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聚苯胺-多糖复合凝胶的制备及其染料吸附性能

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摘 要:为进一步扩展聚苯胺的用途,在聚苯胺的形成过程中加入多糖(如海藻酸钠、壳聚糖等),植酸作为掺杂剂与凝胶促进剂,一步反应得到了聚苯胺-多糖复合凝胶.通过傅里叶红外谱和扫描电子显微镜,对产物的结构与微观形貌进行表征.通过紫外可见光光谱,研究了聚苯胺-多糖复合凝胶对于刚果红、甲基橙和亚甲基蓝等染料的吸附能力,并利用准二级动力学模型研究了其对刚果红吸附行为的吸附动力学.研究结果表明,聚苯胺-多糖复合凝胶具有选择吸附性,对刚果红的吸附效果远大于甲基橙和亚甲基蓝.刚果红的吸附率大于95%,最大吸附量可达57.7 mg/g.聚苯胺-多糖复合凝胶对于刚果红的吸附行为可以用准二级动力学模型进行很好拟合,这些特征表明聚苯胺-多糖复合凝胶有望用于染料废水处理.

关键词:聚苯胺;多糖;凝胶;染料;吸附
中图分类号:TQ424.3;X788 **文献标识码**:A **doi**:10.3969/j.issn.1674-2869.2017.04.007

Synthesis of Polyaniline-Polysaccharide Composite Hydrogels for Dye Adsorption

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Abstract: To expand the application of polyaniline, polysaccharide, such as sodium alginate or chitosan, was introduced into the reaction system of aniline polymerization. Polyaniline-polysaccharide composited hydrogels were successfully obtained in one-step reaction with the aid of phytic acid as both dopant and gel prompter. Fourier-transform infrared spectrometry and scanning electron microscopy were carried out to characterize the structure and morphology of polyaniline-polysaccharide composited hydrogels. Moreover, the dye (congo red, methyl orange, and methylene blue) adsorption properties of the as-prepared polyaniline-polysaccharide composited hydrogels were characterized by ultraviolet and visible spectrophotometry. Adsorption kinetics was studied by pseudo-second-order kinetic model. The result shows that polyaniline-polysaccharide composited hydrogels exhibit selective dye adsorption. The adsorption ability for congo red is better than that for methyl orange and methylene blue. The removal efficiency for congo red is greater than 95 % and the maximum adsorption capacity is about 57.7 mg/g. The adsorption kinetics is well simulated by pseudo-second-order kinetic model. These characteristics make polyaniline-polysaccharide composited hydrogen a promising candidate in the dye waste water treatment.

Keywords: polyaniline;polysaccharide;hydrogel;dye;adsorption

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WU Z L,XIONG H Z,YU X H, et al. Synthesis of polyaniline-polysaccharide composite hydrogels for dye adsorption [J]. Journal of Wuhan Institute Technology,2017,39(4):348-352.

在印染行业中，各种合成有机染料被广泛使用，即使将含少量染料的废水排放到自然环境中，也会严重污染水资源，影响生态系统和人类健康[1-2]. 研究发现，一些染料有较强的毒性，可以致病和致癌[3]. 因此，去除废水中的染料一直是一个重要的环境问题[4]. 目前对于染料废水的处理有絮凝、混凝、生物降解、催化氧化、离子交换、吸附等方法[5-8]. 吸附法是近年处理能力最为优异、应用范围最广的一种方法[9-11]. 所以，制备一种成本低、性能好的吸附剂就成为科研人员的研究目标. 例如，Mahanta等利用2种磺酸掺杂改性聚苯胺，制备了一种对阴离子型染料有显著吸附效果的吸附剂[12]. 聚苯胺由于其良好的电化学可逆性，优良的氧化还原性和良好的环境稳定性，被认为是最具应用前景的一类有机导电聚合物[13-14]. 多糖是一类分子链上含有大量羟基的高分子化合物. 所以，多糖能够吸附各种染料分子和金属离子等[15-16].

