Adsorption Performance of Phosphorus from Industrial Sewage on Ferric Chloride-eggshell

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Abstract. Wasted Eggshell is modified by FeCl₃. The influence of mass concentration of FeCl₃ in different situations, reaction temperature and initial concentration of phosphorus on the adsorption effect was studied, the adsorption kinetics, thermodynamic and adsorption isotherm model are used to simulate the process. The results shows that: The adsorption rate of original eggshell is 33% under the condition of 0.3% FeCl₃, 40°C reaction temperature, and 50 mg/L phosphorus, and the adsorption capacity reaches Phosphorus adsorption rate of FeCl₃-coated is 99.13%, and the adsorption capacity reaches 3.95mg/g, which is reaching the national two grade effluent standard. The adsorption model fitting results shows that the adsorption of phosphorus on modified eggshells was a physical process of spontaneous, endothermic and anisotropy, and the adsorption rate was affected by the internal pore size.

1. Introduction
Phosphorus is widely present in nature. Excessive phosphorus in water mainly comes from domestic sewage, industrial sewage, and agricultural products and so on, it is one of the important factors which cause eutrophication. At present, the mainly method of phosphorus removal include biological, chemical precipitation and adsorption phosphorus removal. The removal rate of phosphorus of chemical is high but too expensive. Although the biological method of phosphorus removal is low in cost but unstable in effect, the reaction speed of adsorption method is high but the adsorption capacity is low [1-6]. This paper will combine the chemical and adsorption method which increase adsorption capacity and reduce costs.

There are a lot of eggshell resources in China, so the reuse of wasted eggshells has considerable practical significance. A large number of pore channels are distributed in the eggshell, which provide sustainable adsorption sites for phosphorus removal and cause the strong adsorption capacity. Phosphorus also can be adsorbed by free iron ions, so ferric chloride-eggshell can improve the adsorption capacity of eggshells [7-12], which is realized the reused of wasted eggshell of iron ion treatment and industrial sewage.
2. Experimental Part

2.1. Experimental Materials and Instruments
Materials: Distilled water, eggshell (from the first canteen of Shenyang Jinzhou University), Potassium dihydrogen phosphate, ferric chloride, concentrated sulphuric acid, potassium antimony oxide tartrate, ammonium moly date and ascorbic acid. All the reagents are analytically pure.

Experimental Instruments: Constant Temperature Oscillating incubator(Shanghai Precision Instrument Company); Electric Thermostat Blasting Dryer( Wujiang Rongxin Oven Manufacturing Plant); Ultraviolet Visible Spectrophotometer( Shanghai Precision Instrument Company).

2.2. Experimental Method

2.2.1. Pretreatment and Modification of Eggshell. Wash up the waste shell and remove the intima, dry at 105°C and grind, leave the 80 mesh sieve and for reserve. Under 25°C, 1g eggshell powder was added to FeCl₃ liquor of 0.05%, 0.1%, 0.3%, 0.5% and 1% of 100ml. After shaking for 9h in constant temperature, the eggshell powder was centrifuged for 5 min at 4000r/min at centrifuge. Eggshell is washed for three times by distilled water and then dried. Blank experiment was carried out when the concentration of FeCl₃ solution was 0%. There are three parallel samples in each group.

2.2.2. Adsorption Isotherm Experiment. The eggshell powder was added into 100ml potassium dihydrogen phosphate liquor which containing 10 mg/L, 20 mg/L, 35 mg/L and 50 mg/L of phosphorus respectively. Under 25°C, after shaking for 9h in constant temperature, took 5ml supernatant, filtered by 0.45 μm filter membrane. Set the phosphorus content and drawn the curve.

2.2.3. Adsorption Kinetics Experiment. The eggshell powder was added into 100ml potassium dihydrogen phosphate liquor which containing 50mg/L of phosphorus. The supernatant was quickly removed at 1, 2, 3, 4, 5, 6, 7, 8, and 9 h in 25°C. After filtration with 0.45 micron membrane, the solution was taken to determine the adsorption capacity of eggshell with time. Drawn the curve of phosphorus removal rate with time.

