REMOVAL OF AROMATIC ORGANIC ACIDS FROM AQUEOUS SOLUTION BY USING CHROME LEATHER WASTE AS AN ADSORBENT

by

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ABSTRACT

Chrome leather shavings were used to prepare adsorbent for removal of aromatic organic acids from aqueous solution. Benzoic acid, *o*-, *m*-, and *p*-phthalic acids, salicylic acid and *p*-hydroxyl benzoic acid, which are common pollutants in waste water, were used as adsorbates in this study to investigate the sorption behavior of the adsorbent made from chrome leather waste. It was found that the sorption capacity of aromatic organic acids on the adsorbent depends largely on the molecular structures of these compounds. The sorption capacity of *o*-phthalic acid on the adsorbent was as high as 2.8mmol/g in experimental conditions, and that of salicylic acid was around 0.41mmol/g. However, no significant sorption was observed in the case of benzoic acid. Sorption isotherms of aromatic organic acids are typically non-linear ones, and can be well fitted by adsorption-partition model. The contributions of adsorption and partition to total sorption of these compounds on the adsorbent were quantitatively described. It was found that, for *o*-phthalic acid, the function of partition is predominant, and for *p*-phthalic acid, adsorption plays a key role. As for *m*-phthalic acid and salicylic acid, the contributions of adsorption and partition to total sorption depend on the concentration of adsorbate. Those results demonstrate that this adsorbent can be applied to remove aromatic organic acids from wastewaters in a wide range of concentration.

RESUMEN

Rebajaduras de Cuero al cromo fueron utilizadas para preparar un adsorbente para remover ácidos orgánicos aromáticos desde soluciones acuosas. Ácido Benzoico, *o*-, *m*-, y ácidos *p*-ftálico, salicílico, y *p*-hidroxi benzoico, los cuales son comúnmente contaminantes en desperdicios acuosos, fueron utilizados como adsorbidos en este estudio investigativo sobre las propiedades de adsorción de desechos del cuero al cromo. Se encontró que la capacidad de adsorción de ácidos orgánicos aromáticos sobre el absorbente depende de la estructura molecular de estos compuestos. La capacidad de adsorción del ácido *o*-ftálico sobre el absorbente fue hasta 2.8mmoles/g bajo condiciones experimentales, mientras que para ácido acetilsalicílico fue alrededor de 0.41mmoles/g. No obstante, no se observó adsorción significante en el caso del ácido benzoico. La adsorción isotérmica de ácidos orgánicos aromáticos es típicamente no lineal y pueden ser descritos por medio de un modelo de una función de partición-adsorción. Las contribuciones de adsorción y partición sobre la absorción total de estos compuestos sobre el absorbente fueron cuantitativamente descritas. Se encontró que, en el caso del ácido *o*-ftálico, la función de partición predomina, mientras que para ácido *p*-ftálico, adsorción juega un papel clave. En cuanto a ácido *m*-ftálico y ácido salicílico, las contribuciones de adsorción y partición en razón a la absorción total dependen de la concentración del adsorbente. Tales resultados demuestran que este adsorbente puede utilizarse en la remoción de ácidos orgánicos aromáticos desde desperdicios acuosos en una amplia gama de concentración.

INTRODUCTION

Nowadays, chrome tanning is still the most popular tanning method in leather-making, and therefore, leather industry would inevitably bring about large amount of chromium-containing leather wastes arisen from trimming, splitting and shaving operations. It was reported that nearly 300,000 metric tons of this solid wastes are generated by leather industry in China each year, and approximately twice of this amount is generated worldwide[1]. However, at present only a few of those wastes have been reused, and most of them are disposed of by landfill or incineration. Recently, due to increasing cost of land disposal and the more strict policies for environmental protection, effective treatment or utilization of chrome leather wastes has raised public attention.

