

Amidoxime-Modified Chitosan for Pigment Red 224 Enrichment through Reversible Assembly

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1. Solubility of AO/Mac-CTS adsorbent in different solvents

Table S1. The condition of AO/Mac-CTS in different solvent environment.

Solvents	Solubility status	Solvents	Solubility status
Distilled water	No	CH ₂ Cl ₂	No
5% aq. NaOH	No	DMF	No
5% aq. HCl	No	DMSO	No
methanol	No	pyridine	No

2. XPS analyses of typical materials

Table S2. The XPS spectra information of AN/Mac-CTS and AO/Mac-CTS.

	Element	Binding Energy(eV)	Assignment	Reference
AN/Mac-CTS	C 1s	285.50	C-H, C-C, CH ₂ -CH ₂ -C≡N	1-2
		286.63	CH ₂ -C≡N, CH ₂ -C≡N	
		287.72	C=O	
	N 1s	399.68	C≡N	1
		402.10	-NH ₃ ⁺	2
AO/Mac-CTS	C 1s	284.92	CH ₂ -CH ₂ -C(NH ₂)=NOH, CH ₂ -C(NH ₂)=NOH, CH ₂ -CH ₂ -C≡N	1-2
		286.33	CH ₂ -C≡N, CH ₂ -C≡N, C-O	
		287.44	CH ₂ -C(NH ₂)=NOH, N-C=O	
	N 1s	399.44	NH ₂ -C=N-OH, C≡N	1
		400.74	NH ₂ -C=N-OH	

3. The effect of pH on the enrichment of pigment red 224

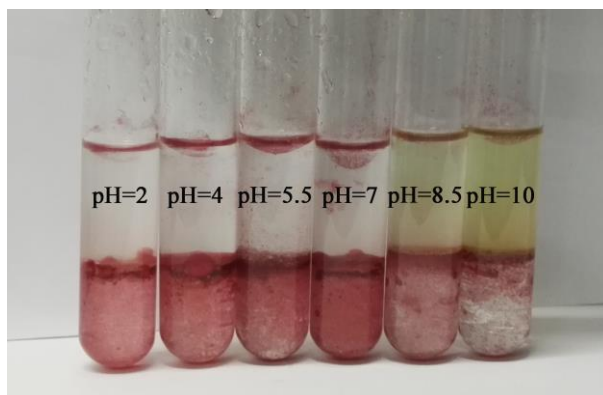


Fig. S1. The effect of pH on the enrichment of pigment red 224. The experiment condition are that $n(\text{Pigment red 224}):n(\text{AO/Mac-CTS}) = 1:4$ and $T=20\text{ }^\circ\text{C}$.

4. Interaction between AO/Mac-CTS and pigment red 224

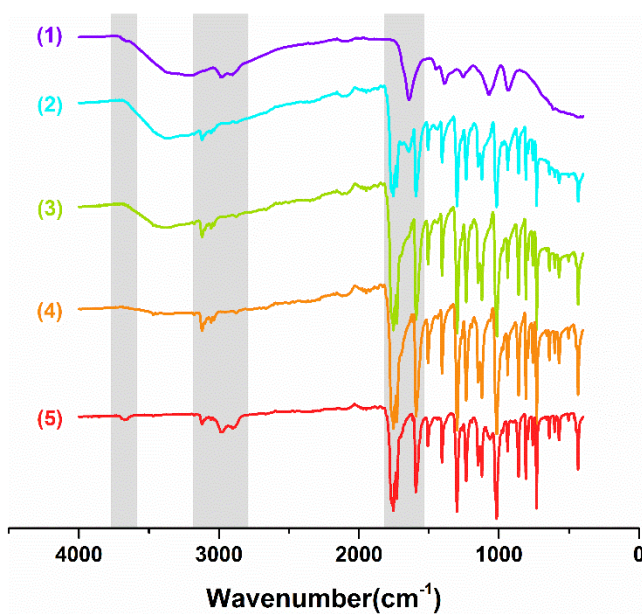
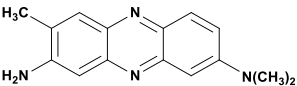
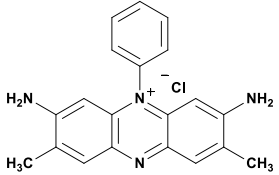
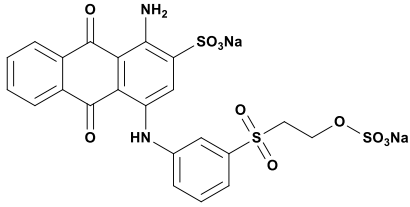


