Korean J. Chem. Eng., **31**(12), 2192-2197 (2014)
DOI: 10.1007/s11814-014-0152-x

pISSN: 0256-1115
eISSN: 1975-7220

Adsorption of methyl orange using self-assembled porous microspheres of poly(*o*-chloroaniline)

Muhammad Naveed Anjum*,*, Khalid Mahmood Zia*, Lihua Zhu**, Haroon-ur-Rashid**,****,**
Mirza Nadeem Ahmad*, Mohammad Zuber*,†, and Heqing Tang**,†**

*Institute of Chemistry, Government College University, Faisalabad 38030, Pakistan
**College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology,
Wuhan 430074, P. R. China
***Institute of Chemical Sciences, University of Peshawar, Peshawar, Pakistan
****Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education,
College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China

(*Received 19 October 2013 • accepted 2 June 2014*)

Abstract−Self-assembled hollow microspheres poly(*o*-chloroaniline) (POC) have been synthesized by simple oxidative polymerization of *o*-chloroaniline using camphor-sulfonic acid (CSA) as dopant acid and ammonium persulfate (APS) as oxidant. The POC microspheres were characterized by means of FTIR, XRD and SEM analysis. Adsorption characteristics of POC spheres were studied by using methyl orange (MO) as adsorbate. It was found that adsorption of MO by POC was better described by pseudo-second-order kinetics than any other kinetic model, such as the pseudo-first-order and intra-particle diffusion models. Langmuir adsorption isotherm model was the best to fit experimental data. The results showed that hollow microspheres of POC can be used as novel and low-cost adsorbent for removal of organic dye from waste water.

Keywords: Adsorption, Methyl Orange, Hollow Microspheres, Poly(*o*-chloroaniline)

INTRODUCTION

Hollow microspheres of conducting polymers have attracted much attention for their unique physical and chemical properties [1-3]. During the last decade, hollow micro or nanospheres have shown promising applications in fields of controlled drug release, stationary phases for separation, chemical sensor and biosensors, and microencapsulation [4-6]. These versatile applications made it an interesting and important subject in the field of material science [7-9]. Hollow microspheres are generally synthesized by using spherical particle as templates [10,11]. Self-assembly method, using 'soft templates' such as micelles, attracts much attention for producing hollow micro or nanospheres of conducting polymers. This approach is inexpensive and simple as it does not involve the required pre- and post-synthesis procedures to prepare and remove the 'hard' templates [12,13]. Wan et al. prepared hollow microspheres of polyaniline (PANI) by self-assembly method with salicylic acid and naphthalene-2-sulphonic acid as dopants [14,15]. Travas-Sejdic reported self-assembly of hollow microspheres of poly(*o*-methoxyaniline) with *p*-toluene sulfonic acid and poly(methyl vinyl etheraltmaleic acid) as dopant acids, and found that the size and morphology of the hollow spheres were dependent on the weight ratio of dopant acid to monomer [16,17]. Hollow spheres of PANI can also be produced from 'alkali-guided' synthesis in which ammonium persulfate (APS) was used to oxidize aniline in alkaline medium of sodium hydroxide or ammonium hydroxide [18].

Dyes are a subject of much interest as they are extensively used in industries such as plastics, paper, leather, cosmetic and textile. The presence of dyes in wastewaters from these industries may pose a potential eco-toxic hazard. Therefore, removing dyes from wastewaters is very important [19-23]. Several techniques such as chemical oxidation, ion-exchange, precipitation, coagulation, filtration and adsorption are used for removal of dyes from wastewaters. Among these, adsorption has the advantage of recycling and reuse of adsorbents [24,25]. For this purpose, several adsorbent materials have been reported such as banana peels, orange peels, activated carbon, neem leaf powder, modified sporopollenin, saw-dust, deoiled soya and rice-husk [26-32]. Similarly, characteristics and photocatalytic degradation [33] and removal of methyl orange [34] using TiO_2 with different composite films have been reported. Azo dye removal from aqueous solution by organic-inorganic hybrid dodecanoic acid modified layered Mg-Al hydrotalcite has also been studied [35]. Moreover, conducting polymers have been used in adsorption of dyes from wastewaters [36,37]. It is well known that PANI emeraldine salt contains a large number of amine and imine functional groups with considerable quantities of positive charges, which render it as an ideal candidate for removal of anionic dyes from waste water [36,37]. Mahanta et al. reported that the adsorption of dye depended on the nature of dopant used to synthesize PANI, and Guo et al. reported that the morphology of PANI also affects the adsorption dye [37]. However, the PANI derivatives have not been studied for adsorption of dye. Herein, we report the synthesis of a hollow microspheres of poly(*o*-chloroaniline) (POC) in aqueous medium by using APS as oxidant, and diaminodiphenylamine (DDPA) as an aniline

