



Bioadsorption of methyl violet from aqueous solution onto Pu-erh tea powder

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ABSTRACT

Chinese unique Pu-erh tea powder (PTP), with leached active ingredients, was used here to adsorb methyl violet (MV), a cationic dye. The effects of several variables on the removal of methyl violet were studied at 25 °C, including pH value, contact time, quantity of the adsorbent, initial concentration, and particle size of the adsorbent. The results showed that the particle size of the adsorbent significantly affected the adsorption process, and the nano-sized PTP particles had the best adsorption efficiency. The equilibrium data was analyzed using Langmuir, Freundlich, and Tempkin isotherms models. The pseudo-second-order kinetics model best explained the MV adsorption by PTP of any particle size. The intra-particle diffusion model was also used to analyze the adsorption process, and it was found that smaller adsorbent particles had a bigger boundary layer effect.

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1. Introduction

China has accounted for 45% of the total dyestuff production around the globe in recent years [1]. Dyes are extensively used in pulp mills, leather, cosmetics, textiles, printing, foods, plastics and dye synthesis [2]. However, about 2% of the dyes flow away with the waste effluents as one ton of dyes are produced [1], threatening aquatic life as well as human beings. Treatment of dye wastewater to eliminate such pollution is necessary [3]. Nowadays, many physical–chemical methods have been used for dye wastewater treatment, including precipitation, coagulation and flocculation, chemical oxidation, reverse osmosis, and ion change [4–8]. Due to the non-biodegradable nature of dyes, adsorption has been considered as a better approach than these other types of treatment methods. Activated carbon was first applied for adsorption but it was too costly. Therefore researchers turned to other biological materials as new types of adsorbents. Many materials have been studied for this purpose such as sewage sludge [9], fly ash [10,11], teak leaves [12], waste apricot [13], rice husk [14], orange peel [15], coir pith [16], phoenix tree leaves [17], and untreated guava leaf powder [18].

Methyl violet is widely used in Gram staining and as anti-allergen and bactericide or pH indicator. It is toxic by releasing toxic substances when decomposed, such as CO, CO₂, NO, etc. For animals or human body, direct contact with methyl violet can cause pain and congestion while inhaling them could irritate the respiratory and gastrointestinal systems [19].

Many researchers investigated the methyl violet removal with biological materials. Doğan and Alkan used perlite as an adsorbent and found the adsorption fits better with Langmuir isotherm, which is a typical physical process [20]. They also used sepiolite for their research work and the results showed that the adsorption process was consistent with the pseudo-second-order kinetic equation and the intra-particle diffusion model [21]. When sunflower seed hull was used as adsorbent, Hameed investigated its equilibrium and kinetics of the adsorption process. He found that Freundlich isotherm and the kinetic pseudo-second-order equation could well describe the adsorption process. The maximum adsorption was 92.59 mg/L [22]. Ofomaja et al. studied the *Mansonia* wood sawdust and demonstrated that the adsorbent particle size significantly affected the adsorption process and the equilibrium data fitted Langmuir and R-P isotherm. Adsorption mechanism could be explained by the mass transfer model [23,24]. Mall et al. studied the kinetic and equilibrium isotherm of methyl violet onto bagasse fly ash and concluded that the R-P isotherm and pseudo-second-order kinetic model fit well with the adsorption process [25]. Mittal et al. used bottom ash and de-oiled soya as adsorbents and the results fit well in the linear forms of Freundlich and Langmuir isotherm, and the Lagergren first order equation [26].

In this study, Yunnan Pu-erh tea was used as an adsorbent for methyl violet removal. Pu-erh tea is microbially fermented Chinese tea made from the leaves of large-leaf species tea plant, with several kinds of microorganisms consisting of *Aspergillus niger*, *Aspergillus glaucus*, and species of *Penicillium*, *Rhizopus*, *Saccharomyces*, and *Bacterium*. In the recent years, Pu-erh tea has gained popularity because of its unique flavor and medicine function. In 2007, the annual production of Pu-erh tea reached 99,000 tons [27]. The large volume consumption of Pu-erh tea produced a lot of tea residuals, thus successful utilization of Pu-erh tea residuals as a new type of dye

