Effective Removal of Organics From Nickel Wastewater By Modified Carbon Adsorption

By Chein-Ho Huang

An effective organic waste treatment for Watts nickel plating wastewater was developed. With the addition of ion exchange (IX) or ion exchange membrane (IXM), the adsorbabilities of organic pollutants onto activated carbon (AC) were increased. Results indicated that IX and IXM behave as insoluble concentrated electrolyte for use in BOD treatment. This treatment is economically advantageous and could be conducted in other industrial wastewater operations.

Although cyanide, chromate, and heavy metal ions are the main pollutants in the electroplating process, it has become increasingly important in recent years to remove organic pollutants from wastewater of some plating processes. For example, a fresh Watts nickel bath usually contains more than 5,000 ppm of organic additives.[1] These additives are consumed during the plating process and undesirable organic impurities are formed. In order to sustain a satisfactory deposit, more organic additives are put into the plating bath. Thus, organic contents gradually increase, resulting in very high concentrations of organic pollutants in the wastewater.

During the pH adjustment process in nickel wastewater operation, these organic pollutants are poorly adsorbed by the nickel hydroxide precipitant, therefore, a BOD (biochemical oxygen demand) treatment is necessary after clarification.[2]

Both oxidation and adsorption methods are used to treat the BOD waste. The most widely accepted method for BOD removal is activated carbon (AC) adsorption. Although AC has been an effective adsorbent for the removal of many organic substances in water, most organic additives of a nickel bath cannot be removed effectively, resulting in high BOD value in the discharge.[3] To overcome this, it is desirable to provide a means of improving the effectiveness of AC.

As predicted in a previous paper,[3] increasing the electrolyte concentration in a solution will promote flocculation or shielding the charge of organic components, consequently increasing the adsorbabilities of these organic additives onto AC.[3,4] In a typical plating wastewater operation, however, the BOD treatment is after clarification of heavy metal ion precipitates. Most electrolytes are removed before BOD treatment; therefore, only very small amounts of electrolyte exist during the BOD treatment. Any electrolyte addition in BOD treatment is inconvenient and may incur other contamination in the discharge; consequently, the BOD treatment has not always been satisfactory in treating Watts nickel wastewater.

Because ion exchange (IX) and ion exchange membrane (IXM) both exhibit electrolyte characteristics and non-dissolution advantages, they should be a practical substitute for the soluble electrolyte.[5] Therefore, they were mixed with AC in the BOD treatment, resulting in an effective operation for BOD removal. With the addition of IX or IXM, we obtain higher adsorbability of organic pollutants onto AC without having other contamination.

This treatment is effective not only for nickel plating wastewater, but for other industrially generated organic pollutants as well.

Experimental Procedure

Sodium benzene sulfonate (SBS), sodium vinyl sulfonate (SVS), sodium dodecylbenzene sulfonate (SDS), and phenol were examined as adsorbates in this work. Adsorption isotherms with 10 g/L activated carbon[a] (AC) were determined for these organic compounds in solution which may contain other electrolytes, IX, and IXM. The concentrations of these organic compounds were 0.1, 0.5, 1.0, 1.5, and 2.0 g/L. All adsorption experiments were mechanically shaken for 15 min. in a thermostatically controlled bath at 30 ± 0.5°C. Preliminary tests showed 15 min. to be sufficient for establishing a 95-percent equilibrium.

After shaking, AC was removed by centrifugation; all the concentrations of organic compounds remaining in solution were determined with ultraviolet spectrophotometry, except the SVS, which was measured by determining BOD according to the standard chromate oxidation method.[6] The difference between the initial and final concentrations was equal to the amount adsorbed by the AC. A blank solution, without any organic species, was also prepared for each test.

Strong acid cation exchange resins,[b,c] weak acid cation exchange resin,[d] strong basic anion exchange resin,[e] and strong cation exchange membrane[f] were used in this work. The AC, IX, and IXM were washed with distilled water until no impurities or debris desorbed into solution were detected.’

Reagent-grade chemicals were used, except for technical-grade nickel sulfate that contained 5.4 ppm Fe, 2.0 ppm Zn, 0.5 ppm Cu, and 2.7 ppm Pb. Infrared spectrophotometry and scanning electron microscopy (SEM) were used to examine surface adsorption of organic species onto IX. X-ray fluorescence and atomic absorption spectrophotometry were used to determine the adsorption of metal ions onto both IX and AC.

Results and Discussion

Organic Pollutants

The main organic pollutants in Watts nickel plating wastewater were the organic brighteners. By Traube’s rule, the non-polar AC will preferentially adsorb the more non-polar Class II brighteners in a polar aqueous solution.[5] On the other hand, anionic Class I brighteners are more polar and have a lower adsorbability onto AC, especially SBS and SVS. Therefore, these two sulfonates were more suitable to demonstrate the effectiveness of IX and IXM on the adsorbabilities of organic pollutants onto AC.