---

†To whom correspondence should be addressed.
E-mail: mohammadzuber@gmail.com, hqtang62@yahoo.com.cn
Copyright by The Korean Institute of Chemical Engineers.

oligomer. In the synthesis of microspheres, the CSA was employed to act as dopant acid, and at the same time the formation of its micelles in aqueous solution plays a vital role in fabrication of hollow microspheres. To the best of our knowledge, this is the first report to fabricate porous microspheres of POC and use them as adsorbent for removal of dye from aqueous solution.

EXPERIMENTAL

1. Chemical Reagents

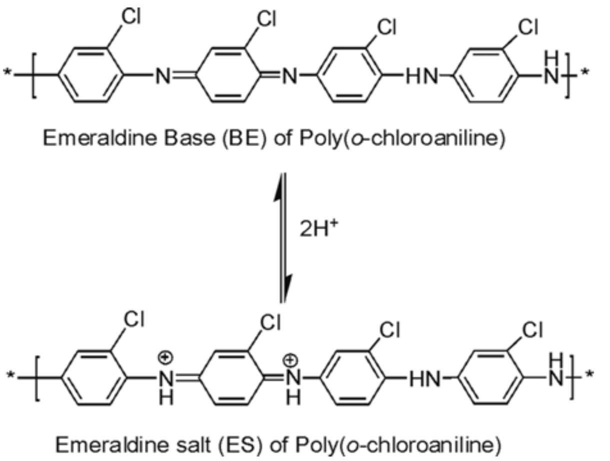
All the chemicals were of analytical grade and used as received. *O*-chloroaniline and ammonium persulfate were procured from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), DDPA from Tokyo Chemical Industries (TCI), Shanghai, China, camphor-sulfonic acids from Aladdin Chemical Reagent Corporation (Shanghai, China) and methyl orange from Tianjin Chemicals (Tianjin, China). All the chemicals were of analytical grade and used as received. Distilled water was used throughout.

2. Synthesis of POC Microspheres

To synthesize POC microspheres, o-chloroaniline (0.48 mmol) was dissolved in 2.5 mL of D-CSA (3 M), with addition of DDPA (0.02 mmol). This mixture solution, being referred to as solution A, was warmed to 60 °C for 1 min and cooled to room temperature (25 °C). A solution of the oxidant (solution B) was prepared by dissolving APS (0.48 mmol) into 2.5 mL of 3M D-CSA solution. Solution B was rapidly added to solution A and then subjected to vigorous stirring for ~30 s. After the completion of polymerization reaction in 4 h, the crude product was washed with water and methanol several times. The cleaned product was dried in oven at 60 °C for 24 h and used for further analysis. The schematic for the preparation of POC microsphere is in Scheme 1.

3. Characterizations

FT-IR spectra were recorded with an IR spectrophotometer (Bruker Vertex 70) between 4,000 and 400 cm^{-1}. UV-visible absorption spectra of the polymers were recorded on a UV-visible spectrometer (Varian Cary 50). The samples were prepared in the pellet form by using spectroscopic grade KBr powder. The morphological images of polymers were observed with scanning electron microscope (SEM, Hitachi S-4800, Japan).



Scheme 1. Schematic formula of EB and its transformation to ES by protonation.