2.2.4. Adsorption thermodynamics experiment. 1 g eggshell powder was added to potassium dihydrogen phosphate solution with phosphorus content of 50 mg/L of 100 ml. The eggshell powder shock for 9 hours at 10°C, 20°C, 25°C, 35°C, and 45°C. After the end of the oscillation, the supernatant was filtered with 0.45μm membrane, the content of orthophosphate in the supernatant was determined. Drawn the curve of phosphorus removal rate and adsorption capacity. Ammonium molybdate spectrophotometry is used to set out the phosphate concentration in water [13].

3. Experimental Results and Discussion

3.1. Effect of Modifier Concentration on Phosphorus Removal Efficiency

Figure 1. Modified eggshell powder
As is shown in Figure 1, modified eggshell power is red brown. The phosphorus concentration in the experimental wastewater was 50mg/L. The phosphorus removal rate was only 33% by the original eggshell. When the concentration of FeCl₃ was 0.3%, the phosphorus removal rate was increased to 90.91% and the residual phosphorus concentration was 0.58mg/L. The removal efficiency of modified eggshell was significantly higher than unmodified eggshell.

Figure 2. Effect of modifier concentration on phosphorus removal efficiency

3.2. Adsorption Isotherm

In order to study the mechanism of phosphorus adsorption on modified eggshell powder, Langmuir (formula 2) model and Freundlich (formula 3) model were used to fit the experimental results. \( \frac{C_e}{X_e} = \frac{C_e}{X_m} + \frac{1}{k_L X_m} \) (2), \( X_e = k_F C_e^{\frac{1}{n}} \) (3). In the formula: \( k_L \), \( k_F \) adsorption equilibrium constant; \( X_m \) is the theoretical maximum adsorption capacity; \( n \) represents the influence of initial concentration of wastewater on adsorption capacity. The fitting parameters of adsorption isotherm are shown in Table 1.

Table 1. The fitting parameters of adsorption isotherm

|                | Langmuir model | Freundlich model |
|----------------|----------------|------------------|
| \( k_L \)      | 29.0064        |                  |
| \( X_m \)      | 1.2182         |                  |
| \( R^2 \)      | 0.9797         |                  |
| \( k_F \)      | -3.56          | 0.9998           |
| \( n \)        | 1.21           |                  |

Freundlich model indicates that the adsorption process is heterogeneous multi-layer adsorption, while Langmuir model represents single-layer adsorption. As is shown in Table 1 of \( R^2 \), we can see that the Freundlich model fits well with the adsorption process, which is indicated that the adsorption of phosphorus on eggshells is more inclined to heterogeneous adsorption [14, 15]. \( 1<n<2 \), indicating that the phosphorus is easy to be absorbed by the eggshell and has a stable adsorption effect.

3.3. Adsorption Kinetics

Figure 3 shows the removal rate of eggshell powder varied with time under 25°C. As time goes on, the phosphorus removal efficiency of eggshell powder increases also. There are two plateau phases because phosphate ions enter the large pore size of eggshell fast, and then infiltrate into the small internal pore slowly until the reaction finished.
Figure 3. Adsorption kinetics curve of eggshell on phosphorus

Langergren quasi first order kinetic model (formula 4) and pseudo two order reaction kinetics model (formula 5) were adopted to fitting influence of the phosphorus removal rate with time variation. \( q_t = q_e \cdot (1 - e^{-k_1t}) \) (4) \( q_t = k_2q_e^2t/(1 + k_2q_e t) \) (5). In the formula: \( q_e, q_t \): the adsorption capacity of eggshell at equilibrium and the adsorption capacity of eggshell at time t; \( k_1, k_2 \): the rate constants of quasi-first-order and second-order reaction kinetics.

