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Surfactants modified egg shells for removal of methyl violet from aqueous solutions

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ABSTRACT

Two surfactant-modified egg shells were prepared and characterized by XRD patterns, FT-TR spectra and scanning electron microscopy (SEM). SEM images showed surfactants-modified egg shells were with more clear porous structures. The methyl violet (MV) removal using egg shell and surfactant-modified egg shells were compared. The MV removal of surfactant-modified egg shells showed better, and that of potassium perfluorooctanesulfonate (PFOS)-modified egg shell is better than that of Sodium octanesulfonate (SOS)-modified one. It can be concluded that the MV removal of surfacant modified egg shell is better when surfactant is more hydrophobic. The adsorption of egg shell fits the pseudo-first-order kinetic model and surfactant modified egg shells fit pseudo-second-order kinetic model. All adsorptions fit Freundlich isotherm. Dubinin-Radushkevich (D-R) isotherm showed the adsorption mainly was a physical adsorption process.

Keywords: Egg shell; Surfactant modified; Methyl violet; Removal; Adsorption

1. Introduction

Dye pollutants from textile paper and other industries are an important source of environmental contamination [1]. Methyl violet (MV) is a basic dye, which has harmful effects on living organisms and its inhalation may cause different illnesses such as headaches, diarrhea and etc [2]. Various techniques have been developed to remove dye pollutants, including biological treatment, adsorption [3], chemical oxidation, coagulation and membrane filtration. Because of its high efficiency, economic feasibility and low energy requirements, adsorption has become the most popular technique [4]. Recently, the study of dye pollutants is increasing, and the selection of adsorbent is very important [5–8]. Activated carbon, as the most commonly used adsorbent, suffers from some drawbacks such as high cost, difficult disposal and regeneration [9]. attention of many investigators have been diverted to the investigation on the feasibility of using low cost, easy obtainable and biodegradable substances [10]. Egg shells, as waste materials, which are everyday generated on a large scale from household, restaurants, food industries, bakeries, etc. The disposal of egg shells is indeed a grave problem to the municipal authorities because of hygiene and sanitation. Recently, egg shells have been found that they can act as a potential adsorbents [11]. However, egg shells are not suitable for treatment of dyes polluants [12] because of its limited adsorption capacity, and how to modify egg shell to enlarge the application in the wastewater treatment is very meaningful. The adsorption is determined by pore structure, which directly has effect on the excellent performance of porous material and also affect its potential use. Surfactants can be used as template agent in synthesis of porous materials and can control aperture structure [13].

In this study, different surfactant-modified egg shells were prepared in order to increase the adsorption capacity for methyl violet. We aimed to evaluate the potentiality of surfactants modified egg shells for removal methyl violet from aqueous solutions. The effects of contact time and initial dye concentrations were investigated. Equilibrium and kinetic analysis were conducted to determine the factors controlling the rate of adsorption and to find out the possibility of using surfactants modified egg shells as low cost adsorbents for dye removal.

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2. Experimental

2.1. Materials and synthesis

The egg shells were collected from the local kitchen workshop. First, the thin membrane adhering to the inside of the egg shell was carefully peeled off. Then the egg shells were washed thoroughly with distilled water and then dried in at 60°C for about 24 h. The dried egg shells were crushed mechanically in a mixer. Two different surfactants were used in synthesis: Sodium octanesulfonate (SOS), potassium perfluorooctanesulfonate (PFOS). All reagents were of analytical reagent grade, made in China. For the synthesis of surfactant modified egg shell, distilled water (20 mL), egg shells (2.0 g) and surfactants (0.1 g) were added to a Teflon reaction vessel. The reaction vessel was put in an oven at 160°C for 8 h. The resulting product was washed thoroughly in distilled water and was dried at 60°C for 24 h. The final sample was characterized by X-ray diffraction, FT-IR spectra , scanning electron microscopy (SEM).

2.2. MV adsorption experiment

Adsorbents (0.05 g) was added to the aqueous solution of MV (5 mL 4.08 mg/L) respectively. The mixture was well oscillated for a fixed time (5–60 min) at 298 K. After adsorption, the concentrations of residual MV was determined by UV-vis spectrophotometer at 577 nm after centrifugation. For a kinetic study, the supernatant was collected at different time intervals for the determination of unabsorbed MV.