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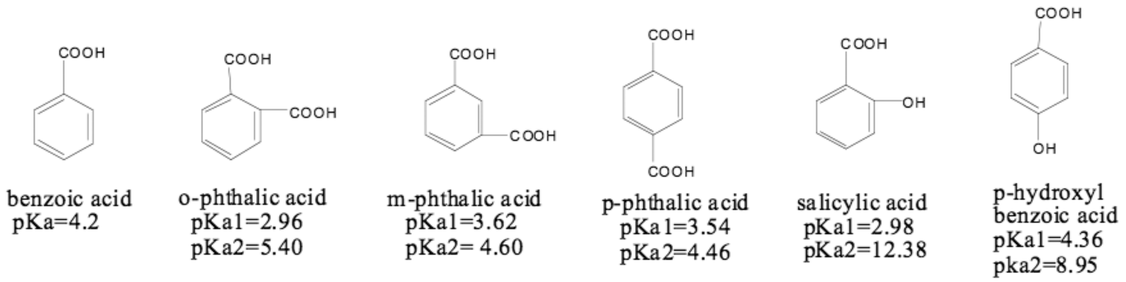

Figure 1: Molecular structure of aromatic organic acids.

In the past decades, many researchers worked on how to utilize chromium-containing leather wastes. Most of them focused on extraction of chromium from the wastes for reuse and recovery of peptides and amino acids that could be used as additives in feeds and fertilizers[2]. Other approaches, such as preparation of leather chemicals from leather wastes3, were also reported recently.

In our previous studies, chromium-containing leather waste had been used as an adsorbent for removing dyes[4] and surfactants[5] from effluent, and it had been found that this adsorbent exhibited excellent sorption ability to these adsorbates. As a kind of modified collagen material, chrome leather waste is rich in functional groups, like carboxyl, hydroxyl and amino, which are able to bind with organic compounds though ionic and hydrogen bonds. Moreover, the chromium combined with collagen has tendency of binding organic compounds through coordination and electrostatic reactions. Hence, chrome leather wastes have potential to be used as a kind of low-cost and effective adsorbent for removal of common organic compounds from wastewaters. Based on the characteristics of chrome leather waste, its sorption behaviors to aromatic organic acids are systematically investigated in this study.

Aromatic organic acids are widely used in ceramics, paper, cosmetic, ink and paint industries[6]. The discharge of effluents containing these organic compounds into environment will cause serious environmental pollution because they are toxic to humans and aquatic life, and can increase chemical oxygen demand (COD) in receiving waters[7]. Therefore, the removal of aromatic organic acids from effluent is imperative. Many technologies for removal of organic pollutants from aqueous solution have been developed, such as sorption, chemical precipitation, membrane filtration, biological degradation and chemical oxidation[8]. Among those methods, sorption is recognized as a simple and effective method for removing organic pollutants from dilute solution. Activated carbon is the commonly used adsorbent for this purpose because of its high sorption capacity to organic compounds[9], but its cost is relatively high.

In recent years, the utilization of industrial wastes as environmental protection materials has attracted considerable attention and is becoming an important research topic in the field of wastes management. Numerous researches of using industrial wastes as adsorbent have been documented. For example, the satisfactory results have been obtained when coal fly ash, mineral, sawdust and protein waste were used for removal of harmful compounds from contaminated water by sorption.[10-13] Therefore, the present work on removing aromatic organic acids from aqueous solution by chrome leather wastes would be significant to explore the utilization of wastes.

EXPERIMENTAL

Materials

Chrome leather waste was obtained from the shaving operation of blue tanned by chrome of 33% basicity without pretreatment of other chemicals. They were washed with deionized water, dried at 60°C for 6h and then ground into granules with particle size 0.1 - 0.2mm. As a result, the adsorbent containing 14.3% water and 3.21% Cr_2O_3 determined by atomic sorption spectrophotometry (CAA7000, Peking East-West Electronic Technology Institute, P. R. China) was obtained. Six typical aromatic organic acids, including benzoic acid, *o*-phthalic acid, *m*-phthalic acid, *p*-phthalic acid, salicylic acid, and *p*-hydroxy benzoic acid were studied. Other chemicals were of analytical reagent grade. The molecular structures of the aromatic organic acids and their pK_a values are shown in Figure 1.