本文采用一步反应，在聚苯胺的形成过程中加入多糖（如海藻酸钠、壳聚糖等），并利用植酸作为掺杂剂与凝胶促进剂，成功制备了聚苯胺-多糖复合凝胶. 整个反应条件温和，操作简单易行，并且聚苯胺-多糖复合凝胶对阴离子型染料具有很好的选择吸附性能.

1　实验部分

1.1　聚苯胺-多糖复合凝胶的制备方法

1）在10 mL去离子水中加入4.5 mL植酸溶液（质量分数为70 %），搅拌5 min；接着加入5 mL的2 mg/mL海藻酸钠水溶液或壳聚糖（质量分数为2 %的乙酸溶液）水溶液搅拌10 min.

2）缓慢加入2.3 mL苯胺，溶液出现乳白色絮状物，持续搅拌30 min.

3）在冰浴条件下，将配好的含有1.43 g过硫酸铵（ammonium persulphate，APS）的5 mL水溶液缓慢滴加入乳白色溶液中，并搅拌5 min，静置反应2 h得到聚苯胺-海藻酸钠复合凝胶（polyaniline-polysaccharide-sodium alginate，PANI-PSA）或聚苯胺-壳聚糖复合凝胶（polyaniline-polysaccharide-chitosan，PANI-PSC）.

1.2　聚苯胺-多糖复合凝胶的表征与测试

采用Nicolet Impacr-420红外光谱（Fourier transform infrared spectroscope，FT-IR）仪、JSM-5510LV扫描电子显微镜（scanning electron microscope，SEM）与TU1901紫外可见分光光度计（ultraviolet and visible spectrophotometer，UV-vis）对样品进行表征.

染料吸附测试：分别配制刚果红（congo red，CR）、甲基橙（methyl orange，MO）及亚甲基蓝（methylene blue，MB）溶液，将0.1 g聚苯胺-多糖复合凝胶放入染料溶液中，在20 ℃下搅拌，以10 min的间隔，取样离心得上清液，用UV-vis检测溶液的染料浓度. 聚苯胺-多糖复合凝胶对染料的吸附率（η，%）和吸附量（q_e，mg/g）的计算公式如下：

$$\eta = \frac{(\rho_o - \rho_e)}{\rho_o} \times 100\% , \tag{1}$$

$$q_e = \frac{(\rho_o - \rho_e)V}{m} , \tag{2}$$

式（1）和式（2）中：ρ_o为待测溶液的染料起始浓度，mg/L；ρ_e为取样溶液的染料浓度，mg/L；V为测试溶液的体积，L；m为复合凝胶的质量，g.

2　结果与讨论

2.1　FT-IR表征

聚苯胺-多糖复合凝胶的FT-IR谱如图1所示. 图1中的1 580 cm^{-1}处出现的特征峰是醌式结构N═Q═N特征振动吸收峰，1 494 cm^{-1}处出现的特征峰是苯式结构N—C—N特征振动吸收峰，1 311 cm^{-1}处出现的特征峰是聚苯胺骨架C—N伸缩振动吸收峰，1 240 cm^{-1}处出现的特征峰是掺杂态聚苯胺C—N伸缩振动吸收峰，823 cm^{-1}处出现的特征峰是由于质子化造成的C—H面外弯曲振动吸收峰，均为掺杂态聚苯胺的特征峰. 3 750 cm^{-1}~2 500 cm^{-1}处的缔合峰证明了多糖的存在.

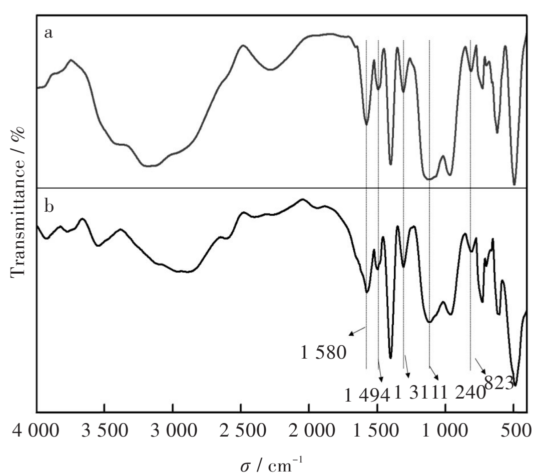

图1　(a) PANI-PSA和(b) PANI-PSC的FT-IR谱

Fig. 1　FT-IR spectra of (a) PANI-PSA and (b) PANI-PSC

2.2　SEM表征

聚苯胺-多糖复合凝胶的SEM图如图2所示. 从图2中可以看出，聚苯胺-多糖复合凝胶是由多

层片结构构成,片层之间分布着大量的孔道结构,这种孔道结构使得聚苯胺的比表面积增加数倍,从而极大地提高了它对染料的吸附效果.