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Nomenclature

| | |
|----------|--|
| a | the Tempkin constant |
| a_2 | rate constant of Elovich |
| b | the Tempkin constant |
| b_1 | Langmuir constant |
| b_2 | rate constant of Elovich |
| C | intercept of intra-particle diffusion equation |
| C_e | the equilibrium concentration of MV dye in the solution (mg/L) |
| C_0 | the initial concentration of MV dye in the solution (mg/L) |
| k_1 | pseudo-first-order apparent rate constant |
| k_2 | pseudo-second-order apparent rate constant |
| K | thermodynamics temperature |
| K_F | the Freundlich constant related with adsorption capacity |
| K_L | the Langmuir affinity constant |
| K_{id} | intra-particle diffusion rate constant |
| m | the mass of adsorbent (g) |
| n | dimensionless exponents of Freundlich |
| Q_e | adsorbed amount at equilibrium (mg/g) |
| Q_t | amount of adsorbate adsorbed at the time t (mg/g) |
| Q_m | the maximum adsorbed amount (mg/g) |
| R_L | dimensionless separation factor |
| t | time of contact (min) |
| V | volume of the solution (L) |

adsorbent could not only help clean dye wastewater but also reduce Pu-erh tea industrial waste. This report represented the first study on the adsorption process and possible adsorption mechanism of Pu-erh tea powder for methyl violet removal.

2. Materials and methods

2.1. Adsorbent

The raw material Pu-erh tea cake was obtained from Yunnan Menghai and was washed several times by both boiled and distilled water to remove its active ingredients, followed by a drying process at 60 °C to constant weight in a vacuum oven. The dried tea was grinded into powder. A small amount of it was screened through different meshes of 40 and 200, and some other was put into a refrigeration ball grinder and grinded fully to the nano-level. Three samples of 40 mesh, 200 mesh, and nano-level were stored in airtight containers.

2.2. Adsorbate solution

The fundamental characteristics of methyl violet (A.R, Sinopharm Chemical Reagent Co., Ltd.) were shown in Table 1. 0.5 g of methyl violet dye was dissolved in 500 mL double-distilled water to obtain 1000 mg/L stock solution. It was then diluted into different desired concentrations.

2.3. Analysis methods

The scanning electron microscopy (SEM) was utilized to observe the surface structure of adsorbents. Functional groups of adsorbent samples were determined by infrared spectroscopy. Specific surface area and the pore volume were measured by BET-N2. The pH_{zpc} (pH at zero point of charge) of PTP was determined with a zeta meter.

2.4. Adsorption tests

The batch adsorption experiments were carried out at 25 °C in vibrating conditions. Supernatant was obtained using a centrifuge (spinning for 20 min at 6000 rpm) and the remaining methyl violet content was analyzed by ultraviolet spectrophotometer (Cary 50 Probe). The pH values ranged from 2 to 10. The adsorbent dosage varied from 0.05 to 0.20 g, when the particle sizes were at 40 mesh, 200 mesh and nano-level, respectively. Isotherm studies were recorded by varying the concentration of methyl violet dye from 50 to 300 mg/L.

The adsorption capacity Q_e (mg/g) after equilibrium was calculated by the following equation:

$$Q_e \text{ (mmol/g)} = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

V is the volume of the solution (L) and m is mass of adsorbent (g).

3. Results and discussion

3.1. Adsorbent characteristics

The SEM micrographs of Pu-erh tea powder at 250×, 1000× and 20000× magnifications were shown in Fig. 1. It could be seen that the surface of PTP was porous and the particle size of smallest sample was about 300 nm. Thus, those were above nano-level particles. As measured, the pore diameter was 6.1369 nm and the specific surface areas were 1.711 m²/g (40 mesh), 5.4721 m²/g (200 mesh), 7.8861 m²/g (nano-level), respectively, which meant PTP worked well as an adsorbent. The IR spectra of PTP (Fig. 2) displayed some adsorption peaks, indicating the complex structure of Pu-erh tea powder. The troughs of OH groups were observed in the range of 3370–3410/cm. The bands observed at about 2910–2850/cm could be assigned to the aliphatic C–H groups. The shoulder at the wave number of 1725/cm could be due to the carbonyl stretch of carboxyl. The trough at 1630–1650/cm represented the C=O stretching. Symmetric bending of CH₃ was observed to shift to 1450/cm. And the peaks at 1140 and 1250/cm could be assigned to C–O stretching and –SO₃ stretching of ether groups, respectively. From the IR spectra, it was clear that PTP possessed several surface functional groups. The result of zeta potential measurements showed that the pH_{zpc} of PTP was 3.6 (Fig. 3).

