Chinese Chemical Letters Vol. 16, No. 9, pp 1209-1212, 2005 1209
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Application of a New Acrylic Ester Resin for Recycling SIPA from its Water Solution

Wei Ben YANG[1,2,3], Ai Min LI[1,3*] Quan Xing ZHANG[1,3], Hong Ming QIAN[3], Jun FAN[1,3], Li Cheng YANG[1,3]

[1] State Key Laboratory of Pollution Control and Resources Reuse, Nanjing University, Nanjing 210093
[2] Nanjing College of Chemical Technology, Nanjing 210048
[3] Jiangsu Engineering & Technology Research Center for Organic Toxicant Control and Resource Reuse, Nanjing 210038

Abstract: A new acrylic ester polymer YWB-7 resin was prepared and characterized. The properties of YWB-7 resin were compared with those of the commercial Amberlite XAD-7, Diaion HP2MG and hypercrosslinked macroporous polymer NDA-150 resins. Both surface area and micropore area of YWB-7 resin were bigger than those of XAD-7 resin and HP2MG resin. The YWB-7 resin was successfully employed to recycle 5-sodiosulfoisophthalic acids (SIPA) from its solutions with and without methanol.

Keywords: Acrylic ester resin, 5-sodiosulfoisophthalic acids (SIPA), hydrogen bonding.

With the development of hypercrosslinked macroporous polymers, hypercrosslinked macroporous polymers produced in many worldwide manufactures are found increasing applications as sorbents for separation or analytical purposes[1-4]. However, the current understanding indicated that hydrophobic interaction is normally dominant force for separation of compounds from the aqueous solution on hypercrosslinked resin. When the compound is easily water-soluble or there are other organic solvents in water solutions, the adsorption capacity of hypercrosslinked macroporous polymers will decrease obviously[5-6].

5-Sodiosulfoisophthalic acids (SIPA), a kind of aromatic sulfonic acid, is an intermediate in the process of the production of 5-sodiosulfoisophthalic acid dimethylester (SIPM). Due to the well solubility and strong hydrophilicity of aromatic sulfonic acids, it makes the difficulty for the recover of SIPA from the water solution in the manufacturing processes. Most of the aromatic sulfonates without hydrophobic alkyl chain are biologically resistant and the treatment efficiency of general chemical and physical methods for these aromatic sulfonic acids is unsatisfactory. In the result they are difficult to remove from wastewater by biological, chemical or physical methods.

In order to solve this problem, many researchers attempt to use new resin to recover organic compounds. For example, the copolymers containing ester groups by

* E-mail: liaimin99@vip.sina.com

hydrogen-bonding adsorption has already become an interesting subject in chemistry and environment science. In this paper, YWB-7 resin, a new cross-linked polymer derived from multifunctional (meth)acrylates, was synthesized and used to remove 5-sodiosulfoisophthalic acid (SIPA) selectively from its aqueous solutions with and without methanol. Amberlite XAD-7 (Rohm and Haas Co., Ltd., Philadelphia, U.S.A), Diaion HP2MG (Mitsubishikasei Co., Ltd., Tokyo, Japan), and NDA-150 (Nanjing University, P. R. China) resins were used as reference. The result showed that it was successfully employed for recycling 5-sodiosulfoisophthalic acids (SIPA) from its solutions with methanol.

Synthesis of YWB-7 resin

YWB-7 resin beads were prepared by suspension polymerization. Firstly, an aqueous phase (450 g) comprised of 0.2% (0.9 g) of hydroxyethyl cellulose, an organic phase (150 g overall mass) comprised of the momomer methyl acrylate, dimethyl acrylate glycol ester and the porogen xylene (1:1 wt.) were formulated separately. Dibenzoyl peroxide (1 wt % relative to monomer) was then introduced into the organic phase. After that the aqueous phase was added to a 1000 mL parallel-sided flanged gastight glass vessel fitted with a metal stirrer, and then the organic phase was added. The stirrer speed was set to be 250 rpm, and the polymerization was allowed to proceed at 348 K for 10 h. At the end of the reaction, the beads were filtered using a 75 μm sieve. The filtered polymer was rinsed three times with hot water, extracted with methanol in a Soxhlet apparatus for 8 h, and then dried in vacuum at 333 K for 8 h. The resulting beads were then fractionated using sieves, and the fraction between 20 meshes and 45 meshes was selected for the experiments.