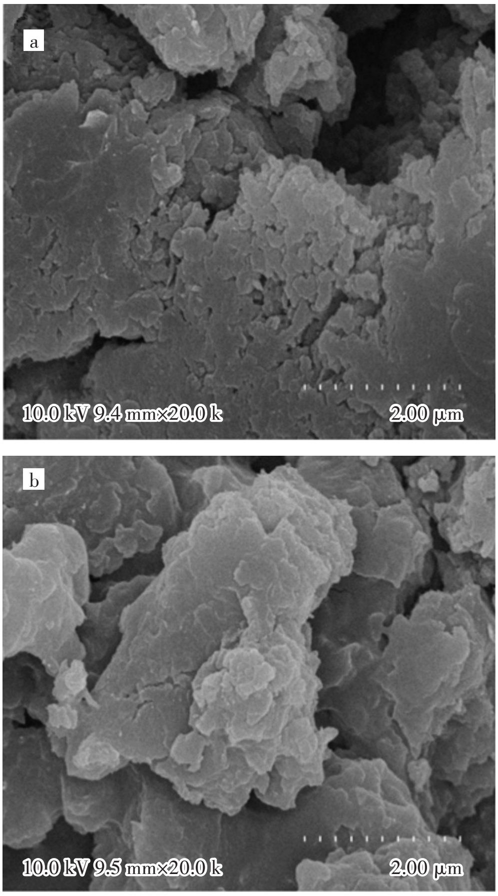

图2 (a) PANI-PSA和(b) PANI-PSC的SEM图

Fig. 2 SEM images of (a) PANI-PSA and (b) PANI-PSC

2.3 吸附性能测试

2.3.1 选择吸附测试 分别配制25 mg/L的CR、MO和MB溶液,分别放入0.1 g的复合凝胶,在20 ℃下搅拌,检测复合凝胶的选择吸附性能. 检测结果如图3所示,复合凝胶对CR、MO这类阴离子型染料能很好地吸附,吸附率都大于95 %;而对MB这类阳离子型染料的吸附率却不足18 %,结果表明聚苯胺-多糖复合凝胶针对离子型染料具有选择吸附性. 之所以有这样的结果,是因为聚苯胺本身带有正电荷,而CR、MO为阴离子型染料,电性与聚苯胺相反,相互吸引,所以具有良好吸附性能;而MB是阳离子型染料,电性与聚苯胺相同,相互排斥,所以吸附效果差.

2.3.2 最大吸附量测试 配制质量浓度分别为10 mg/L、25 mg/L、50 mg/L、100 mg/L的CR溶液,并加入0.1 g复合凝胶,在20 ℃下搅拌,检测聚苯胺-多糖复合凝胶的最大吸附性能. 检测结果如图4所示,在CR的质量浓度小于100 mg/L且搅拌30 min后,复合凝胶将绝大多数CR吸附;在CR质量浓度达到100 mg/L且搅拌100 min后,聚苯胺-多糖复合凝胶对CR吸附达到平衡. 可以计算出,PANI-PSA和PANI-PSC的最大吸附量分别为56.8 mg/g和57.7 mg/g.

