is in the range of 2.1~20.9 kJ/mol [50,52]. From Table 4, the obtained value of ΔH suggests that the adsorption of Orange II by modified

mussel shell powder mainly takes place by physical adsorption, which is consistent with the results of pseudo-first-order kinetic model fitting, $\Delta S = 0.0459 > 0$. It shows that the randomness of solid–liquid interface increases during the adsorption of Orange II dye by modified mussel shell powder, which is a process of entropy increase. In general, the adsorption process of Orange II on modified mussel shell powder is a high temperature process, which is spontaneous, endothermic and of increased entropy.

3.7. Safe disposal of waste adsorbent

Put it in a tube furnace and calcine it at 400°C for 2 h using spent adsorbents for the next reuse. Finally, the obtained particles can be used in roads or landfills.

3.8. Comparison of modified shell powder with other materials

Table 5 summarizes the comparison of the maximum adsorption capacities of several different adsorbents for
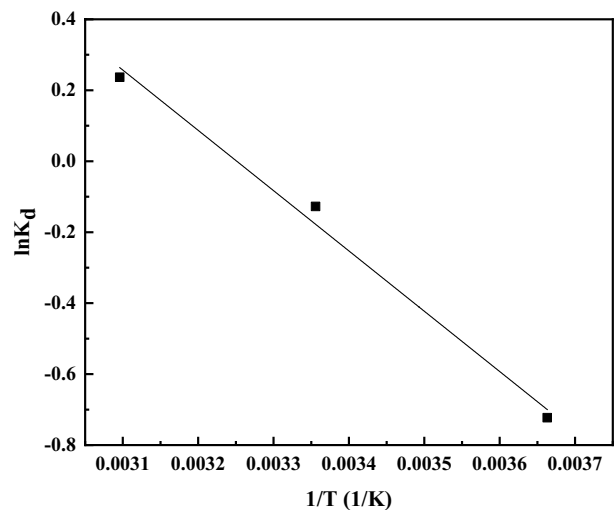

Fig. 8. Adsorption thermodynamics.

Table 4
Thermodynamic parameters of adsorption of Orange II

	ΔG (kJ/mol)		ΔH (kJ/mol)	ΔS (kJ/(mol·K))
273 K	298 K	323 K		
1.588	0.440	−0.708	14.128	0.0459

Table 3
Fitting parameters of intraparticle diffusion model of modified mussel shell powder at different temperatures

T (K)	Whole process			Rapid adsorption			Slow adsorption		
	K_{int1}	b_1	R_1^2	K_{int2}	b_2	R_2^2	K_{int3}	b_3	R_3^2
273	4.236	2.466	0.937	6.099	0.070	0.982	2.623	8.226	0.896
298	6.347	4.686	0.925	9.640	0.551	0.992	3.938	13.21	0.862
323	8.334	5.079	0.947	11.849	0.492	0.995	5.023	16.99	0.973

Table 5
Comparison on Orange II adsorption capacity by modified mussel shell and other reported adsorbents

Adsorbent	q_{max} (mg/g)	References
Biological solid adsorbents	0.6	[53]
Commercial activated carbon	0.73	[53]
Zeolite modified by HDTMA	3.38	[54]
Zeolite	0.63	[54]
CTAB coated zeolite	38.96	[55]
Natural zeolite	8.13	[55]
Modification of palygorskite with STAB	92	[30]
Modification of palygorskite with DOAB	88	[30]
Inorganic–organic bentonite	76	[56]
Deoiled soybean drugs	7.39	[57]
Waste residue	5.93	[57]
Modified mussel shell	65.43	This study

Orange II dye, including the mussel shell powder modified in this paper. As can be seen from Table 5, the adsorption capacity of modified mussels on Orange II dye is better, but it is also lower than that of modified palygorskite and inorganic–organic bentonite, so the modification process still needs to be optimized. However, it has the additional advantages of simple production process, easy to obtain materials and low cost, indicating that the modified mussel shell has a good development prospect for adsorbing Orange II dye.