Sorption isotherm studies

0.1g adsorbent prepared from chrome leather waste was put into 100ml solutions in which the concentration of aromatic organic acids ranged from 0.5mmol/L to 5mmol/L. The pH of solutions was adjusted to 6.0 by using dilute H_2SO_4 or NaOH solution. The sorption was carried out in water-bath shaker (180rpm) at 30°C for 24h. Then, the bulk solutions were centrifuged (GL-20G-II , Shanghai, China) and the concentrations of aromatic organic acids in solutions were measured by using an UV spectrophotometer (Model UV-2510PC, Japan). For each set of experiments, a control experiment without adsorbent was conducted. The equilibrium sorption amount of organic substance on adsorbent, Q_e (mmol/g), was calculated by a mass balance relation as following:

$$Q_e = (C_0 - C_e)\frac{V}{W} \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentration of aromatic organic acid respectively (mmol/L); *V* is the volume of bulk solution (L), and *W* is the mass of adsorbent (g).

TABLE I
Regression Data for Sorption Isotherms of Aromatic Organic Acids on Absorbent.

Adsorbate	Regression Equation	K (L/g)	1/n	Correlation Coeff
m-phthalic acid[a]	logQe=0.298logCe-0.661	0.218	0.298	0.991
p-phthalic acid[a]	logQe=0.0229logCe-0.696	0.202	0.0229	0.998
o-phthalic acid[a]	logQe=0.813logCe+0.170	1.48	0.813	0.994
Salicylic acid[a]	logQe=0.472logCe-0.699	0.199	0.479	0.998
p-hydroxyl benzoic acid[b]	logQe=0.125logCe+0.134	1.36	0.125	0.996

a:initial concentration 1-5mmol/L.
b:initial concentration ≤ 1mmol/L.

TABLE II
Linear Regression Data for Simulated Isotherm at High Concentration and Saturated Adsorption Capacity.[a]

Adsorbate	Regression at High Conc.	Saturated Capacity of Adsorption(mmol/L)	Correlation Coeff
m-phthalic acid	Q_e=0.0430Ce+0.168	0.168	0.995
p-phthalic acid	Q_e=0.00188Ce+0.200	0.200	0.997
o-phthalic acid	Q_e=1.25Ce+0.191	0.191	0.997
salicylic acid	Q_e=0.0657Ce+0.129	0.130	0.988

a:initial concentration of aromatic organic acids >=1.5mmol/L.

Influence of pH on sorption

A series of 1mmol/L aromatic organic acid solutions were prepared with deionized water. As for *m*-phthalic acid and *p*-phthalic acid, they were first dissolved in NaOH solution and then diluted to scale with de-ionized water. The pH of the solutions were adjusted to 2, 3, 4, 5, 6, 7, 8, 9 and10 by using 0.1M HCl or 0.1M NaOH. 0.1g adsorbent was put into 100ml solutions and the sorption experiments were conducted with constant shaking at 30°C for 24h. After sorption, the bulk solutions were centrifuged and the concentrations of aromatic organic acids in solutions were determined by means of UV spectrophotometer. Then the equilibrium sorption amount of aromatic organic acid was calculated by the mass balance relation as shown in Equation (1).

RESULTS AND DISCUSSION

Sorption isotherms of aromatic organic acids on chrome leather waste

The sorption isotherms of six aromatic organic acids on adsorbent are shown in Figure 2. It can be seen that the sorption capacity of o-phthalic acid is outstandingly larger than others. The sorption capacity of *o*-phthalic acid reached 2.8mmol/g when its initial concentration was 5mmol/L. However, benzoic acid with only one carboxyl group shows no sorption at current experimental conditions. Those results indicate that the sorption of aromatic organic acids on chrome leather waste absorbent depends largely on their molecular structures, especially on the number and position of substituting groups on benzene ring.

As for the aromatic organic acids which possess two functional groups, the relative positions of the two groups remarkably influence their sorption capacity. In the cases of *o*-, *m*- and *p*-phthalic acids, the sorption capacity is in the sequence of *o*- phthalic acid >> *m*- phthalic acid > *p*-phthalic acid, as shown in Figure 2. The similar results were also obtained in the sorption processes of salicylic acid and *p*-hydroxyl benzoic acid. This should be due to the fact that ortho- functional groups favor the chelating reaction between them and Cr(III) immobilized on collagen fibers,[14] which leads to higher sorption capacity. Such a chelating reaction is not able to take place in the case of *m*- and *p*-phthalic acids and *p*-hydroxyl benzoic acid.

