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〈研究論文(學術)〉 — 본 연구는 1990년도 지방대학 육성연구비의 지원에 의하여 수행되었음 —

Development of Polymeric Adsorbents for the Treatment of Colored Waste Waters and Re-use of the Treated Water (II)
— Quaternary Aminized Cellulosic Adsorbent —

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有色廢水處理를 위한 高分子 吸着制의 開發과 處理水의 使用 (II)
— 4급 아민화 셀룰로오스 흡착제 —

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Abstract—Quaternary aminized cellulosic adsorbents (CA_{QA}) which exhibit adsorption capacities for anionic dyestuffs for the treatment of colored waste water and re-use of the treated water were studied. The isotherms and thermodynamic parameters of C.I. Acid Orange 7, solution considered as a model of negatively charged coloring matters for CA_{QA}, were determined. Batch method and flow method were employed to determine decoloring capacity of cellulosic adsorbents for Orange 7. The cellulosic adsorbents exhibited much better adsorption capacity than activated carbon. Furthermore the exhausted cellulosic adsorbents could be readily regenerated by washing with dilute sodium hydroxide.

1. Introdution

The control of water pollution and re-use of the water recovered from waste-water treatment are, in these days, one of major scientific activities for the protection of environment and the conservation of resources.

In the present industrial water pollution from dye house has been treated only for the clearance of the waste waters standard and usally treated by combinations of various cleaning methods available today.

Although several methods have been reported for treating dye-waste-stream, the one that appears to be the most feasible is adsorption. The dye-waste-stream passes through a porous material whose surface attracts the dissolved dyestuffs in the stream. When the adsorbent is loaded to capacity, it is regenerated to remove the absorbed impurities of disposal in concentrated form and restored the initial capacity of the adsorbent.

Granular activated carbon is probably the most common industrial adsorbent and has been used to remove the color from dye-waste-stream in some practical fields. While producing substantial reduction in color and oxygen demand, activated carbon systems have some limitations.[1]

Mchay *et al.*[2] reported a mathematical model for the fixed bed adsorption of Telon Blue dye on peat. An adsorption model based on external mass transfer and pore diffusion were developed to predict theorem breakthrough curves for the adsorption of Telon Blue dye.

Khare *et al.*[3] discussed the removal of basic dye from waste water using wollastone as a sorbent. Batch type experiments indicated that low concentration, small particle size of adsorbent, high temperature, and alkaline pH of the solution are favorable for the removal of crystal violet from aqueous solutions.

Park[4] reported that removal of adsorbed dyestuffs and regeneration of adsorption capacity are simpler and more excellent with cellulosic adsorbent than with activated carbon.

Miyata[5] synthesized the adsorbents graft copolymerized with 2-(dimethylamino)ethyl methacrylate onto waste paper pulp. The color removal behavior of the anionic dyes by the adsorbents was investigated.

Furuta[6] reported that cotton yarns graft copolymerized with acrylamide can be used as a adsorbent for the water-recycle-model system in order to remove reactive dyes.

In the present work, adsorption behavior and decoloring of C.I. Acid Orange 7 solution by quaternary aminized cellulosic adsorbents were studied with the aim of developing polymeric adsorbents for the treatment of colored watse waters.

2. Experimental

2.1 Materials

Cellulose powder (Sigma Chem. Co.) and polyvinylalcohol (DP=1500, Junsei Chem. Co.) as matrix of adsorbents were used.

Dye used for a model colored-waster-water was C.I. Acid Orange 7 (denoted as Orange 7) as a anionic dye.

All other chemicals used in this work were first reagent and used without purification.

2.2 Preparation of Quaternary Aminized Cellulosic Adsorbents

Cellulose/PVA mixtures (80 wt% cellulose content) were crosslinked to the desired extent by regulting the mole fraction of triacryloyl hexahydro-s-triazine and diammonium phosphate, and followed by drying and crushing into 150-200 mesh.

Diethylaminoethylation of crosslinked polymer blends was carried out at room temperature a solution containg 15% sodium hydroxide, 15% 2-diethylaminoethyl chloride.

Quaternary aminization[7] of diethylaminoethyl cellulosic adsorbents was carried out under reflux in a boiling 10% solution of methyl iodide in absolute ethanol.