3.9. Dye adsorption mechanism

Combined with FTIR and XPS, we found that it might be due to several active functional groups, such as –OH form a coordination bond with Mn(II) ions. Adsorption processes might include electrostatic interaction, hydrogen bonding, physical adsorption and chemical adsorption. Therefore, the detailed mechanism was difficult to describe. There might be electrostatic interaction between positively charged functional groups on the surface of modified shell powder and negatively charged sites (Orange II) strongly adsorbed from the solution. As the pH_{PZC} value of the modified mussel shell powder is 2.9, when pH increased from 3 to 11, the adsorption capacity of modified mussel shell powder on Orange II dye decreased.

4. Conclusion

The adsorption capacity of Orange II was improved by modifying the discarded mussel shell powder, and the adsorption capacity changed with the change of pH, contact time and temperature. The maximum adsorption capacity was 65.43 mg/g. The results show that both Langmuir and Freundlich models can be used to describe the adsorption process of modified mussel shell powder, and the Langmuir linear model has a better fit for the data in general. Secondly, the quasi-first-order kinetic model is more consistent with the adsorption behavior of modified mussel

shell powder for Orange II dye. In addition, thermodynamic studies show that the adsorption of Orange II by modified mussel shell powder is spontaneous, endothermic and feasible. Therefore, it can be concluded that modified mussel shell powder is an effective adsorbent to remove Orange II dye from wastewater. Mussel shells are a waste product, but can be converted into an adsorbent to serve as a resource.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] L. Dai, W. Zhu, L. He, F. Tan, N. Zhu, Q. Zhou, M. He, G. Hu, Calcium-rich biochar from crab shell: an unexpected super adsorbent for dye removal, Bioresour. Technol., 267 (2018) 510–516.

[2] M.M. El Bendary, E.K. Radwan, M.F. El-Shahat, Valorization of secondary resources into silica-based adsorbents: preparation, characterization and application in dye removal from wastewater, Environ. Nanotechnol. Monit. Manage., 15 (2021) 100455, doi: 10.1016/j.enmm.2021.100455.

[3] A. Kheddo, L. Rhyman, M.I. Elzagheid, P. Jeetah, P. Ramasami, Adsorption of synthetic dyed wastewater using activated carbon from rice husk, SN Appl. Sci., 2 (2020) 2170, doi: 10.1007/s42452-020-03922-5.

[4] V.K. Gupta, I. Ali, Suhas, D. Mohan, Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents, J. Colloid Interface Sci., 265 (2003) 257–264.

[5] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review, J. Environ. Manage., 90 (2009) 2313–2342.

[6] K.S. Bharathi, S.T. Ramesh, Removal of dyes using agricultural waste as low-cost adsorbents: a review, Appl. Water Sci., 3 (2013) 773–790.

[7] S. Jain, R.V. Jayaram, Removal of basic dyes from aqueous solution by low-cost adsorbent: wood apple shell (*Feronia acidissima*), Desalination, 250 (2010) 921–927.

[8] Y. Zhou, L. Ge, N. Fan, M. Xia, Adsorption of Congo red from aqueous solution onto shrimp shell powder, Adsorpt. Sci. Technol., 36 (2018) 1310–1330.

[9] R. Bushra, S. Mohamad, Y. Alias, Y. Jin, M. Ahmad, Current approaches and methodologies to explore the perceptive adsorption mechanism of dyes on low-cost agricultural waste: a review, Microporous Mesoporous Mater., 319 (2021) 111040, doi: 10.1016/j.micromeso.2021.111040.

[10] E.D.V. Giordano, M.E. Brassesco, P. Camiscia, G.A. Picó, N.W. Valetti, A new alternative and efficient low-cost process for the removal of reactive dyes in textile wastewater by using soybean hull as adsorbent, Water Air Soil Pollut., 232 (2021) 1–25.

[11] K. Bharathi, S. Ramesh, Removal of dyes using agricultural waste as low-cost adsorbents: a review, Appl. Water Sci., 3 (2013) 773–790.

[12] K. Ghosh, N. Bar, A.B. Biswas, S.K. Das, Elimination of crystal violet from synthetic medium by adsorption using unmodified and acid-modified eucalyptus leaves with MPR and GA application, Sustainable Chem. Pharm., 19 (2021) 100370, doi: 10.1016/j.scp.2020.100370.

[13] I. Ghosh, S. Kar, T. Chatterjee, N. Bar, S.K. Das, Adsorptive removal of Safranin-O dye from aqueous medium using

coconut coir and its acid-treated forms: adsorption study, scale-up design, MPR and GA-ANN modeling, Sustainable Chem. Pharm., 19 (2021) 100374, doi: 10.1016/j.scp.2021.100374.