3.2. Effect of pH value of the solution on MV–PTP adsorption

The effect of pH on the MV–PTP adsorption was shown in Fig. 4. The adsorption of MV onto PTP was greatly affected by pH of solution. The percentage MV adsorption increased from 30% to 95%

Table 1
The character of dye.

| | |
|---------------------|--|
| Dye name | Methyl violet 2B |
| Generic name | Basic violet 1 |
| λ_{max} | 586 nm |
| Color index number | 42,535 |
| Chemical formula | C ₂₄ H ₂₈ ClN ₃ |
| Molecular structure | |

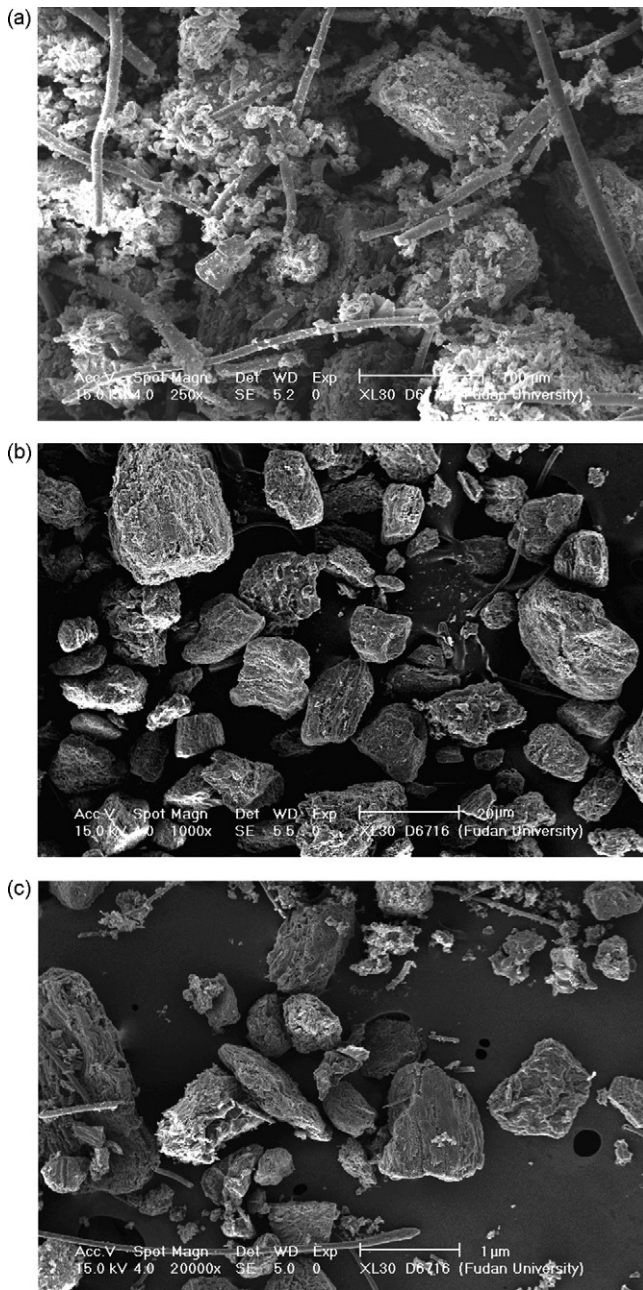


Fig. 1. SEM micrographs of different size particles of PTP (a: 40 mesh, b: 200 mesh, and c: nano-level).

when the pH value increased from 2 to 8. This may be attributed to the fact that the surface charge of PTP is strongly related to the pH values. As mentioned previously, the pH_{zpc} of PTP was 3.6, thus the adsorbent had a positively charged surface at a pH value lower than pH_{zpc} . At a pH value higher than pH_{zpc} , the negatively charged adsorbent surface was favorable for the adsorption of the cationic MV dye. Because of ionization of PTP functional groups, an obviously strong electrostatic attraction existed between the positively charged cationic MV and the negatively charged adsorbent surface. Thus, less adsorption occurred at lower pH. This may also be due to the fact that the excessive H^+ ions competed with cationic MV ions for the adsorption sites. Similar results of the effect of pH were also reported for the adsorption of methylene blue onto pineapple leaf powder [28].