The characteristics of newly synthesized quaternary aminized cellulosic absorbents are listed in Table 1.

Table 1. Characteristics of quaternary aminized cellulosic absorbents (CA_{QA})

Adsorbents	A[a]	BV[b]
CA_{QA}-I	0.52	4.18
CA_{QA}-II	0.80	4.15
CA_{QA}-III	1.12	4.21

[a]charge density (m·eq/g), [b]bed volume (ml/g).

The charge density was determined by potentiometric titration.[8]

2.3 Adsorption Isotherms

Adsorption isotherms were determined from measurements of equilibrium adsorption amount at various dye concentrations under constant temperature.

The amounts of adsorbed dye were measured spectrophotometrically by extraction with DMF.

2.4 Decoloring Capacity and Regeneration

Batch method and flow method were employed to determine decoloring capacity of adsorbents in Orange 7 solution at ambient temperature.

Batch method was carried out by treating Orange 7 solution with adsorbents for 30 min. So was flow method by passing Orange 7 solution through columm filled with adsorbents under constant elution velocity.

Color removal percentage was calculated from the following equation:

Color removal percent(%) = $(D_0 - D_t)/D_0 \times 100$

where D_0 : concentration of dye in untreated Orange 7 solution

D_t : concentration of dye in treated Orange 7 solution

The exhausted adsorbents were regenerated by washing with dilute sodium hydroxide solution.

3. Results and Discussion

3.1 Thermodynamics of Adsorption Isotherms

The adsorption isotherms are shown in Fig. 1. In Fig. 1, the shapes of the isotherms exhibit Langmuir type adsorption which tends to a definite limiting dye concentration on the adsorbent (CA_{QA}) with increasing concentration in solution.

In the case of Langmuir adsorption isotherms,[9] it is well known that the rate of desorption $-d[D]_f/dt$ is proporational to the concentration of dye in the adsorbent, i.e.:

$$-\frac{d[D]_f}{dt} = k_1[D]_f \quad (1)$$

where $[D]_f$ is the concentration of dye in the adsorbent.

The rate of adsorption $d[D]_f/dt$ depends on the concentration of dye in the solution and also upon the number of unoccupied sites, which is proportional to $([S]_f - [D]_f)$.

Thus:

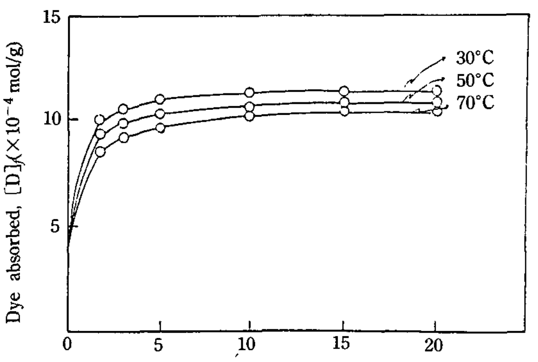

Fig. 1. Adsorption isotherms of the model anion dye, Orange 7, by the CA_{QA}-III at pH 3.

$$\frac{d[D]_f}{dt} = k_2[D]_s([S]_f - [D]_f) \quad (2)$$

where $[S]_f$ is the saturated concentration of dye in the adsorbent, $[D]_s$ the concentration of dye in the solution.

At equilibrium the rates of adsorption and desorption are equal, so that, can be combined: k_1 and k_2

$$[D]_f = k[D]_s([S]_f - [D]_f) \quad (3)$$

or

$$[D]_f = \frac{k[S]_f \cdot [D]_s}{1 + k[D]_s} \quad (4)$$

or inverting (4):

$$\frac{1}{[D]_f} = \frac{1}{k[S]_f} \cdot \frac{1}{[D]_s} + \frac{1}{[S]_f} \quad (5)$$

$[S]_f$ value is easily determined by a graphical method from the reciprocal plot of the adsorption data (see Fig. 2).

The $[S]_f$ value obtained is 11.5×10^{-4}, 11.0×10^{-4} and 10.6×10^{-4} mol/g at 30, 50, and 70℃, respectively.