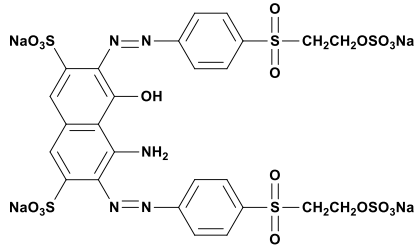
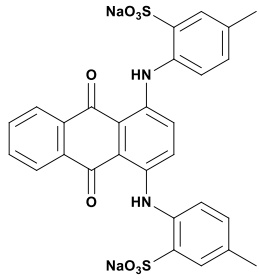
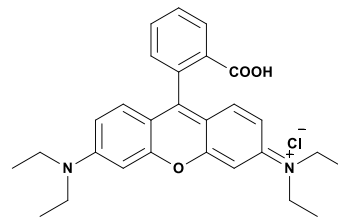
Fig. S2. FTIR spectra of AO/Mac-CTS (1), pigment red 224 adsorbed on AO/Mac-CTS in varying mole ratio ($n(\text{AO/Mac-CTS}):n(\text{Pigment red 224}) = 6:1, 1:1$ and $1:6$ corresponding to (2) - (4) respectively, and pigment red 224 (5).

5. Comparison of dye adsorption performance with other advanced materials

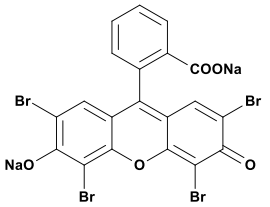
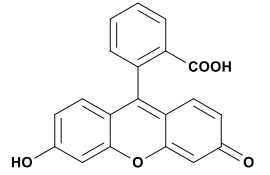
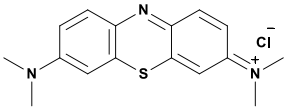
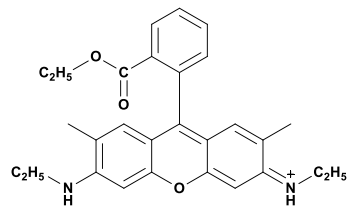
Table S3. Comparison with typical state-of-the-art materials for the treatment of cationic, anionic and neutral dyes which are similar with the structure of PTCDA.

Sample	Solvent	Dye object	T (°C)	pH	Q _e (mg/g)	Ref.
Magnetic multi-wall carbon nanotube nanocomposite	-	 <p>Neutral Red</p>	25	7	20.51	3
Activated carbon prepared by burning-off powder medium density fibreboard with 33min	Water		25	5	50	4
Metal-organic framework [(CH ₃) ₂ NH ₂] ₂ [Cu ₃ O(SO ₄) ₃ Cu ₂ L ₂ (DMF)(H ₂ O)]·9DMF	Ethanol		Room temperature (RT)	-	132	5
Fe ₃ O ₄ nanoparticles	Water	 <p>Safranin O</p>	30	6	96.94	6
Cucurbit[6]uril	DMF	 <p>Reactive Blue 19</p>	25	7	100.5	7
Glycidyl methacrylate- modified chitosan radically copolymered with methyl methacrylate	Water		30	7	189	8