Equilibrium sorption isotherm is fundamentally important in design of sorption process. The parameters of isotherm equation can express surface properties of adsorbent and its affinity to adsorbate. It was found that the sorption data of aromatic organic acids could be well fitted by Freundlich equation using nonlinear least-squares regression.

Freundlich equation is an empirical equation employed to describe multilayer sorption process. The equation is as following:

$$Q_e = KC_e^{1/n} \qquad (2)$$

where C_e and Q_e are the equilibrium concentration (mmol/L) of adsorbate and the amount of compounds absorbed (mmol/g) at equilibrium, respectively; *K* and *n* are Freundlich constants referring to sorption capacity and sorption intensity respectively. This equation can be represented in linear form:

TABLE III
Functions of Adsorption Amount (Q_A) and Partition Amount (Q_P) with Concentrations of Organic Compounds on Chrome Leather Waste.

Adsorbate	Partition amount (QP,_mol/g)	Adsorption amount (QA, _mol/g)
m-phthalic acid	Q_p=43.0Ce	Q_A=218Ce$^{0.298}$-43.0Ce
p-phthalic acid	Q_p=1.88Ce	Q_A=202Ce$^{0.0229}$-1.88Ce
o-phthalic acid	Q_p=1246Ce	Q_A=1479Ce$^{0.814}$-1246Ce
Salicylic acid	Q_p=65.7Ce	Q_A=479Ce$^{0.199}$-65.7Ce

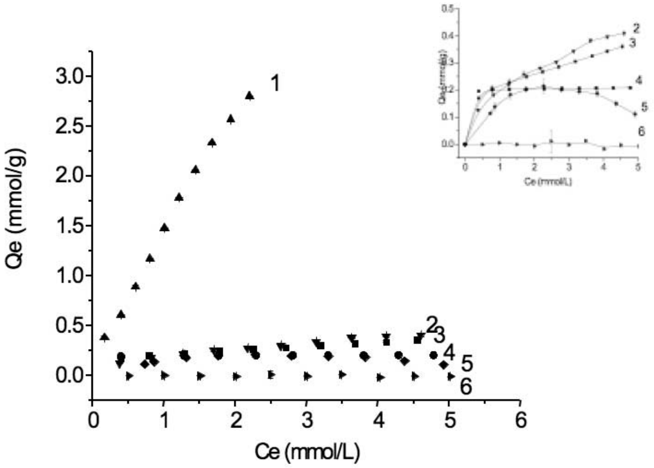

Figure 2: Isotherms of aromatic organic acids on adsorbent (pH=6, 30°C). (1) *o*-phthalic acid, (2)salicylic acid, (3)*m*-phthalic acid, (4)*p*-phthalic acid, (5)*p*-hydroxyl benzoic acid, (6)benzoic acid. Inset: the detailed sorption isotherms of aromatic organic acids except o-phthalic acid.

$$\log Q_e = \frac{1}{n}\log C_e + \log K \tag{3}$$

The values of K and n in equation can be obtained by plotting logQ_e vs logC_e.

The parameters obtained from the Freundlich equation were summarized in Table I. It can be found that all the experimental data fit well to the model of Freundlich isotherm (R^2>0.99). The values of Freundlich affinity index, 1/n, for the aromatic organic acids are all smaller than 1. In general, sorption is designated as 'unfavorable' process when 1/n > 1 and as 'favorable' process when 1/n < 1[15]. Therefore, the sorption of these aromatic organic acids on chrome leather waste should be feasible.

Figure 2 shows that the sorption isotherm of *p*-hydroxyl benzoic acid is different obviously from others. The sorption capacity of *p*-hydroxyl benzoic acid increased with the increase of concentration at first, and then decreased after a maximum value was reached. Freundlich isotherm can not describe the experiment data of *p*-hydroxyl benzoic acid in whole range of concentration. However, the fitting is satisfactory when the concentration of *p*-hydroxyl benzoic acid is lower than 1mmol/L, as presented in Table I. The reason for decrease of sorption capacity in higher concentration range of *p*-hydroxyl benzoic acid needs to be further investigated.