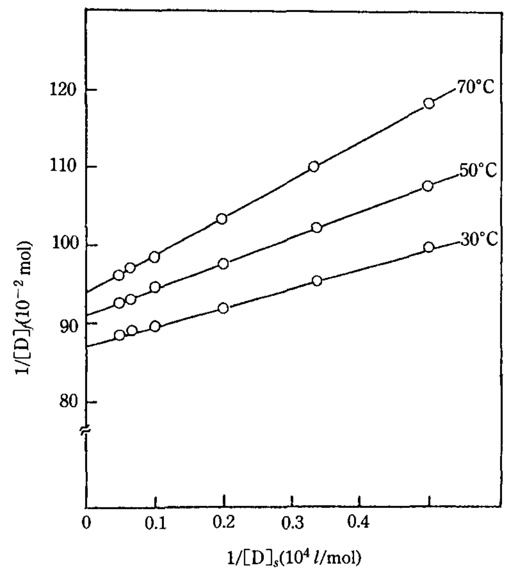

Fig. 2. Reciprocal relationship between the concentration of in solution and the amount of the model anion dye, Orange 7, absorbed by the CA_{QA}-III at pH 3.

The standard affinity of adsorption $-\Delta\mu°$ is calculated by the following Gilbert-Ridial equation [10] adapted for Langmuir adsorption isotherm.

$$-\Delta\mu° = 2RT\ \ln\frac{\theta_D}{1-\theta_D} - 2RT\ \ln[D]_s \quad (6)$$

where R and T are the gas constant and the absolute temperature, respectively. θ_D represented as $[D]_s/[D]_f$ is the fraction of sites occupied by dye. The standard heat of adsorption $\Delta H°$ can be obtained as the following:

$$\frac{\Delta\mu°}{T} = \frac{\Delta H°}{T} + C \quad (7)$$

where C is a constant.

$\Delta H°$ can be evaluated by a graphical method as shown in Fig. 3, since a plot of $\Delta\mu°/T$ against 1/T should yield a straight line (if $\Delta H°$ is contant) with the slope $\Delta H°$.

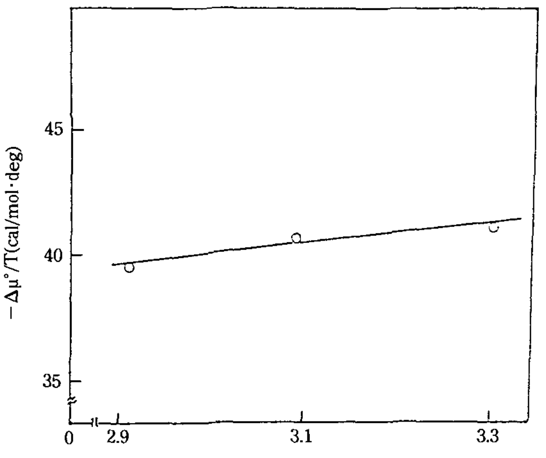

Fig. 3. Relationship between $-\Delta\mu°/T$ and 1/T for the CA_{QA}-III at pH 3.

Table 2. Thermodynamic parameters for adsorption of the model anion dye, Orange 7, by the CA_{QA}-III

Temperature (℃)	$-\Delta\mu°$ (kcal/mol)	$-\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/mol·deg)
30	12.44	30-50℃ 2.38	28.5
50	13.10	50-70℃ 5.22	28.79
70	13.59	Mean : 3.8	28.54

The parameters of the thermodynamics determined by means of above mentioned equations are listed in Table 2.

As shown in Table 2, the affinities of the dye for the adsorbent shows larger values than those of hydrochloric acid for silk.[11]

The mean value of the heat of adsorption is −3.8 kcal/mol in the range 30 to 70℃, and the standard entropy shows positive charge.