2.3. Apparatus

The absorbance at 577 nm was measured on a Perkin-Elmer lambda 17 UV-vis spectrophotometer (P-E Co., America) with 10 mm cell for determination of the concentrations of MV. SEM (Model EPMA-8705QH2, Shimadzu Co., Japan) was used to observe the morphologies of egg shells. The crystalline structures of the egg shells were identified by a D/max-IIIC X-ray diffractometer (Shimadzu, Japan). Fourier Transform Infra-Red (FTIR) spectra were taken with a Spectrum One FTIR spectrophotometer (Perkin-Elmer, America) at room temperature.

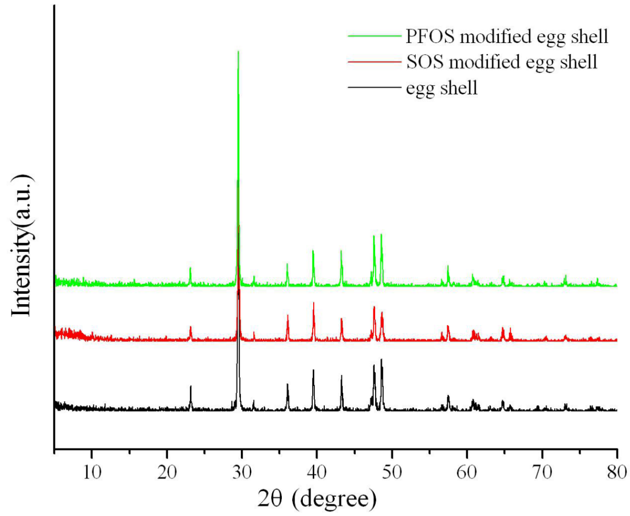

Fig. 1. XRD patterns of egg shells.

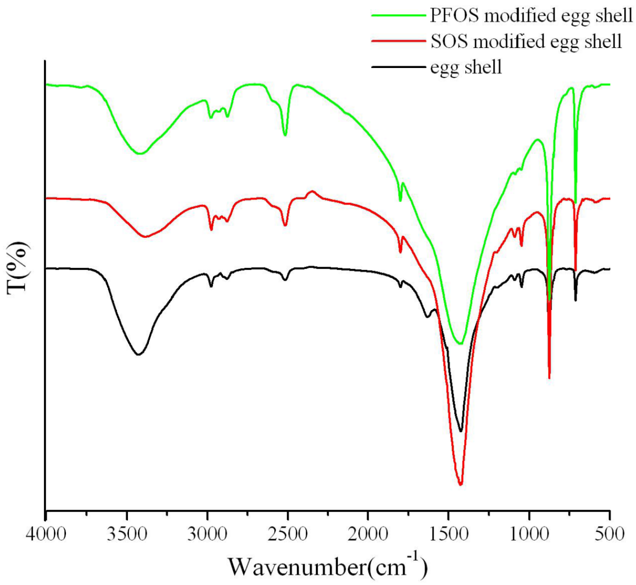

Fig. 2. FT-TR spectra of egg shells.

3. Results and discussion

3.1. Characterization results

Powder XRD patterns of egg shells are shown in Fig. 1. The diffraction peaks of the three egg shells match well with each other. The sharp diffraction peaks indicate that the different surfactants modified egg shells are well crystallized.

Fig. 2 shows the FT-TR spectra of egg shells. The component of egg shell is $CaCO_3$. The characteristic peak of $CaCO_3$ can be all observed in all egg shells. The peak at 1432 cm^{-1} is C-O antisymmetric stretching vibration, the peak at 876 cm^{-1} is the out-of-plane antisymmetric deformation vibration of CO_3^{2-}, and the peak at 724 cm^{-1} is the in-plane deformation vibration of CO_3^{2-}. The characteristic peaks of the three egg shells are consistent with each other, and there is no characteristic peak of surfactants, which indicates that the surfactant modified egg shells are well crystallized and the surfactants are successfully cleaned off after washing by distilled water thoroughly.