4. Adsorption Experiments

We used methyl orange (MO) since it has often been used as a model dye to probe the photo degradation chemistry occurring on semiconductor particles [38]. All of the adsorption experiments were at room temperature. An aqueous solution of MO (500 mg L^{-1}) was prepared by dissolving MO in double distilled water. Aqueous solutions of MO with different concentrations were obtained by diluting the stock solution with water. A calibration curve was plotted between the absorbance (at maximum wavelength 464 nm) and the concentration of MO based on the absorption spectra of the standard solutions (1.25-30 mgL^{-1}) by UV-Vis absorption spectroscopy. To study adsorption kinetics, POC microspheres (10 mg) were dispersed in 40 mL of MO solution (30 mg L^{-1}) and the mixture was stirred magnetically. An appropriate amount (2 mL) of the mixture was taken out at predetermined time intervals and centrifuged at 5,000 rpm for 5 min. The residual concentration of MO in the supernatant liquid was determined by UV-Vis absorption spectroscopy. For the isotherm experiments, the contact time was controlled at 3 h. The amount of MO adsorbed on the POC microspheres was calculated according to Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where q_e is the amount of MO adsorbed per gram of POC microspheres at equilibrium (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of MO (mg L^{-1}), respectively, V is the volume of solution (L), and m is the mass of the added POC microspheres.

RESULTS AND DISCUSSION

1. Structural Characterization

Structural characterization of the hollow microspheres was by using SEM analysis, and SEM images are presented in Fig. 1. The SEM images show the porous and hollow micro-spherical morphology in the synthesized product. The microspheres were about 10 μm in diameter, and the diameters of the hollow pores in the microspheres were more than 500 nm.

The UV-visible absorption spectra of as-prepared and de-doped POC were also studied [39]. The spectrum of the as-prepared POC shows the absorptions around 900 nm and 400 nm ascribed to the π-π^* transition of the polarons, indicating that POC is in its doped state [40,41]. The FTIR spectrum of POC shows two bands at about 1,502 and 1,577 cm^{-1}, which can be assigned to the non-symmetric C_6 ring modes. The presence of these two bands clearly shows that the polymers are composed of the amine and imine units. The detailed FTIR interpretation is presented elsewhere [39]. The XRD pattern of POC hollow microspheres shows that the product is amorphous and only one broad peak centered at $2\theta=25°$ may be ascribed to the periodicity parallel to the polymer chain [42,43]. The XRD pattern of the POC hollow microsphere was presented in our previous studies [39].

In our experiments, when CSA was mixed in water, it formed micelles, and further mixing with monomer these micelles filled the monomer droplets as shown in Fig. 2. After the addition of APS, two types of polymerizations led to the formation of porous spheres. The first one occurred among the monomers in the same micelle (intra micelle) and the second one between the monomers in dif-