[14] K. Ghosh, N. Bar, A.B. Biswas, S.K. Das, Removal of methylene blue (aq) using untreated and acid-treated eucalyptus leaves and GA-ANN modelling, Can. J. Chem. Eng., 97 (2019) 2883–2898.

[15] S. Bhattacharya, N. Bar, B. Rajbansi, S.K. Das, Adsorptive elimination of Cu(II) from aqueous solution by chitosan-nanoSiO$_2$ nanocomposite—adsorption study, MLR, and GA modeling, Water Air Soil Pollut., 232 (2021) 161, doi: 10.1007/s11270-021-05070-x.

[16] B. Singha, N. Bar, S.K. Das, The use of artificial neural networks (ANN) for modeling of adsorption of Cr(VI) ions, Desal. Water Treat., 52 (2014) 415–425.

[17] Q. Wang, F. Jiang, X.-K. Ouyang, L.-Y. Yang, Y. Wang, Adsorption of Pb(II) from aqueous solution by mussel shell-based adsorbent: preparation, characterization, and adsorption performance, Materials, 14 (2021) 741, doi: 10.3390/ma14040741.

[18] L. Ji, W. Song, D. Wei, D. Jiang, L. Cai, Y. Wang, J. Guo, H. Zhang, Modified mussel shell powder for microalgae immobilization to remove N and P from eutrophic wastewater, Bioresour. Technol., 284 (2019) 36–42.

[19] L. He, J. Meng, Y. Wang, X. Tang, X. Liu, C. Tang, L.Q. Ma, J. Xu, Attapulgite and processed oyster shell powder effectively reduce cadmium accumulation in grains of rice growing in a contaminated acidic paddy field, Ecotoxicol. Environ. Saf., 209 (2021) 111840, doi: 10.1016/j.ecoenv.2020.111840.

[20] C. Xia, X. Zhang, L. Xia, Heavy metal ion adsorption by permeable oyster shell bricks, Constr. Build. Mater., 275 (2021) 122128, doi: 10.1016/j.conbuildmat.2020.122128.

[21] S. Chowdhury, P. Saha, Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies, Chem. Eng. J., 164 (2010) 168–177.

[22] J.-I. Lee, J.-K. Kang, S.-H. Hong, C.-G. Lee, S. Jeong, S.-J. Park, Thermally treated *Mytilus coruscus* shells for fluoride removal and their adsorption mechanism, Chemosphere, 263 (2021) 128328, doi: 10.1016/j.chemosphere.2020.128328.

[23] W. Kim, R. Singh, J.A. Smith, Modified crushed oyster shells for fluoride removal from water, Sci. Rep., 10 (2020) 5759, doi: 10.1038/s41598-020-60743-7.

[24] N.A.A. Salim, N.H. Abdullah, M.R. Khairuddin, M.A.Z.R. Arman, M.H. Khamidun, M.A. Fulazzaky, A.R.M. Yusoff, M.H.D. Othman, M.H. Puteh, Adsorption of phosphate from aqueous solutions using waste mussel shell, MATEC Web Conf., The 12th International Civil Engineering Post Graduate Conference (SEPKA) – The 3rd International Symposium on Expertise of Engineering Design (ISEED) (SEPKA-ISEED 2018), 250 (2018) 06013.

[25] C. Namasivayam, A. Sakoda, M. Suzuki, Removal of phosphate by adsorption onto oyster shell powder—kinetic studies, J. Chem. Technol. Biotechnol., 80 (2005) 356–358.

[26] W.F. Sye, Y.C. Chen, S.F. Wu, Evaluation of natural porous crab shell powder used for the enrichment of sulfur compounds from gaseous samples, J. Chin. Chem. Soc., 50 (2003) 73–79.

[27] A. Das, N. Bar, S.K. Das, Adsorptive removal of Pb(II) ion on *Arachis hypogaea*'s shell: batch experiments, statistical, and GA modeling, Int. J. Environ. Sci. Technol., (2022), doi: 10.1007/s13762-021-03842-w.

[28] F. Zhu, J. Ma, Q. Ji, H. Cheng, S. Komarneni, Visible-light-driven activation of sodium persulfate for accelerating Orange II degradation using ZnMn$_2$O$_4$ photocatalyst, Chemosphere, 278 (2021) 130404, doi: 10.1016/j.chemosphere.2021.130404.