The surface conditions of the three egg shells are analyzed by scanning electron microscopy (SEM). Typical results are shown in Fig. 3. Because surfactant is a template for porous material, the nature of surfactants has effect on the porous structure [14]. It is clear that SOS- and PFOS-modified egg shells are easy to aggregate. The porous structure of SOS- and PFOS- modified egg shells are clearer than egg shell. Furthermore, the average size of PFOS modified egg shells (0.36 μm) is bigger than that of SOS modified egg shells (0.28 μm). It can be concluded that surfactants can modify the pore size of egg shells. The critical micelle concentration (CMC) of PFOS and SOS were $2.03 \cdot 10^{-4}$ and 0.0139 mol L^{-1} respectively [15]. In the fluorinated surfactants, substitution of the larger and highly electronega-

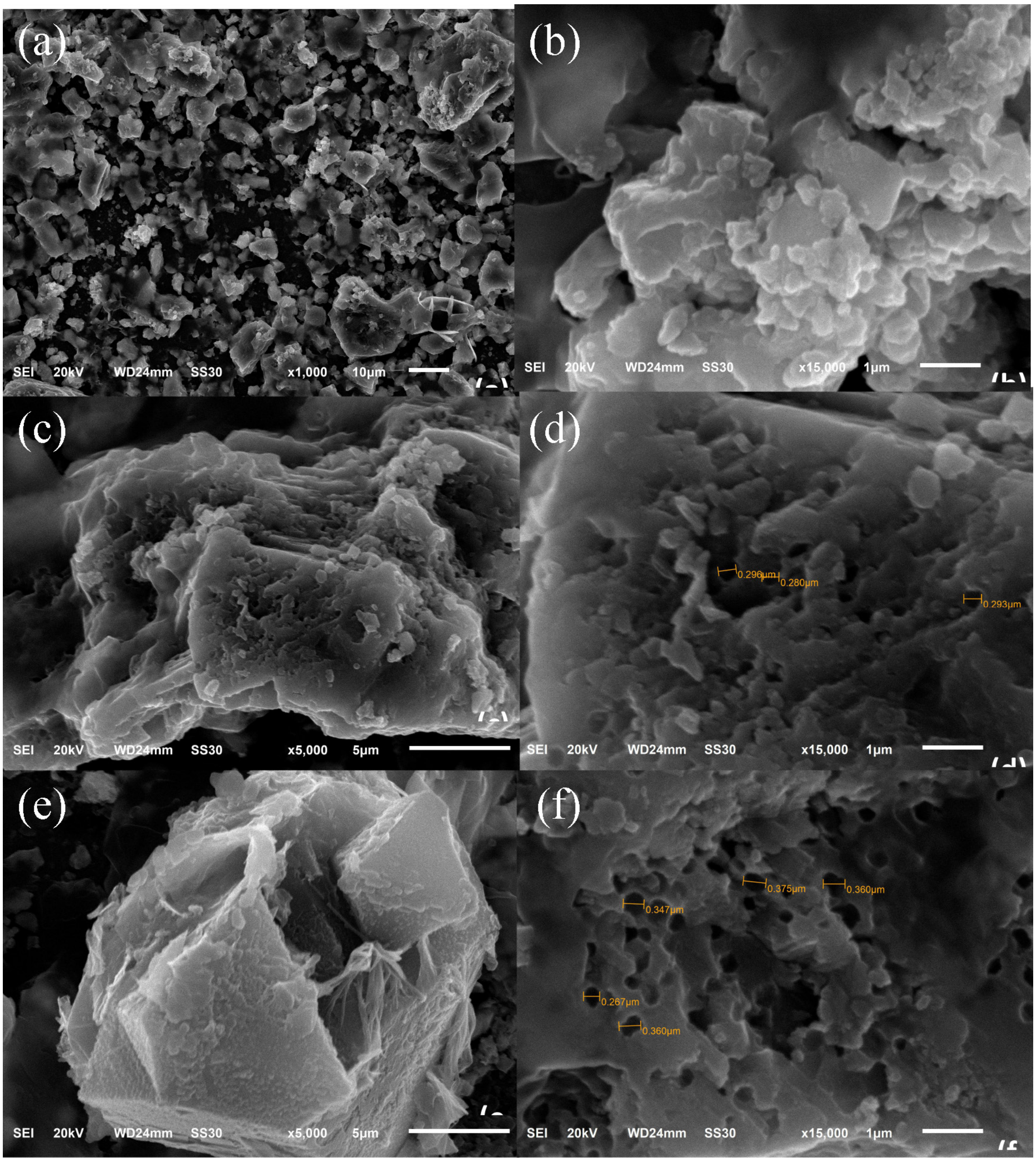

Fig. 3. SEM images of egg shell (a,b), SOS modified egg shell (c,d) and PFOS modified egg shell (e,f).

tive fluorine atom for the smaller hydrogen increases the amphiphilic nature of the surfactant and lowers the surface tension and critical micelle concentration. PFOS is more hydrophobic than SOS [16], so it can be concluded that once surfactant is more hydrophobic, that the pore size of surfactants modified egg shells is bigger. The pore size distribution is shown in Fig. 4. It showed that pore size distribution main exhibited larger pores in PFOS modified egg shells.