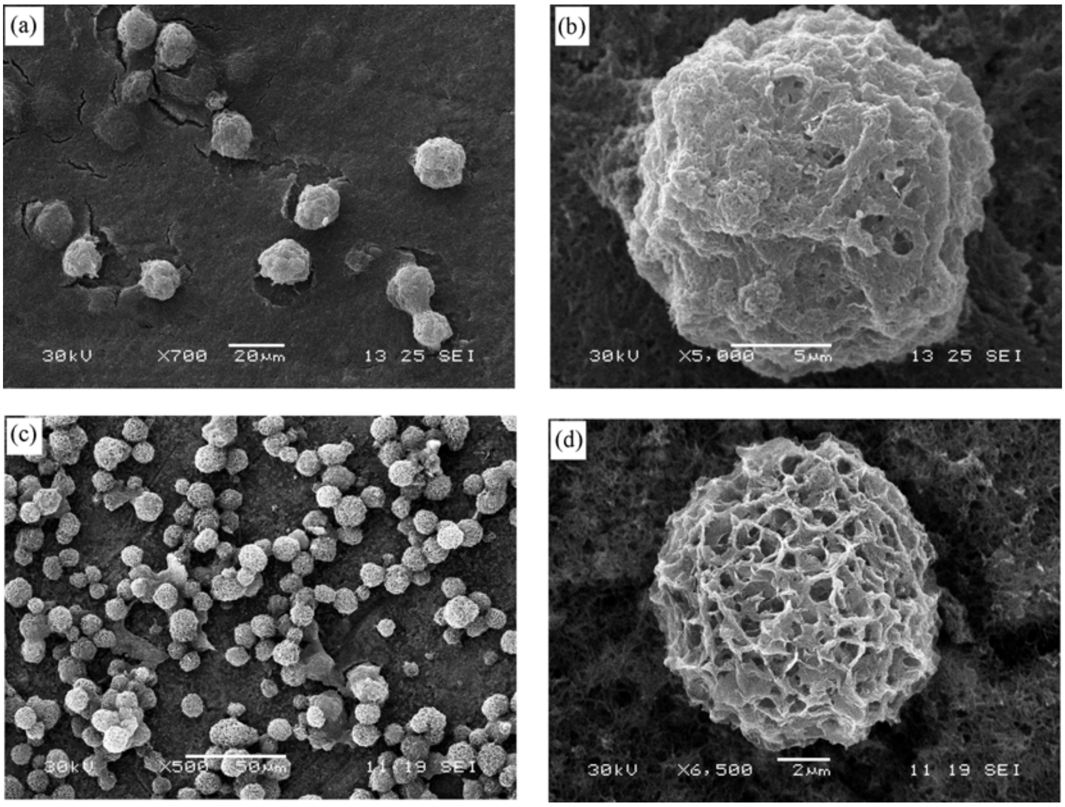


Fig. 1. SEM images of POC microspheres: (a)-(b) as synthesized and (c)-(e) after being washed with distilled water.

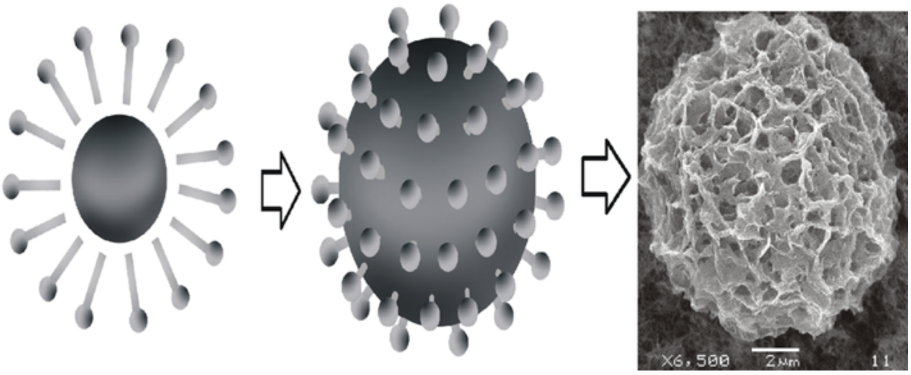


Fig. 2. Graphical illustration of formation of porous microspheres of POC.

ferent micelles (inter micelle) [44]. After the polymerization was completed, CSA remained in the pores, which can be removed by simple dilution or washing by centrifugation. During washing or diluting by water, the CSA molecules diffused out of pores, giving microspheres a porous hollow shape. The SEM image (Fig. 1) of as-prepared microspheres contains CSA in it, which is also demonstrated by the UV-visible spectrum.

2. Use of POC Microspheres as Adsorbents

The different adsorption parameters were studied using various advanced techniques. Fig. 3(a) represents the UV-visible spectra of standard methyl orange aqueous solution with different concentrations: 1.25 mg/L to 30.0 mg/L. The value of absorbance increases with increase in concentration of the standard methyl orange solution. On the basis of the absorbance value, a straight line was obtained in the standard curves.

Herein, we synthesized and used POC porous microspheres as adsorbent for removal MO dye and found that POC porous microspheres can be used as good adsorbent. Fig. 4 shows the kinetic curve of MO adsorption on porous POC microspheres. In the first several minutes, the adsorption process is fast, leading to fast increase of the adsorption amount of MO (q). Then, the q value is further increased but somewhat slowly, until it reaches a saturated value. Fig. 5 shows the pseudo-first-order and pseudo-second-order kinetic plots for the adsorption of MO on POC microspheres according to the pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

