



Chemisorption effects on the separation of phthalimide from anthranilic acid solution by using the polymeric adsorbents

Fei Zhenghao^{*}, Fang Jie, Yang Shanshan, Liu Zongtang, Shi Weizhong, Wu Xiuhong and Chen Jian

Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection, Institute of Applied Chemistry & Environmental Engineering, Department of Chemistry, Yancheng Teachers University, Jiangsu, China

ABSTRACT

Functional groups modified polymeric adsorbents were designed based on semiempirical molecular orbital theory, and the newly polymeric adsorbent named FZH124 modified with 1,2,4-benzenetricarboxylic anhydride was prepared. The static adsorption and desorption characteristics for phthalimide or anthranilic acid in aqueous solution at the temperature range of 288-318K on FZH124 or NDA150 were studied to confirm the existence of chemisorption effects, which was interpreted by the approximate orbital energy level difference between adsorbent and phthalimide calculated with the semiempirical molecular orbital method PM3. The result indicates that chemisorption effects exist in the adsorption system of phthalimide in aqueous solutions with FZH124 at the proper temperature. The capacities of phthalimide adsorbed onto the polymeric adsorbents modified with 1,2,4-benzenetricarboxylic anhydride were increased greatly, and the mechanism for the adsorption was investigated further. The separation method of phthalimide from anthranilic acid solution was also designed.

Keywords: Chemical modification; Phthalimide; Molecular orbital; Separation method

INTRODUCTION

Adsorption method is a better available technology for recovering organic compounds from wastewater. However, the polymeric adsorbents in hand hardly have high adsorption capacities for phthalimide, such as NDA or ZH series[1-3] having high adsorption capacities for phenols, anilines and benzoic acid, and thus a new resin having good adsorption efficiency for phthalimide is needed to separate phthalimide from the wastewater containing anthranilic acid and sodium chloride.

In this paper, the functional groups were designed from calculation with the semiempirical molecular orbital (MO) method and chemically modified onto the cluster of the adsorption resin during the post-crosslinking of chloromethyl low crosslinking macroporous poly-styrene resin. The new polymeric adsorbent having both the lower LUMO energy level and the higher HOMO energy level was prepared according to some references [1-3]. Mechanism for adsorbing phthalimide was investigated, and the method of separating phthalimide from anthranilic acid was designed as well.

EXPERIMENTAL SECTION

1 Molecular Orbital (MO) Calculation

The electronic state of adsorbents and adsorbates can be determined by semiempirical molecular orbital calculations with HyperChem 7.0. In our case PM3 has been chosen as it gives satisfactory results because all the parameters for most of the atoms are available in PM3. All these methods are semiempirical and used for the quantum calculation

of molecular electronic structure in computational chemistry and based on the neglect of differential diatomic overlap integral approximation. The interaction energy between adsorbate and adsorbent is calculated on the basis of the frontier orbital theory (FOT) proposed by Fukui *et al*[4]. The electronic state of the cluster models adopting the minimum cluster size to get the more appreciable influence on the energy level have been calculated and the electronic state of adsorbents can be determined by semiempirical molecular orbital method of PM3.

2 Preparation and Characterization of Adsorbent of FZH124

Spherical adsorbent NDA150 was available from Jiangsu Jinsan Environmental Technology Co. LTD of China. The initial synthesis of low-crosslinked macroporous styrene-divinylbenzene copolymer and its chloromethylation were undertaken as described in the literature[1-3].

The specific surface area and the pore distribution of the adsorbents were calculated, respectively by BET and BJH methods via the nitrogen adsorption and desorption curves at 77K using a Micromeritics ASAP-2010 automatic surface area analysis instrument (Micromeritics Instrument, Norcross, USA). The residual chloride content and carboxyl group amounts were determined by Volhard method [5] and Boehm method [6,7], respectively.

3 Sorption of Phthalimide or Anthranilic Acid onto the Resin Beads

The sorption of phthalimide or anthranilic acid onto the adsorbents was performed by using batch experiments. A given amount of beads (100 mg) was added into phthalimide or anthranilic acid aqueous solution (100 mL) at a known concentration, constant temperature of 288~318K or another 288K fallen from 318K (288K*), and constant rate 110rpm in a thermostat oscillator under dark environment. After a desired period of sorption, the concentration of phthalimide or anthranilic acid was measured by HPLC. The adsorbance of phthalimide or anthranilic acid onto the adsorbents were calculated. The initial pH value of phthalimide or anthranilic acid aqueous solution was not adjusted.