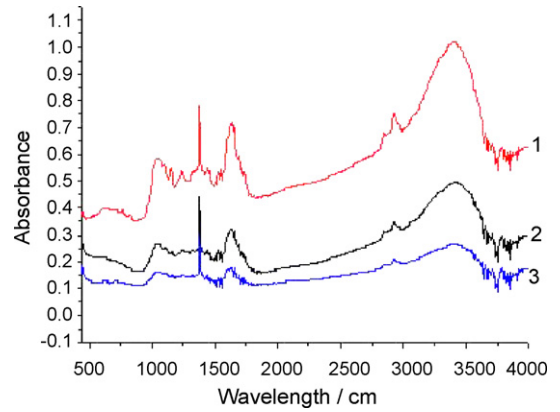


Fig. 2. IR spectra of Pu-erh tea powder (1: 40 mesh, 2: 200 mesh, and 3: nano-particle).

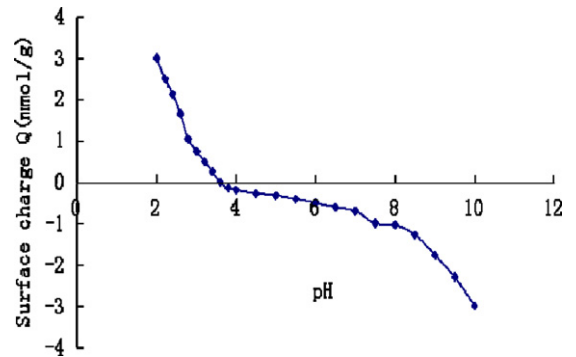


Fig. 3. Surface charge of PTP as a function of pH.

3.3. Effect of adsorbent dosage on MV removal

The effect of PTP dosage on MV removal was shown in Fig. 5. The percentage of MV removal increased with adsorbent dosage and then reached a saturation value. The optimal PTP dosage for MV removal was 0.12 g for 100 mL solution with the initial MV concentration of 100 mg/L. This increase was due to the additional surface area of PTP for adsorption. Similar results had been reported by Uddin et al. [29].

3.4. Effect of particle size on adsorption of MV

Effect of different size particles with 40 mesh, 200 mesh, and nano-level on adsorption of MV was investigated. As shown in Fig. 6, MV was better removed from the solution by smaller PTP particles,

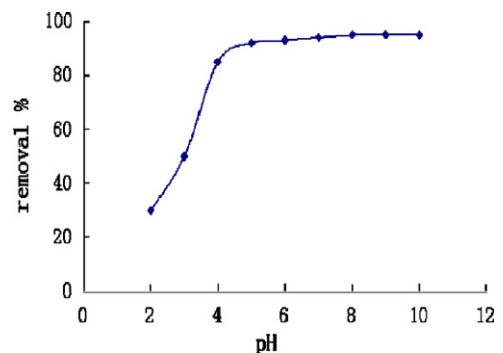


Fig. 4. Effect of pH on the adsorption of MV by PTP ($W=0.2$ g, 40 mesh; $C_0=100$ mg/L; $V=100$ mL).

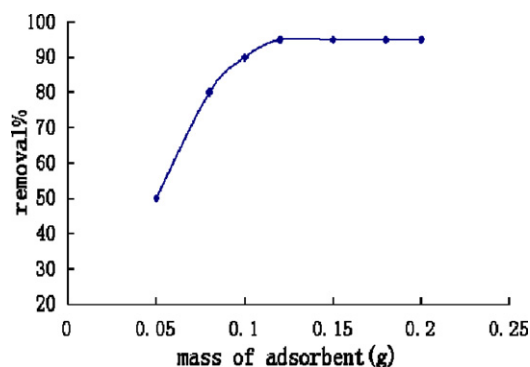


Fig. 5. Effect of adsorbent mass on the adsorption of MV by PTP (40 mesh adsorbent; $C_0 = 100$ mg/L; $V = 100$ mL).

and the equilibrium time was shorter with smaller particles. These trends could be attributed to the fact that smaller PTP particles provide more special surface areas and therefore offer more adsorption sites for MV. Additionally, more adsorption sites could reduce the competition among MV ions, thus the equilibrium time could be shorter. The present observations were in good agreement with previous findings by Ponnusami et al. [30].

3.5. Adsorption isotherms

In order to represent the equilibrium adsorption process, three different isotherm equations were used for experimental data analysis.