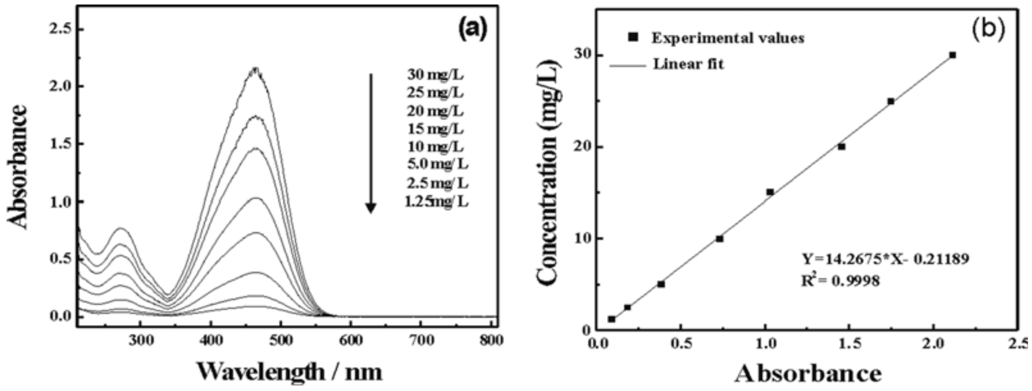


Fig. 3. (a) UV-visible spectra of standard methyl orange (MO) aqueous solution with different concentrations; (b) the relation between the concentration and absorbance at 464 nm, the line represent the linear fit of the experimental values.

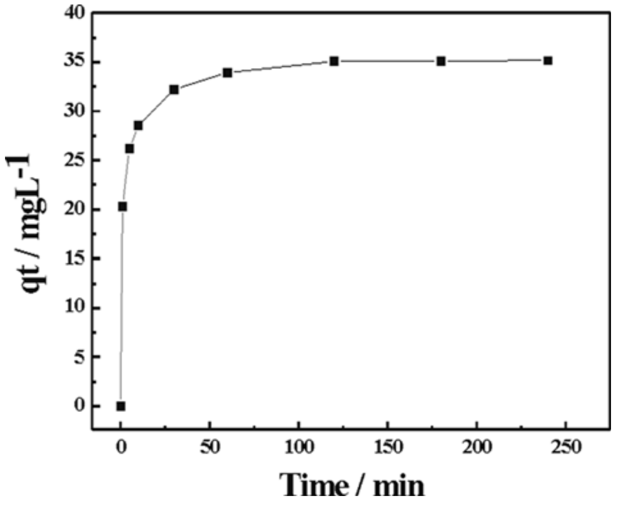


Fig. 4. Adsorption kinetic curves for the adsorption of MO on POC microspheres.

and pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the amount (mg g^{-1}) of dye adsorbed on the POC microspheres at equilibrium and at time t (min), respectively, k_1 and k_2 is the rate constants (g mg^{-1} min).

Eq. (3) can be written as

$$\frac{q_t}{1} = \frac{h}{1 + kq_e t}$$

where h can be regarded as the initial sorption rate as q_t/t, when t approaches 0, Hence

$$h = kq_e^2$$

Thus, a plot of t/q_t against t should give a linear relationship with a slope of $1/q_e$. The result shows that the plot of t/q_e and t is linear with $R^2=0.9998$. This shows that the adsorption of MO by POC porous microspheres can be better described by the pseudo-second-order model as compared to pseudo-first-order model (Fig. 5).

The experimental equilibrium adsorption data can be further analyzed by using different isothermal models: the Langmuir (4), Freundlich (5) and Temkin (6 & 8) equations:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \tag{4}$$

where q_m is the maximum monomolecular adsorption capacity (mg g^{-1}), and k_L the Langmuir constant (L mg^{-1}).

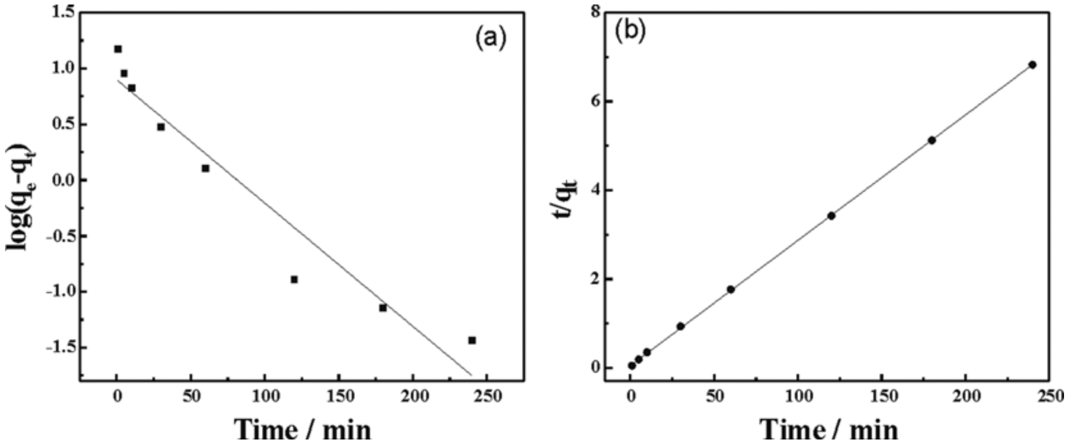


Fig. 5. A pseudo-first-order (a) and pseudo-second-order (b) kinetic plot for the data in Fig. 4.