In order to further understand the sorption mechanism of *m*-, *p*- and *o*-phthalic acids and salicylic acid on adsorbent, the adsorption-partition model was used to describe the experimental results. According to the theory of this model, the sorption of organic compounds on adsorbent consist of two simultaneous processes, partition and adsorption.[16-17] The adsorption is a surface phenomenon that occurs at solid-liquid interface, while the partition process is attributed to the interaction between adsorbate and solid phase. The total equilibrium sorption amount (Q_e) of an aromatic organic acid on chrome leather waste can be defined as:

$$Q_e = Q_A + Q_P \tag{4}$$

where Q_A is the sorption amount contributed by adsorption and Q_P is the sorption amount contributed by partition.

In a mixed system of adsorption and partition, partition increases linearly with the increase of equilibrium concentration, whereas adsorption increases non-linearly with the increase of equilibrium concentration and reaches saturation rapidly[18]. Anyway, the sorption isotherm at high concentration could approach linearity, and it can be written as[16-18]:

$$Q_e = K_p C_e + N \tag{5}$$

where K_p is partition coefficient; K_pC_e is the contribution of partition to sorption; N is the saturated adsorption capacity obtained from high concentration data. Linear regression data for fitting isotherms at high concentration is listed in Table II.

Based on the equations (2), (4), (5), the contributions of partition and adsorption to sorption can be determined, respectively. The results are shown in Table III. The plots of Q_e, Q_A and Q_P versus C_e based on the equations in TABLE III are shown in Figure 3.

As shown in Figure 3, partition increases linearly with the increase of equilibrium concentration and adsorption changes non-linearly with equilibrium concentration. Studies showed that non-linear adsorption depends on the chemical characteristics of adsorbent, while partition is linear because it is governed by equilibrium phase distribution theories.[16-17]

As for *o*-phthalic acid, partition effect is much stronger than adsorption effect in whole range of concentration tested, while for *p*-phthalic acid, the results are contrary. In the cases of *m*-phthalic acid and salicylic acid, there is a critical equilibrium concentration, where the effects of adsorption and partition on

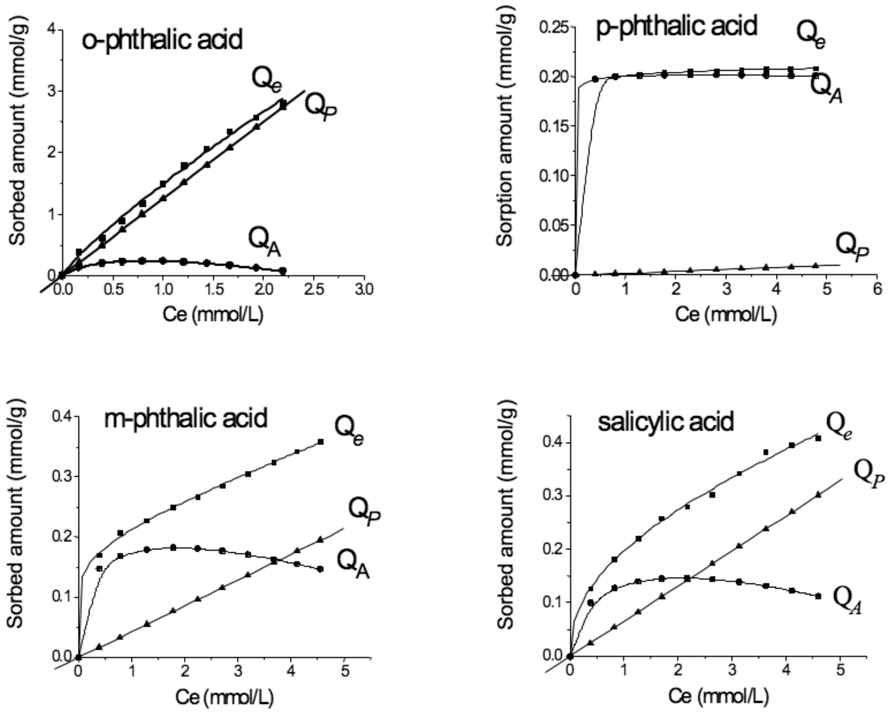

Figure 3: Adsorption and partition contributions to the total sorption amount of *m*-, *p*- and *o*-phthalic acids and salicylic acid on adsorbent.