The Langmuir theory presumes a specific homogeneous type of the adsorption with the adsorbent [31], i.e., once a molecule of MV takes a site, no other one can take same site. The linear form of the Langmuir model was used the following equation:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m \times K_L \times C_e} \quad (2)$$

The Freundlich isotherm assumes that adsorption process occur heterogeneous surfaces and the capacity of adsorption is related to the concentration of MV at the equilibrium [32]. A linear form of Freundlich is expressed as follows:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Tempkin isotherm assumes that the heat of the adsorption decreases linearly with coverage due to adsorbent–adsorbate interaction, and adsorption process is characterized by a uniform distribution of binding energies [33]. Tempkin isotherm is represented by the following equation:

$$Q_e = a + b \ln C_e \quad (4)$$

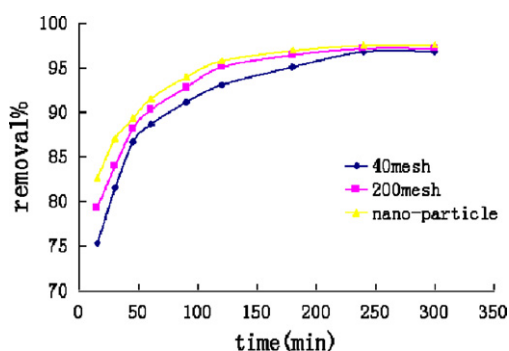


Fig. 6. Effect of particle size on removal of dye by PTP ($W = 0.2$ g; $C_0 = 100$ mg/L; $V = 100$ mL).

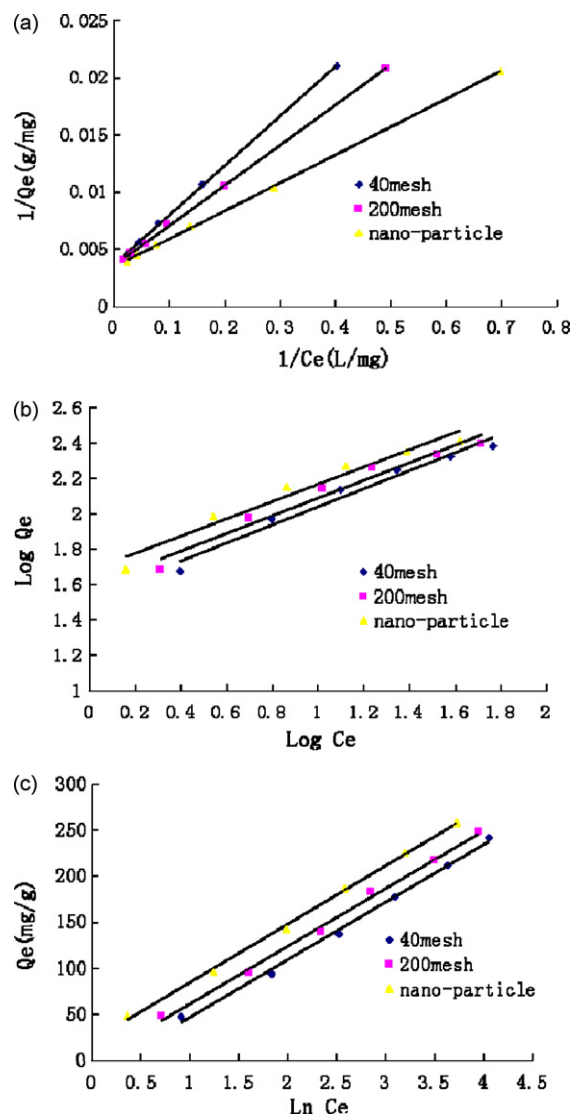


Fig. 7. Adsorption isotherm models of MV adsorption onto PTP at 25 °C.

where Q_e is the adsorbed amount at the equilibrium (mg/g), Q_m is the maximum adsorbed amount (mg/g), C_e is the equilibrium concentration of MV dye in the solution (mg/L), K_L , K_F are the equilibrium constants, and a , b , and n are constants.

The linearized Langmuir, Freundlich and Tempkin isotherms were shown in Fig. 7 and the parameters for different models were shown in Table 2.