3.2. Adsorption of MV

The applicable of egg shells to different concentration MV are compared, as shown in Fig. 5. It shows that the MV removal efficiency of surfactants modified egg shells are better, and the MV removal efficiency of PFOS modified egg shells with the largest pore size is the highest. It can be explained that there will be larger surface area when pore size is smaller, but if the aperture is too small, there is a disadvantage for absorbing large molecular dyes [17,18]. Because the larger pore not only contributes to the adsorption, but also provides a wide channel for the diffusion of adsorbents. The size of MV is 1.31 nm, and the size of the aperture is enough for entering dye molecules. Therefore, the MV removal efficiency of PFOS modified egg shells is the highest.

The adsorption capacity for MV at different time was compared, as shown in Fig. 6. It is clear that the adsorption capacity of PFOS modified egg shells is the highest and can keep a constant after 25 min. Egg shells also can reach

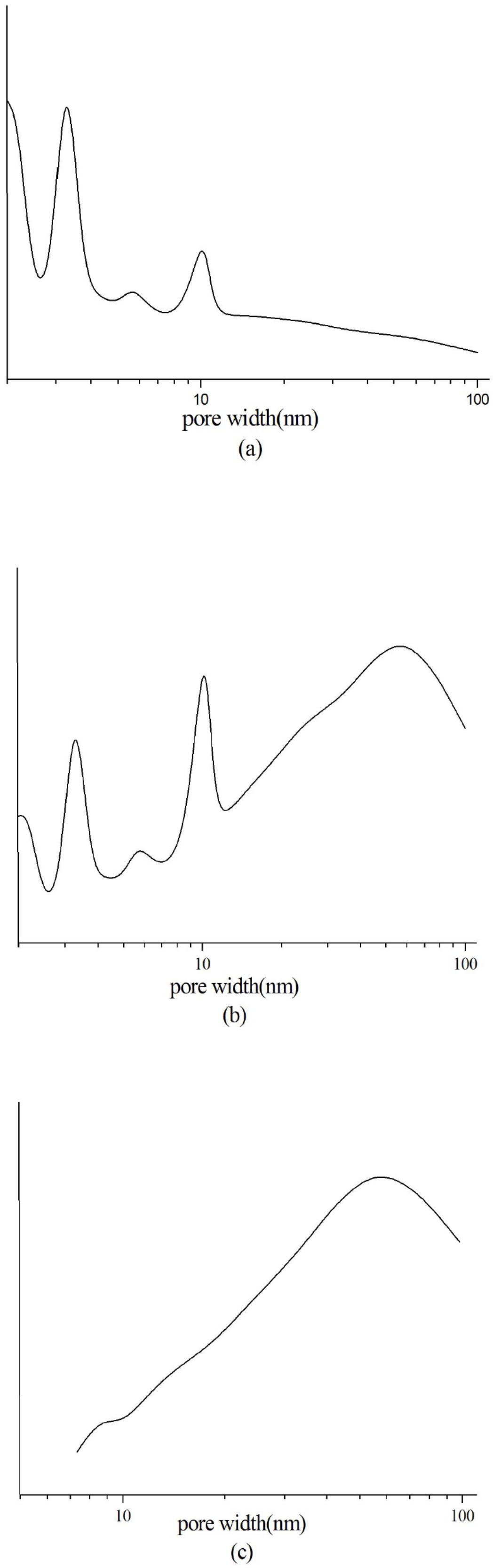

Fig. 4. Pore size distribution of egg shell (a), SOS modified egg shell (b) and PFOS modified egg shell (c).