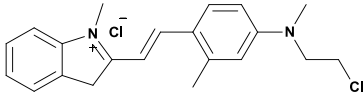
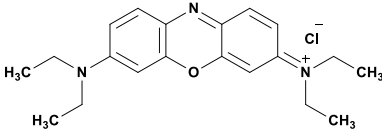
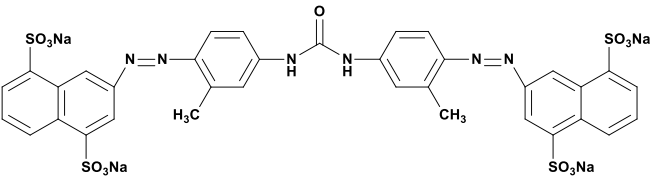
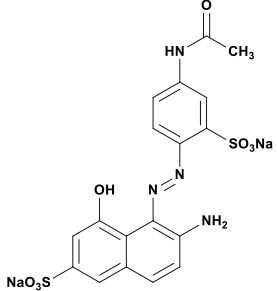
Continued Table S3

Sample	Solvent	Dye object	T (°C)	pH	Q _e (mg/g)	Ref.
Microalgae immobilized by polysulfone nanofibrous web	Water	 <p>Remazol Black 5</p>	23	6	36.5	9
Cross-linked amino-starch	Water		25	4	245.42	10
Magnetic nanoparticles modified with aminoguanidine	Water	 <p>Acid Green 25</p>	25	1.3	121.1	11
Phase-selective gelators methyl 4,6-O-[(4-methylphenyl)methylene]-2,3-di-O-hexadecanoyl-α-D-glucopyranoside	Water	 <p>Rhodamine B</p>	RT	-	24	12

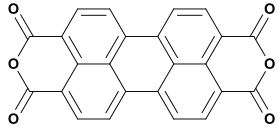
Continued Table S3

Sample	Solvent	Dye object	T (°C)	pH	Q _e (mg/g)	Ref.
Graphene oxide-chitosan hydrogel	Water	 <p>Eosin Y</p>	21	7	326	13
Hyperbranched poly(ether amine) nanogel/chitosan	Water	 <p>Fluorescein</p>	25	-	2.39	14
Amidoximated poly(acrylonitrile) particles	Water	 <p>Methylene Blue</p>	RT	-	90.53	15
		 <p>Rhodamine 6 G</p>			74.17	

Continued Table S3

Sample	Solvent	Dye object	T (°C)	pH	Q _e (mg/g)	Ref.
Starch/acrylonitrile-amidoxime	Water	 <p>Basic Violet 7</p>	25	7	7.3	16
		 <p>Basic Blue 3</p>			7.2	
		 <p>Direct Yellow 50</p>			2.1	
		 <p>Acid Red 37</p>			3.1	

Continued Table S3

Sample	Solvent	Dye object	T (°C)	pH	Q _e (mg/g)	Ref.
AO/Mac-CTS	H ₂ O -CHCl ₃	 PTCDA	10	7	315.79	This work