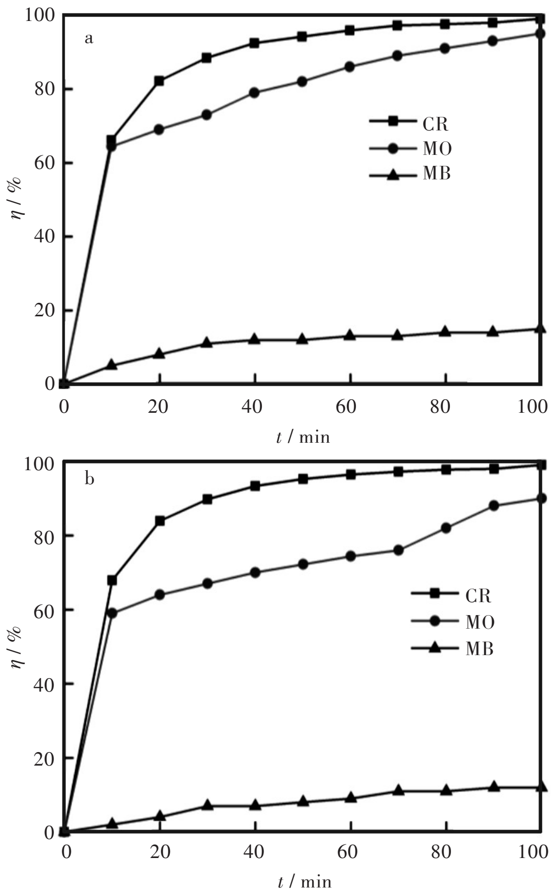

图3 (a) PANI-PSA和(b) PANI-PSC对不同类染料的选择吸附

Fig. 3 Selective adsorption of different dyes on (a) PANI-PSA and (b) PANI-PSC

2.3.3 吸附动力学研究 在20 ℃且复合凝胶用量为0.1 g的情况下,采用准二级动力学方程(pseudo-second-order kinetic),拟合复合凝胶吸附CR在不同起始质量浓度下的准二级动力学曲线,拟合的参数和曲线分别如表1、表2和图5所示.

准二级动力学方程为:

$$\frac{\mathrm{d}q_{\mathrm{e}}}{\mathrm{d}t}=k_2(q_{\mathrm{e}}-q_t)^2\ , \quad (3)$$

式(3)中: k_2 为方程的速率常数; q_{e} 为复合凝胶的吸附量, mg/g. 对式(3)积分,并且采用边界条件 $q_t=0$ 和 $t=0$ 得到公式(4):

$$\frac{t}{q_t}=\frac{1}{k_2q_{\mathrm{e}}^2}+\frac{t}{q_{\mathrm{e}}}\ , \quad (4)$$

式(4)中: t 为时间, min. 结果表明聚苯胺-多糖复合凝胶吸附CR的吸附动力学能很好的被准二级动力学模型拟合.

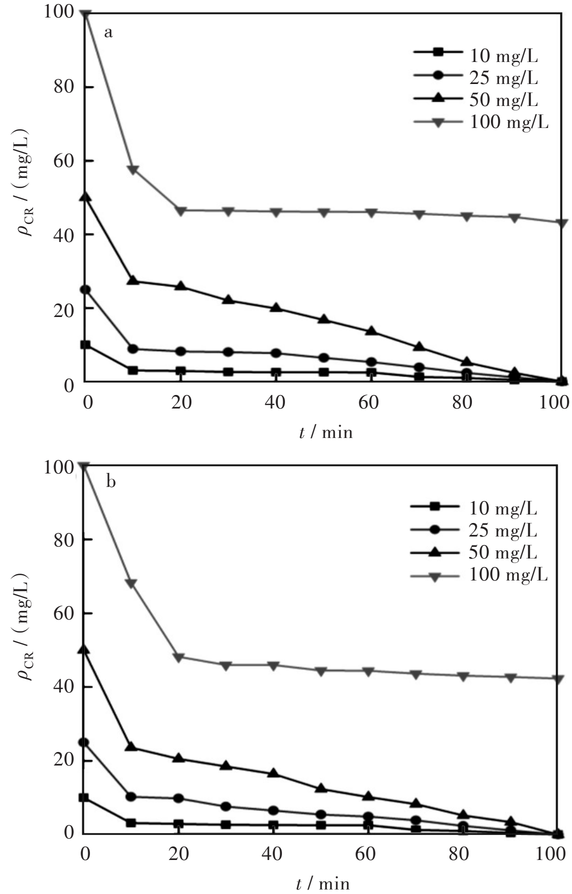

图4 (a) PANI-PSA和(b) PANI-PSC对不同质量浓度CR的吸附

Fig. 4 Mass concentrations of CR adsorption on (a) PANI-PSA and (b) PANI-PSC

表1 PANI-PSA吸附CR的准二级动力学拟合方程及参数

Tab. 1 Fitted equations and parameters of CR adsorption on PANI-PSA by pseudo-second-order kinetic model