The results showed that how well the isotherms fit the process: Langmuir is better than Tempkin which is better than Freundlich. The correlation coefficient (R^2) for Langmuir and Tempkin were both above 0.99, which indicated that the adsorption process occurred almost on homogeneous surfaces. As PTP particles got smaller from 40 mesh to nano-level, the maximum adsorbed amount increased from 277.78 to 294.12 mg/g, with K_L increased from 0.083 to 0.138, which manifested that the smaller particles provided more surface area and adsorbing sites for adsorption.

The characteristics of Langmuir equation could be expressed by a dimensionless separation factor R_L [34]:

$$R_L = \frac{1}{1 + b_1 C_0} \quad (5)$$

where C_0 is the initial concentration (mg/L) and b_1 (L/mg) is the Langmuir constant. The parameter R_L demonstrates the shape

Table 2
Isotherm parameters for removal of MV by PTP at 25 °C.

| Particle sizes | Langmuir | | | Freundlich | | | Tempkin | | |
|----------------|--------------|-------|--------|------------|------|--------|---------|--------|--------|
| | Q_m (mg/g) | K_L | R^2 | K_F | n | R^2 | a | b | R^2 |
| 40 mesh | 277.78 | 0.083 | 0.9995 | 33.93 | 1.96 | 0.9715 | -15.51 | 62.489 | 0.9960 |
| 200 mesh | 285.71 | 0.099 | 0.9994 | 39.06 | 2.00 | 0.9623 | -1.088 | 62.594 | 0.9961 |
| Nano-particle | 294.12 | 0.138 | 0.9995 | 47.95 | 2.05 | 0.9595 | 21.551 | 63.321 | 0.9982 |

nature of isotherm:

- $R_L > 1$ unfavorable adsorption process
- $0 < R_L < 1$ favorable adsorption process
- $R_L = 0$ irreversible adsorption process
- $R_L = 1$ linear adsorption

The values of R_L in this study were 0.040, 0.033 and 0.024, indicated that the adsorption of MV onto PTP was favorable.

3.6. Adsorption kinetics

The pseudo-first-order kinetic model was appropriate for lower concentration, with the equation expressed as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{6}$$

The rate of pseudo-second-order reaction depends on the amount of adsorbed solution, the surface of adsorbent and the amount of adsorption at the equilibrium. The model was represented in the following linear form [35]:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \tag{7}$$

The simple Elovich model was expressed in the form:

$$Q_t = a_2 + b_2 \ln t \tag{8}$$

In Eqs. (6)–(8), Q_t is the amount of dye adsorbed at time t (mg/g), Q_e is the adsorption capacity at equilibrium (mg/g), k_1, k_2, a_2, b_2 are the rate constants of these models, and k_1 and k_2 are the apparent rate constants.

During this study, the three different kinetic models were discussed in Fig. 8 and the related parameters were shown in Table 3.

As shown, the R^2 values of the pseudo-second-order model exceeded 0.999, which suggested that the overall rate of the MV-PTP adsorption process was controlled by a chemical process. These results were consistent with previous reports [36]. From Table 3, it could be observed that decrease in PTP particle size resulted in increase in the adsorption rate of MV adsorption.

In most cases, it was reported that adsorption process advanced proportionally with $t^{1/2}$, the Weber–Morris plot, rather than t , where t is the contact time [37]. The model was represented using the following equation:

$$Q_t = K_{id} t^{1/2} + C \tag{9}$$

where K_{id} is the intra-particle diffusion rate constant. According to the equation, when the mechanism of the adsorption follows the intra-particle diffusion process, the plot of Q_t versus $t^{1/2}$ must be a straight line with a slope K_{id} and the intercept C . The value of

Table 3
Kinetics parameters for the removal of MV by PTP.

| Particle size | First order | | Second order | | Elovich | | |
|---------------|-------------|--------|--------------|--------|---------|--------|--------|
| | K_1 | R^2 | K_2 | R^2 | a | b | R^2 |
| 40 mesh | 0.0135 | 0.9656 | 0.383 | 0.9991 | 7.3696 | 56.303 | 0.9835 |
| 200 mesh | 0.0194 | 0.9972 | 0.261 | 0.9998 | 7.1698 | 60.276 | 0.9877 |
| Nano-particle | 0.0194 | 0.9986 | 0.176 | 0.9999 | 5.9584 | 66.788 | 0.9921 |