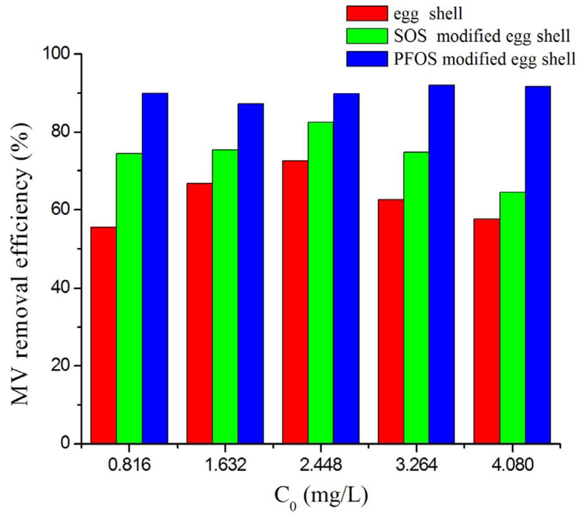

Fig. 5. MV removal efficiency of egg shells.

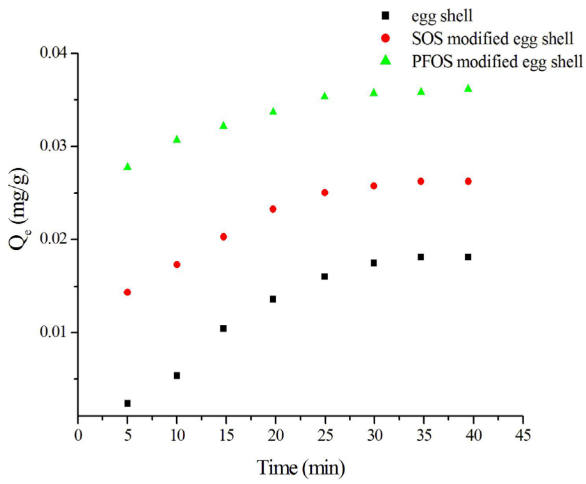

Fig. 6. The adsorption capacity of egg shells at different time.

adsorption equilibrium after 30 min. Therefore, 30 min is selected in experiment.

3.3. Kinetics for the adsorption of MV on egg shells

The time-dependent adsorption capacity is obtained to study the kinetics for the adsorption of MV on egg shells. The adsorption model which describes the adsorption of a solute onto a solid surface can be expressed in the following way [19]:

$$\frac{dq}{dt} = k_1\left(q_e - q_t\right) \tag{1}$$

where k_1 is the apparent pseudo-first-order constant (min^{-1}), q_t is the extent of adsorption at time t (in mg·g^{-1}), and q_e is the extent of adsorption at equilibrium (mg·g^{-1}). This law is used to describe process in which the reaction rate, *dq/dt*, is proportional to the number of available adsorption sites, $(q_e - q_t)$. The linear, integrated form of this equation for the

Table 1
Surface area and pore volumes of egg shells

	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Pore volume (cm^3/g)
Egg shell	0.3432	0.3609	0.001851
SOS modified egg shell	0.5118	0.8147	0.002547
PFOS modified egg shell	0.6847	0.9279	0.003940

boundary conditions; $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, can be written as:

$$ln\left(q_e - q_t\right) = lnq_e - k_1 t \tag{2}$$

Hence, the rate equation is obeyed when a linear relationship exists between $log(q_e - q_t)$ and t, in which case k_1 may be estimated from the gradient of the plot. Similarly, the expression can be used to describe adsorption process in which the reaction rate is proportional to the square of the number of available adsorption sites.

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{3}$$

where k_2 is the apparent pseudo-second-order rate constant (in $g \cdot mg^{-1} \cdot min^{-1}$), and can be integrated and rearranged thus:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

gradient of a linear plot of t/q_t against t.

The pseudo-first-order and pseudo-second-order kinetic models to the adsorption of MV onto egg shells have been tested by fitting the experimental data to the models, and it is found that the adsorption process of egg shells accords with pseudo-first-order kinetic model, and pseudo-second-order kinetic model affords a more appropriate description of the adsorption process of surfactants modified egg shells, as shown in Figs. 7 and 8.