[29] F. Zhu, Q. Ji, Y. Lei, J. Ma, Q. Xiao, Y. Yang, S. Komarneni, Efficient degradation of Orange II by core shell CoFe$_2$O$_4$–CeO$_2$ nanocomposite with the synergistic effect from sodium persulfate, Chemosphere, 291 (2022) 132765, doi: 10.1016/j.chemosphere.2021.132765.

[30] B. Sarkar, Y. Xi, M. Megharaj, R. Naidu, Orange II adsorption on palygorskites modified with alkyl trimethylammonium and dialkyl dimethylammonium bromide—an isothermal and kinetic study, Appl. Clay Sci., 51 (2011) 370–374.

[31] S. Mubarak, M. Zia-ur-Rehman, M.N. Chaudhry, Modified eggshells as cost effective adsorbent for the treatment of arsenic(III) contaminated industrial effluents, Asian J. Chem., 27 (2015) 1995–2000.

[32] H. Yin, L. Liu, M. Lv, L. Feng, J. Zhou, Metal-modified mussel shell for efficient binding of phosphorus in eutrophic waters, Int. J. Environ. Res., 14 (2020) 135–143.

[33] J. Ma, J. Zou, B. Cui, C. Yao, D. Li, Adsorption of Orange II dye from aqueous solutions using phosphoric-acid modified clam shell powder, Desal. Water Treat., 51 (2013) 6536–6544.

[34] J.N. Murphy, C.M. Schneider, K. Hawboldt, F.M. Kerton, Hard to soft: biogenic absorbent sponge-like material from waste mussel shells, Matter, 3 (2020) 2029–2041.

[35] D. Zhang, K. Zhang, X. Hu, Q. He, J. Yan, Y. Xue, Cadmium removal by MgCl$_2$ modified biochar derived from crayfish shell waste: batch adsorption, response surface analysis and fixed bed filtration, J. Hazard. Mater., 408 (2021) 124860, doi: 10.1016/j.jhazmat.2020.124860.

[36] R. Slimani, I. El Ouahabi, S. Benkaddour, H. Hiyane, M. Essoufy, Y. Achour, S. El Antri, S. Lazar, M. El Haddad, Removal efficiency of textile dyes from aqueous solutions using calcined waste of eggshells as eco-friendly adsorbent: kinetic and thermodynamic studies, Chem. Biochem. Eng. Q., 35 (2021) 43–56.

[37] B. Zhao, J.-e. Zhang, W. Yan, X. Kang, C. Cheng, Y. Ouyang, Removal of cadmium from aqueous solution using waste shells of golden apple snail, Desal. Water Treat., 57 (2016) 23987–24003.

[38] H.T. Van, L.H. Nguyen, X.H. Nguyen, T.H. Nguyen, T.V. Nguyen, S. Vigneswaran, J. Rinklebe, H.N. Tran, Characteristics and mechanisms of cadmium adsorption onto biogenic aragonite shells-derived biosorbent: batch and column studies, J. Environ. Manage., 241 (2019) 535–548.

[39] X. Wang, Z. Zhang, Y. Zhao, K. Xia, Y. Guo, Z. Qu, R. Bai, A mild and facile synthesis of amino functionalized CoFe$_2$O$_4$@SiO$_2$ for Hg(II) removal, Nanomaterials, 8 (2018) 673, doi: doi: 10.3390/nano8090673.

[40] Y. Shen, N. Jiang, S. Liu, C. Zheng, X. Wang, T. Huang, Y. Guo, R. Bai, Thiol functionalization of short channel SBA-15 through a safe, mild and facile method and application for the removal of mercury(II), J. Environ. Chem. Eng., 6 (2018) 5420–5433.

[41] J. Shen, S. Zhang, Z. Zeng, J. Huang, Y. Shen, Y. Guo, Synthesis of magnetic short-channel mesoporous silica SBA-15 modified with a polypyrrole/polyaniline copolymer for the removal of mercury ions from aqueous solution, ACS Omega, 6 (2021) 25791–25806.