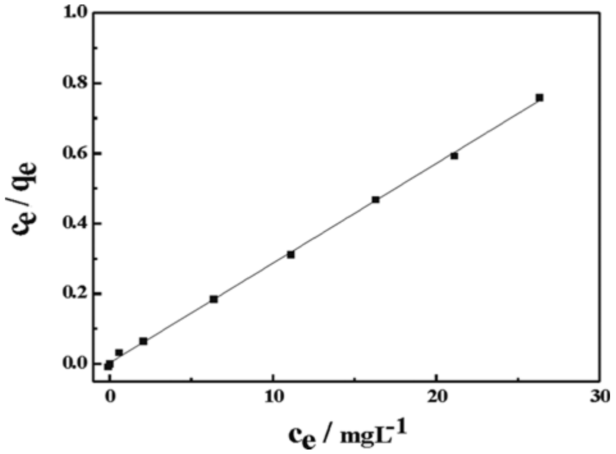


Fig. 6. Langmuir adsorption isotherm of MO on POC porous microspheres.

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{5}$$

The Temkin isotherm contains a factor that explicitly takes into the account adsorbent-adsorbate interactions, and its derivation is characterized by a uniform distribution of binding energies. The model is given by the following equation:

$$q_e = \frac{RT}{b}\ln(A_T C_e) \tag{6}$$

$$q_e = \frac{RT}{b}\ln A_T + \left[\frac{RT}{b}\right]\ln C_e$$

$$B = \frac{RT}{b_T}$$

$$q_e = B\ln A_T + B\ln C_e \tag{7}$$

where A_T is the Temkin isotherm equilibrium binding constant (L/g); b_T is Temkin isotherm constant; R is the universal gas constant (8.314 J/mol/K); T is Temperature at 298 K and B is a constant related to heat of sorption (J/mol).

Eq. (7) can be written as:

$$q_e = a + b\log C_e \tag{8}$$

Table 1. Comparison of the methyl orange (MO) adsorption capacity of various adsorbents

Adsorbents	Adsorption capacity (mg g^{-1})	References
Modified sporopollenin	5.23	[29]
Activated carbon	9.49	[27]
Orange peel	20.5	[26]
Banana peel	21	[27]
POC[a] porous microspheres	35.21	This work
Hypercrosslink polymer	70.923	[54]
Polyaniline microspheres	154.56	[37]
NH_3^+-MCM-41[b]	366.57	[55]
PANI[c] hollow spheres	384.62	[38]

[a] Poly(*o*-chloroaniline)

[b] Ammonium functionalized mobile crystalline material No. 41

[c] Poly(aniline)

Fig. 6 shows the adsorption isotherm of MO on POC porous microspheres, which shows that the experimental equilibrium adsorption of MO onto POC microspheres follows a typical Langmuir-isotherm model. Fig. 6 also shows that the adsorption MO on porous POC microspheres follows the Langmuir isotherm model (correlation coefficient R^2=0.9991) as compared to other models (Fig. 7). Based on Eq. (4), the value of q_m was found to be 35.21 mg g^{-1} of MO on the porous POC microspheres.

Table 1 compares adsorption capacities of POC porous microspheres with other adsorbents used for the adsorption of MO available in the literature. It can be seen that the POC porous spheres can be a promising material for the dye removal from aqueous solution.