6. References

- (1) Zhao, Y.; Wang, X.; Li, J.; Wang, X. K., Amidoxime functionalization of mesoporous silica and its high removal of U(VI). *Polym. Chem.* **2015**, *6* (30), 5376-5384.
- (2) Ho, T. T.; Bremmell, K. E.; Krasowska, M.; Stringer, D. N.; Thierry, B.; Beattie, D. A., Tuning polyelectrolyte multilayer structure by exploiting natural variation in fucoidan chemistry. *Soft Matter* **2015**, *11* (11), 2110-2124.
- (3) Gong, J. L.; Wang, B.; Zeng, G. M.; Yang, C. P.; Niu, C. G.; Niu, Q. Y.; Zhou, W. J.; Liang, Y., Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *J. Hazard. Mater.* **2009**, *164* (2–3), 1517-1522.
- (4) Gomes, J. A. F. L.; Azaruja, B. A.; Mourão, P. A. M., From MDF and PB wastes to adsorbents for the removal of pollutants. *Appl. Surf. Sci.* **2016**, *380*, 119-126.
- (5) Yao, S.; Xu, T.; Zhao, N.; Zhang, L.; Huo, Q.; Liu, Y., An anionic metal-organic framework with ternary building units for rapid and selective adsorption of dyes. *Dalton Trans.* **2017**, *46*, 3332-3337.
- (6) Ghaedi, M.; Hajjati, S.; Mahmudi, Z.; Tyagi, I.; Agarwal, S.; Maity, A.; Gupta, V. K., Modeling of competitive ultrasonic assisted removal of the dyes – Methylene blue and Safranin-O using Fe₃O₄ nanoparticles. *Chem. Eng. J.* **2015**, *268*, 28-37.
- (7) Xie, X.; Li, X.; Luo, H.; Lu, H.; Chen, F.; Li, W., The Adsorption of Reactive Blue 19 Dye onto Cucurbit[8]uril and Cucurbit[6]uril: An Experimental and Theoretical Study. *J. Phys. Chem. B* **2016**, *120* (17), 4131-4142.
- (8) Jiang, X.; Sun, Y.; Liu, L.; Wang, S.; Tian, X., Adsorption of C.I. Reactive Blue 19 from aqueous solutions by porous particles of the grafted chitosan. *Chem. Eng. J.* **2014**, *235*, 151-157.
- (9) Keskin, N. O. S.; Celebioglu, A.; Uyar, T.; Tekinay, T., Microalgae Immobilized by Nanofibrous Web for Removal of Reactive Dyes from Wastewater. *Ind. Eng. Chem. Res.* **2015**, *54* (21), 5802-5809.

- (10) Cheng, R. M.; Ou, S. J.; Li, M. J.; Li, Y. J.; Xiang, B., Ethylenediamine modified starch as biosorbent for acid dyes. *J. Hazard. Mater.* **2009**, *172* (2–3), 1665-1670.
- (11) Li, D. P.; Zhang, Y. R.; Zhao, X. X.; Zhao, B. X., Magnetic nanoparticles coated by aminoguanidine for selective adsorption of acid dyes from aqueous solution. *Chem. Eng. J.* **2013**, *232* (10), 425-433.
- (12) Zhang, X.; Song, J.; Ji, W.; Xu, N.; Gao, N.; Zhang, X.; Yu, H., Phase-selective gelators based on closed-chain glucose derivatives: their applications in the removal of dissolved aniline/nitrobenzene, and toxic dyes from contaminated water. *J. Mater. Chem. A* **2015**, *3* (37), 18953-18962.
- (13) Chen, Y.; Chen, L.; Bai, H.; Li, L., Graphene oxide-chitosan composite hydrogels as broad-spectrum adsorbents for water purification. *J. Mater. Chem. A* **2013**, *1* (6), 1992-2001.
- (14) Li, J.; Su, Z.; Xu, H.; Ma, X.; Yin, J.; Jiang, X., Supramolecular Networks of Hyperbranched Poly(ether amine) (hPEA) Nanogel/Chitosan (CS) for the Selective Adsorption and Separation of Guest Molecules. *Macromolecules* **2015**, *48*, 2022-2029.
- (15) Ajmal, M.; Demirci, S.; Siddiq, M.; Aktas, N.; Sahiner, N., Amidoximated poly(acrylonitrile) particles for environmental applications: Removal of heavy metal ions, dyes, and herbicides from water with different sources. *J. Appl. Polym. Sci.* **2016**, *133* (7), 43032-43043.
- (16) Abdelaal, S. E.; Gad, Y. H.; Dessouki, A. M., Use of rice straw and radiation-modified maize starch/acrylonitrile in the treatment of wastewater. *J. Hazard. Mater.* **2006**, *129* (1–3), 204-215.