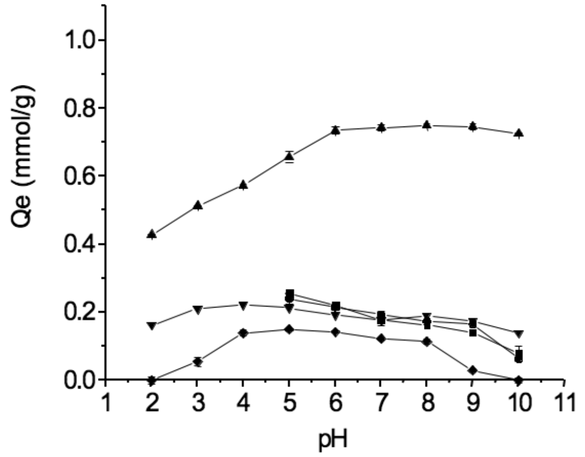

Figure 4: Effect of pH on sorption capacity of aromatic organic acids. (■*m*-phthalic acid; ●*p*-phthalic acid; ▲*o*-phthalic acid; ▼ salicylic acid; □*p*-hydroxyl benzoic acid)

total sorption are equal. This means that the sorption is dominated by adsorption when the equilibrium concentration is lower than the critical concentration; otherwise, partition plays an important role in the range of higher equilibrium concentration.

Effect of pH on Sorption

The effects of pH value on sorption of aromatic organic acids are shown in Figure 4. The initial pH for *m*- and *p*-phthalic acids determinations was set as 5.0 in experiments because their solubility is very low at lower pH range. pH is one of the important factors influencing sorption process. It affects not only the state of adsorbate in solution, but also the surface charge of adsorbent.

The pH_{pzc} (corresponding to the point of zero charge) of chrome leather waste determined is around 6.0. It implies that the adsorbent surface is positively charged in the pH range lower than 6.0, and is negatively charged when pH is higher than 6.0. Figure 4 shows that the sorption capacity of *o*-phthalic acid increases with the increase of pH, and almost keeps constant as pH exceeds 6.0. The increase of sorption capacity in pH range of 2.0-6.0 should be attributed to the increasing ionization of *o*-phthalic acid, which favors the interaction between it and Cr(III) in absorbent. When pH is higher than 6.0, the sorption amount of *o*-phthalic acid does not appear to be affected by pH, indicating that electrostatic interaction has little effect on all the sorption process. The high sorption capacity of *o*-phthalic acid might be mainly due to the chelating reaction between ortho- carboxyl groups and adsorbent. As for *m*- and *p*-phthalic acids, this chelating reaction is not able to take place, so their sorption capacities are remarkably lower than that of *o*-phthalic acid.

The chelating reaction between *p*-hydroxyl benzoic acid and absorbent can not take place, and this kind of reaction also seldom happens between salicylic acid and absorbent since the pK_{a2} of salicylic acid is as high as 12.38, as indicated in Figure 1. Therefore, chemical sorption of these two compounds on the adsorbent is relatively weak and electrostatic forces play an important role in adsorption process. Their sorption capacities are slightly increased in low pH range due to both chemical and electrostatic forces[19] and decreased as pH over 6 because of dominant effect of electrostatic repulsion between ionized aromatic organic acid and negatively charged adsorbent.

CONCLUSIONS

The adsorbent prepared from chrome leather waste was able to adsorb *m*-, *o*- and *p*-phthalic acids, salicylic acid and *p*-hydroxyl benzoic acid from aqueous solution. But benzoic acid can not be adsorbed by the adsorbent. The sorption capacity and sorption mechanism of these aromatic organic acids on the adsorbent depends largely on their molecular structures. The sorption of *o*-phthalic acid is mainly through chelating reaction between ortho- carboxyl groups and Cr(III) of adsorbent, and its sorption capacity is the highest among these aromatic acids. Other aromatic organic acids are adsorbed through both chemical and electrostatic interactions, and their sorption capacities are more influenced by pH. In summery, this research indicates that chrome leather wastes can also be utilized in preparing environmental protection materials.

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