CONCLUSIONS

Hollow microspheres of POC were synthesized via self-assembly process wherein CSA played a key role in framing hollow porous morphology. The mechanism proposed for the formation of microspheres was supported by the SEM and UV-visible spectroscopic data. Adsorption kinetics of POC porous microspheres were studied by using methyl orange (MO) as an adsorbate. It was revealed

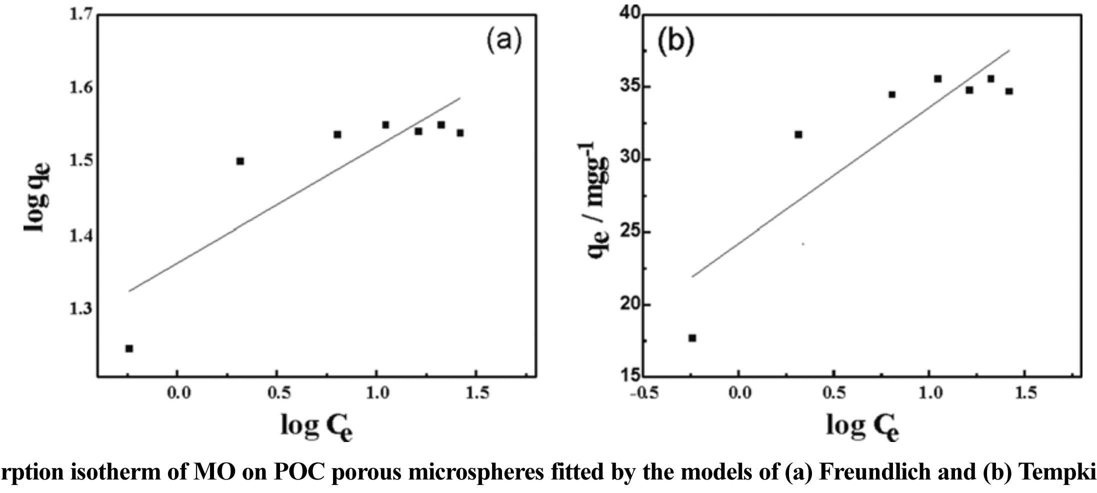


Fig. 7. Adsorption isotherm of MO on POC porous microspheres fitted by the models of (a) Freundlich and (b) Tempkin.

that the adsorption of MO by POC followed pseudo-second-order kinetics and Langmuir-type isotherm model with a favorable adsorption. The results demonstrated that porous microspheres can be a good and cheap candidate for the removal of dyes from aqueous industrial wastes.

ACKNOWLEDGEMENTS

The authors are gratefully thankful to Analysis and Testing Centre, Huazhong University of Science and Technology, China and Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, South-Central University for Nationalities, Wuhan, China. Financial support of Higher Education Commission, Islamabad, Pakistan is highly appreciated and acknowledged for the conduct of this research work.