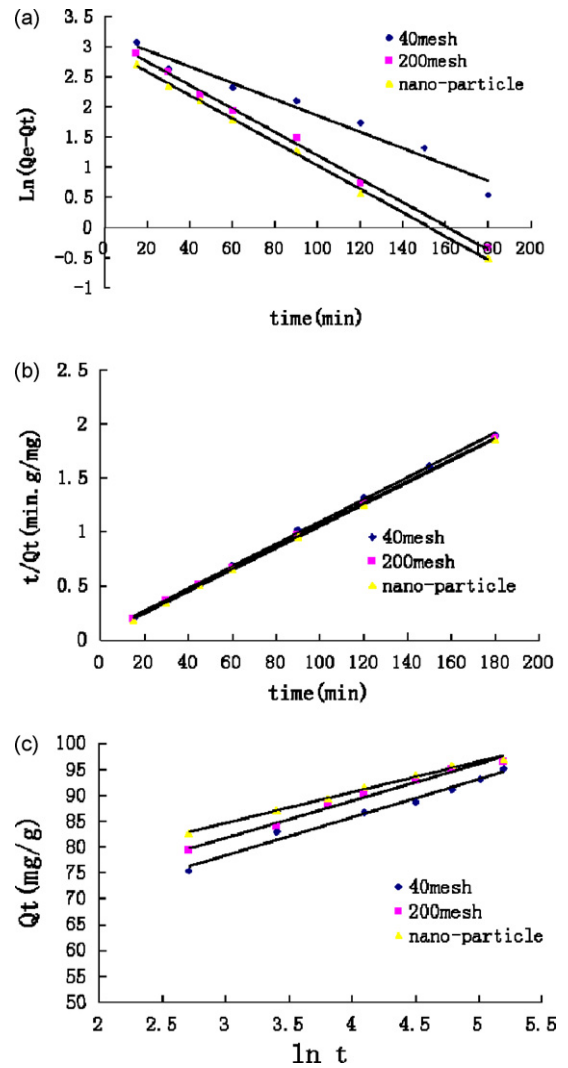


Fig. 8. kinetic models for adsorption of MV onto PTP at 25 °C.

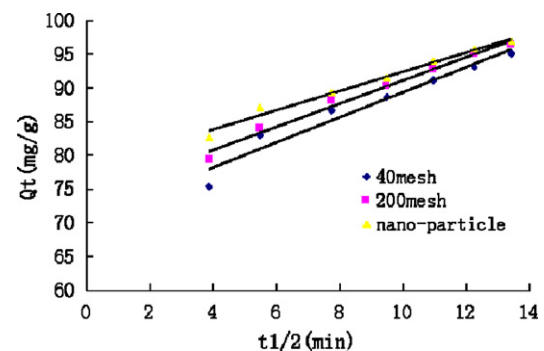


Fig. 9. Plots for evaluating intra-particle diffusion rate constant for adsorption of MV onto PTP at 25 °C.

Table 4
Intra-particle diffusion constant for different PTP particle sizes.

| Particle size | K_{id} | C |
|---------------|----------|--------|
| 40 mesh | 1.8666 | 70.713 |
| 200 mesh | 1.7290 | 73.846 |
| Nano-particle | 1.4320 | 78.109 |

intercept C shows the thickness of the boundary layer. The larger intercept indicates a thicker boundary layer [38]. The deviation of the straight lines from the origin may due to the transformation of the rate during the initial and the final stages of adsorption (Fig. 9). At the same time, this deviation may indicate that the pore diffusion is not the unique factor controlling the rate of the process.

It could be seen in Table 4 that with PTP particles getting smaller, the slope K_{id} decreased from 1.8666 to 1.432, and the intercept C increased from 70.713 to 78.109, which could be explained that a large number of smaller particles provided a larger surface area for MV removal and larger surface for adsorption thus enhanced the boundary layer effect.

4. Conclusion

In the present investigation it had been clearly shown that Pu-erh tea powder could be potentially used as a low cost adsorbent for methyl violet removal from an aqueous solution. System variables such as pH, adsorbent dosage and particle size of Pu-erh tea powder were investigated. Three isotherms and kinetic equations were employed in modeling the adsorption mechanism. It was found that the isotherm fit the Langmuir and the kinetics fit the pseudo-second-order equation with higher correlation coefficient. Intra-particle diffusion model was found to determine the rate of progress of the adsorption process. It showed that smaller particles exhibited bigger boundary layer effect.

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