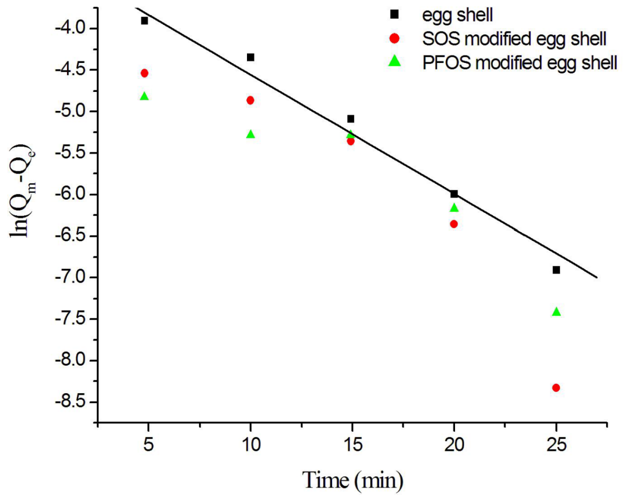

Fig. 7. Plots of pseudo-first-order kinetic for the adsorption of MV on egg shells.

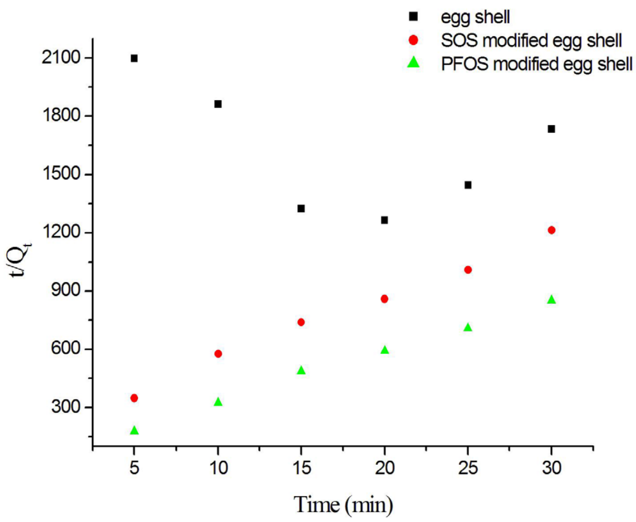

Fig. 8. Plots of pseudo-second-order kinetic for the adsorption of MV on egg shells.

3.4. Adsorption isotherms for MV on egg shells

To describe the adsorption isotherm and analyze the equilibrium data more scientifically, Langmuir adsorption isotherm and Freundlich adsorption isotherm are employed.

The Langmuir isotherm is expressed as :

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} K_L + \frac{C_e}{q_{\max}} \tag{5}$$

where c_e (mg L^{-1}) is the equilibrium concentration of MV, q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_{max} (mg g^{-1}) is the maximum adsorption capacity in calculation, and the K_L (L mg^{-1}) is the Langmuir adsorption constant, related to free energy of adsorption. The plot between c_e/q_e and c_e is obtained from the Langmuir model, as shown in Fig. 9. The inserted figure is magnification of PFOS modified egg shell. It is clear that all egg shells don't obey the Langmuir model.

The Freundlich equation is given as:

$$Q_e = K_F C_e^{\,1/n} \tag{6}$$

where K_F represents the Freundlich constant and $1/n$ is corresponding to adsorption capacity and adsorption intensity, respectively. A linear plot of lnQ_e versus lnC_e is obtained from the model as shown in Fig. 10. It shows that the all adsorptions fit the Freundlich model well.

The Dubinin-Radushkevich (D-R) isotherm model was applied to the data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent. The linear form of the D-R isotherm is given as:

$$lnQ_e = lnQ_D - B_D\left[RTln\left(1 + 1/Ce\right)\right]^2 \tag{7}$$

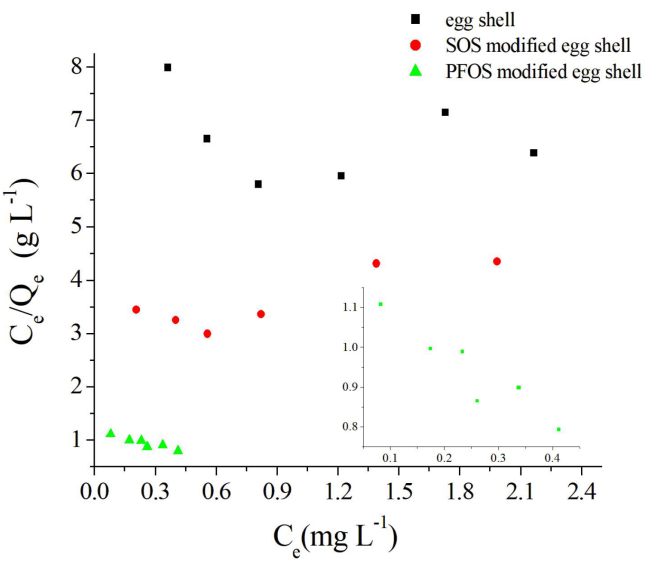

Fig. 9. Langmuir plots of the isotherm for MV adsorption onto egg shells.