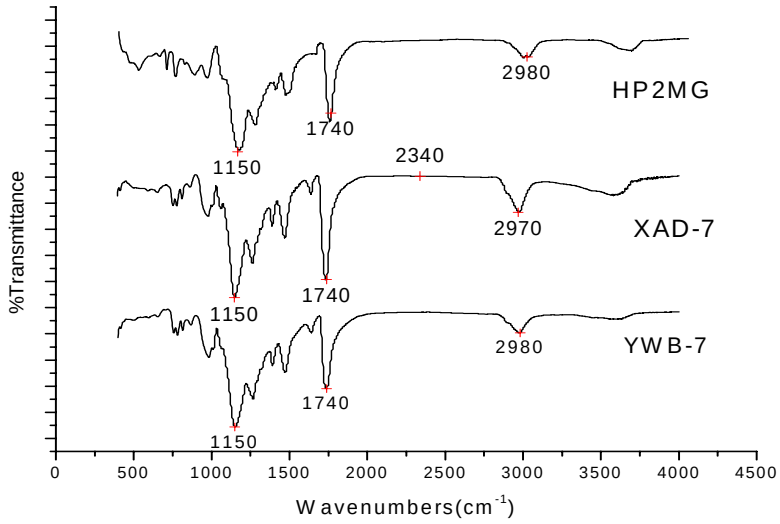
Comparison of the properties of resins

Table 1 listed the properties of the four resins. Both surface area and micropore area of YWB-7 resin were bigger than those of Amberlite XAD-7 and Diaion HP2MG resin. The content of oxygen, carbon, and hydrogen of YWB-7 resin was similar to XAD-7 and HP2MG, which suggested that the structure of YWB-7 resin was in agreement with that of the two other acrylic ester resins. The structure of resin could be inferred by the IR

Table 1 Properties of the four resins

Property	YWB-7	XAD-7	HP2MG	NDA-150
Structure	Polymethacrylate	Polymethacrylate	Polymethacrylate	Oxygen modified polystyrene
BET surface area (m^2/g)	663.8	510.9	459.7	906.1
Micropore Area (m^2/g)	107.17	71.38	103.73	529
Average pore diameter (nm)	4.79	7.29	9.16	6.8
Porosity (mL/g)	0.041	0.026	0.041	0.272
Oxygen content (%)	29.14	30.44	29.86	5.95
Carbon content (%)	63.15	61.76	62.54	84.64
Hydrogen content (%)	7.71	7.80	7.60	9.41

Figure 1 IR spectra of the three acrylic ester resins



spectra. **Figure 1** showed the IR spectra of the three acrylic ester resins. The characteristic peak of carbonyl and acetyl group at 1740 cm^{-1} and ester group at 1150 cm^{-1} testified that the three resins were all acrylic ester resin.