ρ_o / (mg/L)	拟合方程 equations	参数 parameters
10	t/q_t=0.130t+0.170	0.999 8
25	t/q_t=0.055t+0.083	0.999 7
50	t/q_t=0.032t+0.029	0.999 9
100	t/q_t=0.018t+0.006	0.999 9

表2 PANI-PSC吸附CR的准二级动力学拟合方程及参数

Tab. 2 Fitted equations and parameters of CR adsorption on PANI-PSC by pseudo-second-order kinetic model

ρ_o / (mg/L)	拟合方程 equations	参数 parameters
10	t/q_t=0.131t+0.177	0.999 9
25	t/q_t=0.061t+0.090	0.998 5
50	t/q_t=0.037t+0.011	0.999 9
100	t/q_t=0.018t+0.006	0.999 9

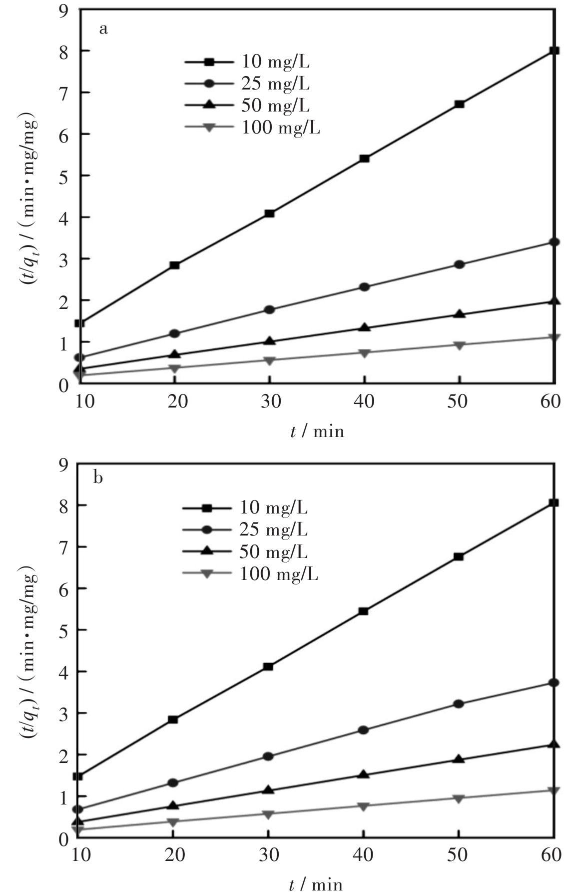

图5 (a) PANI-PSA和(b) PANI-PSC在不同起始质量浓度下吸附CR的准二级动力学曲线

Fig. 5 Pseudo-second-order kinetic plots of different mass concentrations of CR adsorption on (a) PANI-PSA and (b) PANI-PSC

3 结 语

本文采用一步反应,在聚苯胺的形成过程中加入多糖(如海藻酸钠、壳聚糖等),并利用植酸掺杂剂与凝胶促进剂,成功制备了聚苯胺-海藻酸钠复合凝胶与聚苯胺-壳聚糖复合凝胶. 聚苯胺-多糖复合凝胶具有较好的选择吸附性能,可以在短时间内对阴离子型染料有很大的吸附容量. 经测试可得,在CR起始浓度为100 mg/L,经过100 min后,PANI-PSA和PANI-PSC的最大吸附量分别为56.8 mg/g和57.7 mg/g. 聚苯胺-多糖复合凝胶对于CR的吸附行为可以用准二级动力学模型进行很好地拟合. 这类聚苯胺-多糖复合凝胶可用于染料废水处理.

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