Desorption experiment

After adsorption at 288K*, FZH124 and NDA150 were filtered from the solution and desorbed with 100mL distilled water at 318K, and the concentration of desorbed phthalimide was determined.

RESULTS AND DISCUSSION

1 Choose of modified functional group

The HOMO energy is a measure of how hard it is to remove an electron from a neutral molecule and the LUMO energy is a measure of how hard it is to add an electron to the neutral molecule. The calculated results with PM3 methods for the different modified functional group are shown in Table 1. Obviously 2,4-dicarboxyl-1-benzoyl group having both the lower LUMO energy level and the higher HOMO energy level for phthalimide as modified functional group will be chosen.

Table 1 The calculated results with PM3 methods for the different modified functional group

Modified functional group	LUMO (ev)	HOMO (ev)	Modified functional group	LUMO (ev)	HOMO (ev)
1,2,4-benzenetricarboxylic anhydride	-0.668	-7.479	phthalicacidanhydride	-1.834	-8.288
acetylaniline	0.524	-9.021	hydroxylbenzene	0.160	-9.263
dimethylamine	0.476	-9.031	benzoyl	-0.048	-9.143

2 Equilibrium Adsorption

In our experiment, NDA150 hardly adsorb phthalimide from aqueous solutions. The equilibrium adsorption isotherms of phthalimide on the FZH124 adsorbent and those of anthranilic acid on the NDA150 adsorbent at the temperature of 288K, 303K, 318K and 288K* are respectively shown in Fig. 1a~1b. Due to small difference of specific surface area and average pore diameters between NDA150 and FZH124 (as shown in Table 2), it is obvious that the specific surface area and average pore diameters of adsorbents are not the key factors for adsorbing phthalimide.

It is well known that the increasing temperature was disadvantageous for the adsorption capacities in a physical process like that in Fig. 1b, in which the adsorption capacities for anthranilic acid at 288K and 288K* are almost equal to each others. However, when the physical and chemical transition of adsorption exists, the adsorption would be selective for some groups [8], which results in the increasing chemical adsorption capacities with the increase of the temperature. Therefore, the active carboxyl group in FZH124 would be easy to interact with the imidogen group of phthalimide, which caused the increase of adsorption capacity of phthalimide when the temperature increased. In

addition, due to the chemical irreversible process and the physical reverse process, FZH124 had the highest adsorption capacities at 288*K. Obviously, the irreversible chemisorption existed in the adsorption system as shown in Fig. 1a.

3 Semi empirical MO Study

The semiempirical MO method (PM3) was applied to the cluster models of adsorbent surface and the energy levels were calculated. Energy levels of the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) are listed in Table 3. It is identifiable that there existed irreversible chemisorption when GAC adsorbed many aromatic compounds because GAC has the high HOMO energy level and the low LUMO energy level[9,10]. In this study, the higher HOMO energy level of FZH124 and the lower LUMO energy level of phthalimide will be of importance for interpretation of irreversible chemisorption.

It is obvious from Table 3 that the HOMO value of FZH124 is as high as that of GAC, which results in the decrease of the energy difference (only 6.291eV) between the LUMO of adsorbate and the HOMO of adsorbent. According to the Hammond postulate, when this difference is lower than the potential energy barrier separating the precursor state and the irreversible state, the irreversible chemisorption will occur[10].