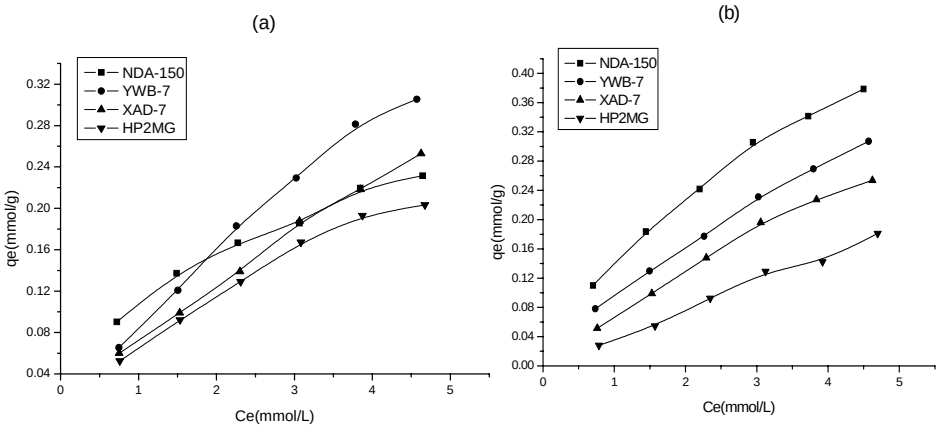
Applications of the resins

Figue 2 showed the equilibrium adsorption isotherms of SIPA solutions on YWB-7, XAD-7, HP2MG, and NDA-150 resins respectively. **Figue 2** (b) indicated that the adsorption capacities of SIPA on four resins were in the following order: NDA-150 > YWB-7 > XAD-7> HP2MG, which were contributed to the surface area of resins.

Figue 2 (a) showed that the adsorption capacities of SIPA on NDA-150 in solutions with 5% methanol (v/v) decreased compared with those in solutions without methanol, while the capacities of adsorption on acrylic ester resins had no obvious difference in two kinds of solutions. This was presumably due to the fact that the main interaction between NDA-150 resin and adsorbate was hydrophobic interaction, which should decrease in solutions with methanol. The main interaction between the acrylic ester resins and adsorbate was hydrogen bonding interaction, which did not affect by methanol in the range of the oxygen content of the acrylic ester resin about 30 %(**Table 1)**. Because the surface area of YWB-7 resin was largest in three acrylic ester resins, the amount of polar groups such as carbonyl group, acetyl group and hydroxyl group on the surface of YWB-7 resin should be larger than XAD-7 resin and HP2MG resin[7-8]. Although the NDA-150 resin contained about 5.95% oxygen which might contribute to the hydrogen bonding in a certain conditions, the strength of hydrogen bonding of NDA-150 resin might be less than that of acrylic ester resins in the same conditions, because the amount of polar groups on the matrix of NDA-150 resin is extremely low compared

with that of the acrylic ester resins. The adsorption capacities of SIPA in solutions with methanol on YWB-7 resin were the best compared with other three resins.

Figue 2 Equilibrium adsorption isotherms for SIPA solutions with and without methanol on four resins at 288 K: (a) 5%methanol in SIPA solution; (b) SIPA solution without methanol.



q_e is the equilibrium adsorption capacity (mmol/g), C_e is the equilibrium concentration (mmol/L)

Acknowledgment

We gratefully acknowledge the generous support provided by Jiangsu Province Hi-Tech Fund:(GB2003030) and Jiangsu Province Natural Science Fund:(2004088).

References

1. A. M. Li, Q. X. Zhang, *React. Funct. Polym.*, **2001**, *49*(3), 225.
2. A. M. Li, Q. X. Zhang, *Chemosphere*, **2002**, *47*(9), 981.
3. A. M. Li, Q. X. Zhang, *Sep. Sci. Technol.*, **2002**, *37*(14), 3211.
4. A. M. Li, Q. X. Zhang, *J.Environ.Sci.*, **2002**, *14*(4), 457.
5. P. K. Jerabek, *React. Funct. Polym.*, **1999**,*41*, 21.
6. J. Hradil, E. K. Ralova, *Polymer*, **1998**, *39* (24), 6041.
7. K. Tanaka, H. Chikara, W. Hu, *et al., J. Chromatogr. A*, **1999**, 850(1-2), 187.
8. H. M. Anasthas, V.G. Gaikar, *React. Funct. Polym.*, **2001**, *47* (1), 23.

Received 25 November, 2004