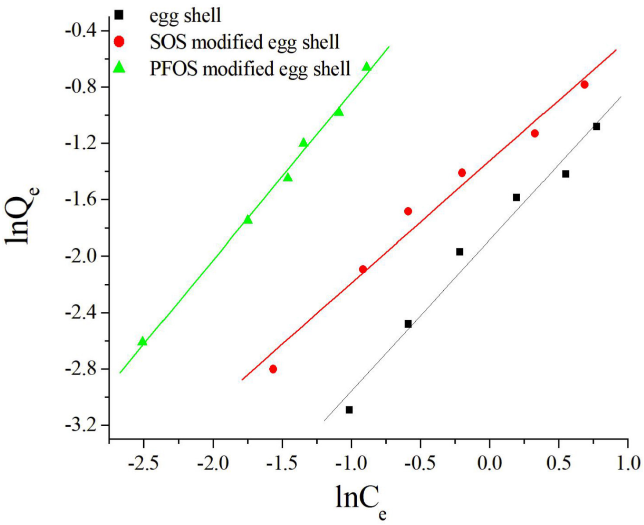

Fig. 10. Freundlich plots of the isotherm for MV adsorption onto egg shells.

The apparent energy of adsorption, E was calculated as:

$$E = \frac{1}{(2B_D)^{\frac{1}{2}}} \tag{8}$$

The constants Q_D (mol/g) is the D-R constant representing the theoretical saturation capacity and B_D (mol^2/J^2) is a constant related to the mean free energy of adsorption per mol of the adsorbate, R is the ideal gas constant, (8.314 J/ mol K) , $T(K)$ is the temperature of adsorption and E (kJ/mol) is the mean free energy of adsorption per molecule of the adsorbate when transferred to the surface of the solid from infinity in solution. The plot of lnQ_e against [RTln(1+1/Ce)]^2 is shown in Fig. 11 and E of different egg shells were calculated to be 1.29, 2.76 and 6.13 kJ/mol

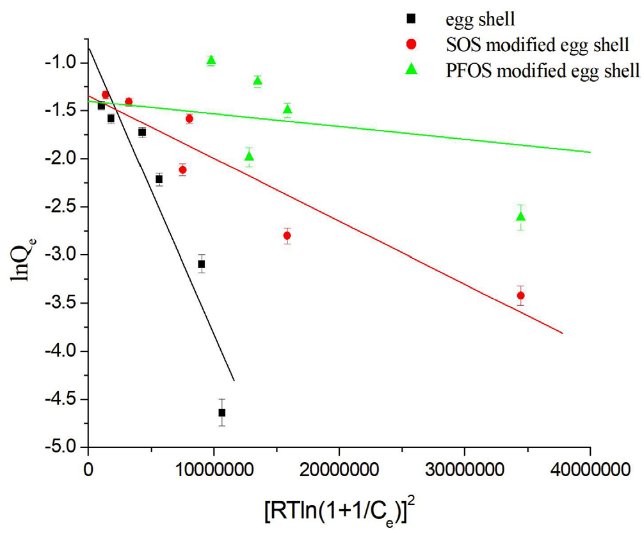

Fig. 11. D-R adsorption isotherm for MV adsorption onto egg shells.

respectively. If the value of E lies between 8 and 16 kJ/mol the sorption process is a chemisorption one, while values of below 8 kJ/mol indicates a physical adsorption process (Choy et al., 1999). The value indicated physical adsorption process between egg shells and MV.

4. Conclusion

In this work, surfactants modified egg shells are introduced as adsorbents for the adsorptive removal of MV from wastewater, and the adsorptions are compared with that of egg shells. The results indicate that pseudo-second-order kinetic model matches with the adsorption of MV onto surfactants modified egg shells. It is found the MV removal of PFOS-modified egg shells is better than SOS –modified one. The carbon chain length of PFOS and SOS are the same, but C-F bond makes the surfactants PFOS more hydrophobic. It can be concluded that the MV removal of surfactants modified egg shells is better when the surfactants is more hydrophobic. Therefore, surfactants can be used to modify egg shells to make them more suitable for treatment of dyes pollutants.

Acknowledgments

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