Table 2 Surface properties of two adsorption resins

Properties	NDA150	FZH124
Specific surface area (m ² /g)	906	893
Average pore radius (nm)	1.25	1.19
Microporous area (m ² /g)	529.0	418.4
Microporous volume (mL/g)	0.252	0.187
Residual chloride content (%)	3.46	3.30
Carboxyl group amounts (mmol/g)	---	2.38

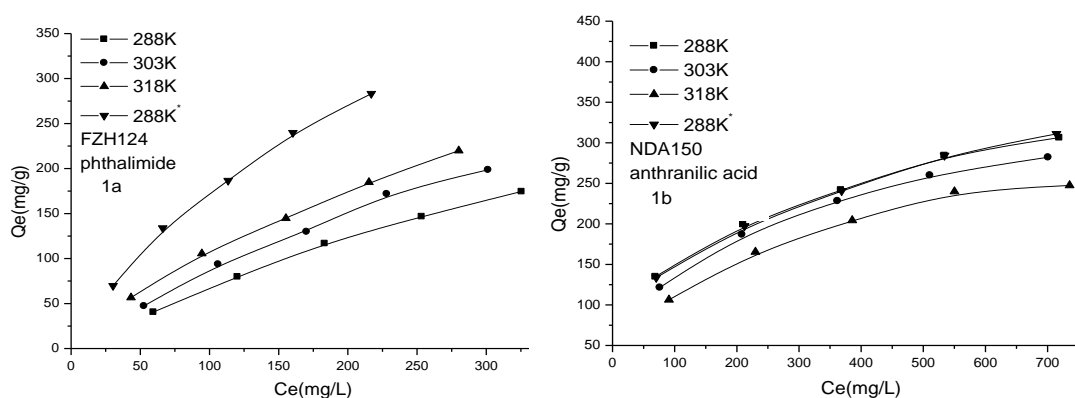


Fig.1 The equilibrium adsorption isotherms of adsorbates on the adsorbents at 288-318 K

Table 3 HOMO and LUMO energy levels of adsorbents and adsorbate calculated by PM3

Adsorbent	HOMO (eV)	LUMO (eV)
GAC	-7.356	-1.935
NDA150	-9.163	0.245
FZH124	-7.479	-0.668
phthalimide	-10.292	-1.188
anthranilic acid	-8.379	-0.270

4 Comparison of Desorption Conditions

Different solvents were used respectively to desorb the adsorbents reached the static adsorption equilibrium, and the results are given in Table 4.

Obviously, anthranilic acid adsorbed onto NDA150 can be desorbed easily by using methanol, and the desorption efficiency reaches 91%, while methanol just desorb a part of amount of phthalimide from FZH124. However, the desorption efficiency could be improved greatly when the solvents are alkalized, which will be a forceful proof that there existed irreversible chemisorption for FZH124 adsorbing phthalimide from aqueous solution.

Table 4 The results of desorption at different solvents

Adsorbent	Adsorbate	Desorption solvent	Desorption efficiency (%)
NDA150	anthranilic acid	Methanol	91.4
		Methanol: 4% NaOH = 1:1	93.1
		4% NaOH	94.4
FZH124	phthalimide	Methanol	72.1
		Methanol: 4% NaOH = 1:1	86.4
		4% NaOH	90.8

5 Separation Plan of Phthalimide from Anthranilic Acid in Aqueous Solution

It is shown above that NDA150 can selectively adsorb the anthranilic acid from the aqueous solution containing anthranilic acid and phthalimide, and FZH124 resin has higher adsorption capacity for phthalimide, which appears that NDA150 and FZH124 may be used for selective separation of phthalimide and anthranilic acid from the wastewater containing these two chemicals. Anthranilic acid in wastewater may be separated from phthalimide when the wastewater flows through the adsorption column filled with NDA150, and then phthalimide will be recovered when the outlet wastewater flows through FZH124 column.

CONCLUSION

The static adsorption and static desorption experiments for phthalimide in aqueous solution at the temperature range of 288~318K with the prepared adsorption resin modified with 1,2,4-benzenetricarboxylic anhydride were studied, and the following conclusions were drawn.

- (1) Due to both the lower LUMO energy level and the higher HOMO energy level, the polymeric adsorbent FZH124 modified with 1,2,4-benzenetricarboxylic anhydride has high adsorption selectivity for phthalimide in aqueous solution, where the active carboxyl group in FZH124 is easy to interact with the imidogen group of phthalimide.
- (2) Because NDA150 hardly adsorbs phthalimide but it has high adsorption capacity for anthranilic acid, phthalimide in wastewater from producing 1,2-benzisothiazoline-3-one may be separated from anthranilic acid when the wastewater flows through the adsorption column filled with NDA150 and then phthalimide will be recovered when the outlet wastewater flows through FZH124 column.

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