REFERENCES

1. Y. Yang, Y. Chu and F. Yang, *Mater. Chem. Phys.*, **92**, 164 (2005).
2. M. A. Abidian, H. D. Kim and D. C. Martin, *Adv. Mater.*, **18**, 405 (2006).
3. L. Zhang, Z. Zhang, P. A. Kilmartin and J. Travas-Sejdik, *Macromol. Chem. Phys.*, **212**, 2674 (2011).
4. C. S. Guo and C. M. Li, *Phys. Chem. Chem. Phys.*, **12**, 12153 (2010).
5. S. Virji, J. Huang, R. B. Kaner and B. H. *Nano Lett.*, **4**, 491 (2004).
6. B. M. Lee, J. E. Kim, F. F. Fang, H. J. Choi and J. F. Feller, *Macromol. Chem. Phys.*, **212**, 2300 (2011).
7. K. Ramanathan, M. A. Bangar and Y. M. Yan, *J. Am. Chem. Soc.*, **127**, 496 (2005).
8. S. Y. Park, M. S. Cho and C. A. Kim, *Colloid Polym. Sci.*, **282**, 198 (2003).
9. K. Ishizu, H. Tanaka and R. Saito, *Polymer*, **37**, 863 (1996).
10. L. Yang, Z. Yang and W. J. Cao, *Colloid Interface Sci.*, **292**, 503 (2005).
11. L. Hao, C. Zhu, C. Chen, P. Kang, Y. Hu, W. Fan and Z. Chen, *Synth. Met.*, **139**, 391 (2003).
12. L. Zhang, H. Peng, P. A. Kilmartin, C. Soellar, R. Tilley and J. Travas-Sejdic, *Macromol. Rapid Commun.*, **29** 598 (2008).
13. J. Han, G. Song and R. Gou, *Adv. Mater.*, **18**, 3140 (2006).
14. L. Zhang, M. Wan and Y. Wie, *Macromol. Rapid Commun.*, **27** 888 (2006).
15. Z. Wei and M. Wan, *Adv. Mater.*, **14**, 1314 (2002).
16. L. Zhang, H. Peng, P. A. Kilmartin, C. Soellar and J. Travas-Sejdic, *J. Phys. Chem. C.*, **113**, 9128 (2009).
17. J. Sui, L. Zhang, H. Peng, J. Travas-Sejdic and P. A. Kilmartin, *Nanotechnology*, **20**, 415 (2009).
18. X. Wang, N. Liu, X. Yan, W. J. Zhang and Y. Wie, *Chem. Lett.*, **34**, 42 (2005).
19. P. C. Vandevivere, R. Bianchi and W. Verstraete, *J. Chem. Technol. Biotechnol.*, **72**, 289 (1998).
20. W. Luo, M. E. Abbas, L. Zhu, K. Deng and H. Q. Tang, *Anal. Chim. Acta*, **629**, 1 (2008).
21. L. Wang, L. Zhu, W. Luo, Y. Wu and H. Q. Tang, *Ultrason. Sonochem.*, **14**, 253 (2007).
22. W. Luo, Z. Chen, L. Zhu, F. Chen, L. Wang and H. Q. Tang, *Anal. Chim. Acta*, **588**, 117 (2007).
23. M. S. Chiou and G. S. Chuang, *Chemosphere*, **62**, 731 (2006).
24. G. Annadurai, G. Chellapandian and M. R. V. Krishnan, *Environ. Monit.*, **59** 111 (1999).
25. G. Annadurai, R. S. Juang and D. J. Lee, *J. Hazard. Mater.*, **92**, 263 (2002).
26. K. P. Singh, D. Mohan, S. Sinha, G. S. Tondon and D. Gosh, *Ind. Eng. Chem. Res.*, **42**, 1965 (2003).
27. A. Sharma, K. G. Bhattacharya and G. Krishna, *Ind. J. Chem. Technol.*, **12**, 285 (2005).
28. A. Ayar, O. Gezici and M. Kucukosmanoglu, *J. Hazard. Mater.*, **147**, 186 (2007).
29. V. K. Grag, M. Amita, R. Kumar and R. Gupta, *Dyes Pigm.*, **63**, 243 (2004).
30. V. K. Gupta, I. Ali, Suhas and D. Mohan, *J. Colloid Interface Sci.*, **265**, 257 (2003).
31. A. N. Chowdhury, S. R. Jasmeen and M. M. Hosain, *Polym. Adv. Technol.*, **15**, 633 (2004).
32. M. M. Ayad and A. E. Ahmad. *J. Phys. Chem. C.*, **114**, 14377 (2010).
33. S Artkla, K. Wantala, B. Srinameb, N. Grisdanurak, W. Klysubun and J. Wittayakun, *Korean J. Chem. Eng.*, **26**, 1556 (2009).
34. J. He, Q. Z. Cai, Q. Luo, D. Q. Zhang, T. T. Tang and Y. F. Jiang, *Korean J. Chem. Eng.*, **27**, 435 (2010).
35. L. Nong, C. Xiao and W. Jiang, *Korean J. Chem. Eng.*, **28**, 933 (2011).
36. D. Mahanta, G. Madras, S. Radhakrishnan and S. Patil, *J. Phys. Chem. B.*, **113**, 2293 (2009).
37. L. H. Ai, J. Jiang and R. Zhang, *Synth. Met.*, **160**, 762 (2010).
38. K. Dai, H. Chen, T. Peng, D. Ke and H. Yi, *Chemosphere*, **69**, 1361 (2007).
39. M. N. Anjum, PhD Thesis, Library, Huazhong University of Science and Technology, P. R. China (2012).
40. M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Polymer*, **36**, 3113 (1994).
41. I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, *Macromolecules*, **33**, 3237 (2000).
42. C. J. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).
43. Y. Sahin, S. Percin, M. Sahin and G. Ozkan, *J. App. Polym. Sci.*, **19**, 2302 (2004).
44. M. N. Anjum, L. Zhu, Z. Luo, J. Yan and H. Q. Tang, *Polymer*, **52**, 5795 (2011).