[42] Z. Zhang, K. Xia, Z. Pan, C. Yang, X. Wang, G. Zhang, Y. Guo, R. Bai, Removal of mercury by magnetic nanomaterial with bifunctional groups and core-shell structure: synthesis, characterization and optimization of adsorption parameters, Appl. Surf. Sci., 500 (2020) 143970, doi: 10.1016/j.apsusc.2019.143970.

[43] S. Dandil, D.A. Sahbaz, C. Acikgoz, High performance adsorption of hazardous triphenylmethane dye-crystal violet onto calcinated waste mussel shells, Water Qual. Res. J., 54 (2019) 249–256.

[44] S. Gao, W. Zhang, Z. An, S. Kong, D. Chen, Adsorption of anionic dye onto magnetic Fe$_3$O$_4$/CeO$_2$ nanocomposite: equilibrium, kinetics, and thermodynamics, Adsorpt. Sci. Technol., 37 (2019) 185–204.

[45] A.G. El-Shamy, An efficient removal of methylene blue dye by adsorption onto carbon dot @ zinc peroxide embedded poly vinyl alcohol (PVA/CZnO$_2$) nano-composite: a novel reusable adsorbent, Polymer, 202 (2020) 122565, doi: 10.1016/j.polymer.2020.122565.

[46] L. Ji, Q. Xiao, L. Zhu, S. Komarneni, J. Ma, CDs@Cr$_2$O$_3$ catalytic degradation of Orange II based on non-radical pathway, Mater. Chem. Phys., 287 (2022) 126257, doi: 10.1016/j.matchemphys.2022.126257.

[47] B. Qiu, J. Guo, X. Zhang, D. Sun, H. Gu, Q. Wang, H. Wang, X. Wang, X. Zhang, B.L. Weeks, Polyethylenimine facilitated ethyl cellulose for hexavalent chromium removal with a wide pH range, ACS Appl. Mater. Interfaces, 6 (2014) 19816–19824.

[48] B. Qiu, J. Guo, X. Zhang, D. Sun, H. Gu, Q. Wang, H. Wang, X. Wang, X. Zhang, B.L. Weeks, Z. Guo, S. Wei, Polyethylenimine facilitated ethyl cellulose for hexavalent chromium removal with a wide pH range, ACS Appl. Mater. Interfaces, 6 (2014) 19816–19824.

[49] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using flyash, a low-cost adsorbent, Ind. Eng. Chem. Res., 41 (2002) 3688–3695.

[50] K.G. Akpomie, F.A. Dawodu, Efficient abstraction of nickel(II) and manganese(II) ions from solution onto an alkaline-modified montmorillonite, J. Taibah Univ. Sci., 8 (2014) 343–356.

[51] S. Meski, N. Tazibt, H. Khireddine, S. Ziani, W. Biba, S. Yala, D. Sidane, F. Boudjouan, N. Moussaoui, Synthesis of hydroxyapatite from mussel shells for effective adsorption of aqueous Cd(II), Water Sci. Technol., 80 (2019) 1226–1237.

[52] Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol., 61 (2008) 229–242.

[53] C. Hung-Lung, L. Kuo-Hsiung, C. Shih-Yu, C. Ching-Guan, P. San-De, Dye adsorption on biosolid adsorbents and commercially activated carbon, Dyes Pigm., 75 (2007) 52–59.

[54] X. Jin, M.-q. Jiang, X.-q. Shan, Z.-g. Pei, Z. Chen, Adsorption of methylene blue and Orange II onto unmodified and surfactant-modified zeolite, J. Colloid Interface Sci., 328 (2008) 243–247.

[55] X. Jin, B. Yu, Z. Chen, J.M. Arocena, R.W. Thring, Adsorption of Orange II dye in aqueous solution onto surfactant-coated zeolite: characterization, kinetic and thermodynamic studies, J. Colloid Interface Sci., 435 (2014) 15–20.

[56] J.F. Ma, J.M. Yu, B.Y. Cui, D.L. Li, J. Dai, Adsorption and catalysis of Orange II from wastewater by inorganic–organic bentonite, Adv. Mater. Res., 340 (2012) 236–240.

[57] V. Gupta, A. Mittal, V. Gajbe, J. Mittal, Removal and recovery of the hazardous azo dye acid orange 7 through adsorption over waste materials: bottom ash and de-oiled soya, Ind. Eng. Chem. Res., 45 (2006) 1446–1453.