3.2 Evaluation of the Decoloring Capacity and Regeneration

Decoloring capacities of cellulosic adsorbents including the granular activated carbon in the mo-

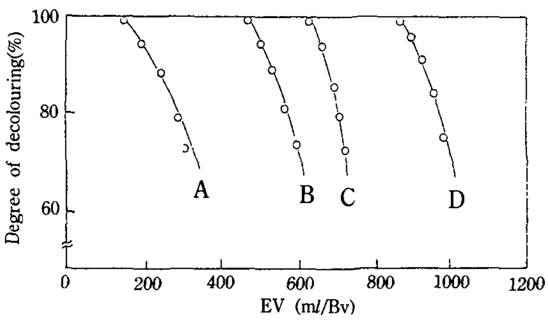

Fig. 4. Effect of various adsorbents on the decolouring of model anion dye, Orange 7, solution.
A: activated carbon (granular), B: CA_{QA}-I, C: CA_{QA}-II, D: CA_{QA}-III

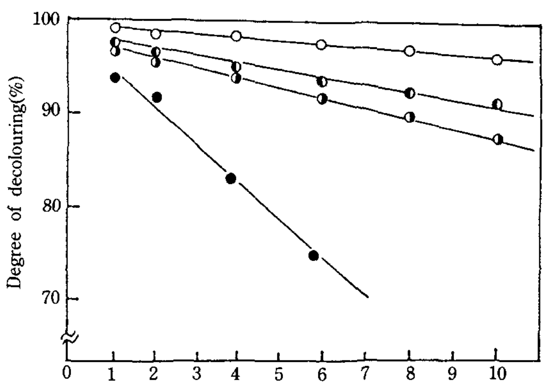

Fig. 5. Relationship between the decolouring of model anion dye, Orange 7, solution and the number of regeneration of various adsorbents.
●: activated carbon(granular), ◑: CA_{QA}-I, ◐: CA_{QA}-II, ○: CA_{QA}-III

del anion dye, Orange 7, solution were measured at ambient temperature by flow and batch methods. Results obtained are showed in Fig. 4 and Fig. 5.

The results indicate that decoloring capacities of the cellulosic adsorbents are generally much than those of granular activated carbon, and that the decoloring capacity increases with the increase of charge density.

The ionic functionality of cellulosic adsorbents except for granular activated carbon is easily regenerated by the treatment of adsorbents with dilute sodium hydroride solution, and have more than 90% efficiency for about 10 cycles.

Conclusions

Quaternary aminized cellulosic adsorbents (CA_{QA}) were prepared to develop the polymeric adsorbents for the treatment of colored waste water. Adsorption behaviour and decoloring capacity of a model anionic dye, C.I. Acid Orange 7 by the CA_{QA} were investigated.

Adsorption isotherms are Langmuir type and the affinity of the dye for the CA_{QA} decreases with increasing temperature. The mean value of the standard heat of adsorption is −3.8 kcal/mol in the range 30 to 70℃. The entropy is positive charge.

The decoloring capacities of the CA_{QA} were generally much better than those of granular activated carbon. The decoloring capacity increased with the increase of charge density. The ionic functionality of the CA_{QA} was easily regenerated by treating with dilute sodium hydroxide.

References

1. P.A. Schweizer, "Handbook off separation techniques for chemical engineer," 2nd ed., Chap. 1.13, R.R. Donnelley and Sons Company (1988).
2. G. Mckay and S.J. Allen, *J. Sep. Processor Technol.*, **4**, 8 (1983).
3. R.C. Kapoor, A. Prakash, and S.L. Kalami, *J. Indian Chem. Soc.*, **61**, 600 (1984).
4. S.M. Park, *J. Kor. Soc. of Dyers and Finishers*, **4**, No. 2, 84 (1992).
5. N. Miyata, *Sen-I Gakkaishi*, **42**, 468 (1986).
6. H. Furuta, *Sen-I Gakkaishi*, **43**, 499 (1987).
7. C.L. Hoffpauir and J.D. Guthrie, *Text. Res. J.*, **20**, 617 (1950).
8. G.J. Shugar, R.A. ShuGar, L. Bauman, and R.S. Bauman, "Chemical Technicians' Ready reference handbook," 2nd ed., Chap. 26, 579, McGraw-Hill Book Company (1981).
9. T. Vickerstaff, "The Physical Chemistry of Dyeing," Chap. 3.98, Oliver and Boyd Company (1954).
10. E.K. Ridial and G.A. Gilbert, *Proc. Roy. Soc.*, **A182**, 335 (1974).
11. H. Kato, *Sen-I Gakkaishi*, **31**, 168 (1975).