Table 2. The fitting parameters of adsorption kinetics

| Initial phosphorus concentration/(mg·L⁻¹) | quasi-first-order reaction kinetics | quasi-second-order reaction kinetics |
|-----------------------------------------|-----------------------------------|-------------------------------------|
|                                         | \( q_e \)/(mg·g⁻¹) | \( k_f \)/(min⁻¹) | \( R^2 \) | \( q_e \)/(mg·g⁻¹) | \( k_2 \)/(min⁻¹) | \( R^2 \) |
| 50                                      | 4.94 | 0.0032 | 0.9851 | 4.94 | 0.0008 | 0.9978 |

Langergren dynamic model is used to express the relationship between time and the phosphorus removal rate in table 2. From the values of \( R^2 \) in the table, it can be seen that quasi-second-order reaction kinetics can be better fitted of the adsorption kinetic characteristics of eggshell phosphorus removal process, indicating that there are physical and chemical adsorption exist simultaneously in the reaction process [16]. It is possible that iron radicals have adsorption characteristic of phosphate, and it also have positive electricity which can increase the adsorption sites for absorbing the phosphate. There is a large amount of calcium carbonate in eggshell acts as a chemical precipitation for phosphorus removal.

3.4. Adsorption Isotherm

Temperature is one of the main factors which affect the adsorption process. The thermodynamics process is shown in Figure 4. In the process of adsorption, the adsorption capacity and phosphorus removal rate of eggshell increased with the increase of temperature. The highest removal rate reached 99.13% at 45°C. It indicates that the adsorption of phosphorus by eggshell is an endothermic reaction process. The parameter \( \Delta G \), \( \Delta H \) and \( \Delta S \) of the thermodynamic equation are used to analyze the adsorption characteristics.
The thermodynamic equations are calculated by using the following formulae: 
\[ k_d = \frac{X_e}{Ce} \] 
\[ \ln k_d = \Delta S/R - \Delta H/RT \] 
\[ \Delta G = \Delta H - T \Delta S \]. In the formula: \( k_d \) is the equilibrium partition coefficient; \( \Delta G, \Delta H \) and \( \Delta S \) are Gibbs free energy, enthalpy and entropy changes; \( X_e \) is the equilibrium adsorption capacity of eggshell to phosphorus; \( Ce \) is the equilibrium concentration of phosphorus; \( R \) is the ideal gas constant. The value of \( \Delta G \) can be further calculated from \( \Delta H \) and \( \Delta S \).

| T/°C | \( K_d \) | \( \Delta G /\text{KJ} \cdot \text{mol}^{-1} \) | \( \Delta H /\text{KJ} \cdot \text{mol}^{-1} \) | \( \Delta S /\text{J} \cdot \text{mol}^{-1} \) |
|------|---------|---------------------------------|---------------------------------|------------------|
| 15   | 2.877   | -2.596                          |                                 |                  |
| 20   | 3.083   | -3.436                          |                                 |                  |
| 25   | 8.450   | -4.278                          | 45.863                          | 168.2            |
| 35   | 11.108  | -5.960                          |                                 |                  |
| 40   | 11.458  | -6.802                          |                                 |                  |

As is shown in table 2, the range of Gibbs free energy change for physical adsorption is 0-20 KJ/mol, indicating that the reaction process belongs to physical adsorption and does not absorb energy from the outside [17]. \( \Delta H>0 \) shows that the adsorption of eggshell powder is endothermic reaction; \( \Delta G \) decreases continuously while the temperature increases, \( \Delta S>0 \), indicating that the degree of confusion on the reaction interface increases [18], which improving the phosphorus removal rate of eggshell powder, it is consistent with the results of adsorption isotherm.

4. Conclusion

(1). The adsorption process of modified eggshell powder was significantly fitted with the Freundlich model, and the adsorption process was multi-molecular layer adsorption.

(2). The adsorption of phosphorus by modified eggshell powder can be well fitted with the quasi-second-order reaction kinetics, physical and chemical adsorption exist simultaneously in the adsorption process, and the difference of eggshell structure and internal pore size causes two platform periods.

(3). Adsorption of phosphorus by modified eggshell powder is a spontaneous endothermic reaction process. Increasing temperature is beneficial to the reaction.

(4). The effect of FeCl3 modified eggshell powder on phosphorus removal was significantly improved, the reuse of industrial sewage can be realized.

Acknowledgments
This work was financially supported by major scientific projects of Shenyang Jianzhu University fund.
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