[a] Powdered activated carbon, Yakuri Chemicals, Osaka, Japan.
[b] Amberlite IRA 120, E. Merck, Darmstadt, Germany.
[c] #1, E. Merck, Darmstadt, Germany.
[d] #4, E. Merck, Darmstadt, Germany.
[e] Amberlite IRA 400, E. Merck, Darmstadt, Germany.
[f] R-1010, RAI Research Corp., New York, NY.

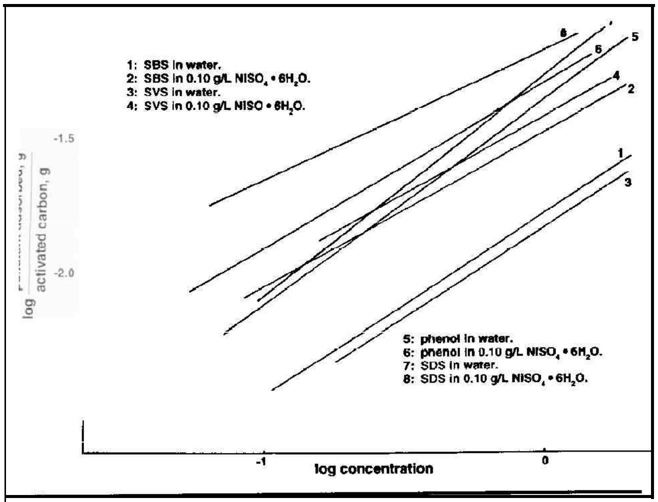

Fig. 1—Equilibrium isotherms of organic pollutants, using activated carbon at 30°C in both water and 0.1 g/L $NiS0_4.6H_20$.

Cleaning is necessary for satisfactory plating. Surfactants added in the cleaning process must also exist in the nickel wastewater. Thus SDS, a typical anionic surfactant, was also selected for study as an organic pollutant. Besides, in order to show the future applications of this work in other industrial processes, the frequently used organic pollutant, phenol, was also selected for study.

Freundlich's isotherm was applied to these four organic pollutants from sample solutions onto AC at concentrations ranging from 0.5 to 2.0 g/L. Some typical isotherm results of these pollutants are shown in Fig. 1, where x is amount (g) of pollutant adsorbed, m is the weight (g) of AC, and C is the pollutant concentration (g/L).

As predicted in our earlier work, although most organic pollutants could not be removed completely by the AC, with the effects of flocculating and charge shielding, the adsorbabilities of organic pollutants onto AC was increased by the presence of the electrolyte.' This phenomenon was especially noteworthy in the case of an organic pollutant which has larger polar moiety. As shown in Fig. 1, both SBS and SVS had larger polar moieties, resulting in a higher increase of adsorbability when 0.1 g/L of nickel sulfate ($NiSO_4$• $6H_20$) was added into the system being studied. On the other hand, phenol and SDS had small polar moieties and experienced little effect from the added electrolyte.

For reasons of clarity, average adsorbability results were adopted in the following results and discussion. Adsorbability of higher adsorbate concentration means the average adsorbability of initial adsorbate concentrations of 2.0, 1.5, and 1.0 g/L, whereas the adsorbability of lower adsorbate concentration means the average adsorbability of initial adsorbate concentrations of 1.0,0.5, and 0.1 g/L. All results showed that adsorbabilities were higher at higher adsorbate concentrations than at lower concentrations.

The concentration of electrolyte had an obvious effect on the adsorbability of the organic pollutant onto AC. As shown in Table 1, the adsorbability of SBS onto AC increased with

Table 1
Amenability to Adsorption of Sodium Benzene Sulfonate

Bath	Specific conductivity* of bath	Adsorbate concentration	Adsorbability (Adsorbate, g / AC) IX-free	0.5 g/L #1 resin
water	1.45	high	0.021	0.041
		low	0.010	0.018
0.05 g/L Ni**	6.61	high	0.037	0.046
		low	0.016	0.020
0.10 g/L Ni	11.6	high	0.039	0.044
		low	0.017	0.018
0.20 g/L Ni	20.0	high	0.044	0.045
		low	0.019	0.020
0.50 g/L Ni	41.4	high	0.047	0.048
		low	0.022	0.022
1.00 g/L Ni	73.8	high	0.052	0.050
		low	0.025	0.024
5.00 g/L Ni	252.7	high	0.069	0.067
		low	0.029	0.030
10,0 g/L	435.2	high	0.078	0.077
		low	0.033	0.034
30.0 g/L Ni	988.3	high	0.080	0.079
		low	0.036	0.038
Dil. Watts bath***	5430.7	high	0.062	0.080
		low	0.041	0.041
Watts bath	5921.7	high	0.096	0.094
		low	0.043	0.040
10 g/L Na_3HPO_4. $12H_20$	812.9	high	0.035	0.042
		low	0.015	0.018
10 g/L Na_2HPO_4. $12H_20$	525.2	high	0.043	0.051
		low	0.016	0.020
10 g/L NaH_2PO_4• H_2O	451.1	high	0.047	0.053
		low	0.018	0.024

*All specific conductivities are expressed in $10^{-5}ohm^{-1}cm^{-1}$.
**Ni = $NiS0_4$. $6H_20$.
***Watts bath diluted with 20% w/w water.

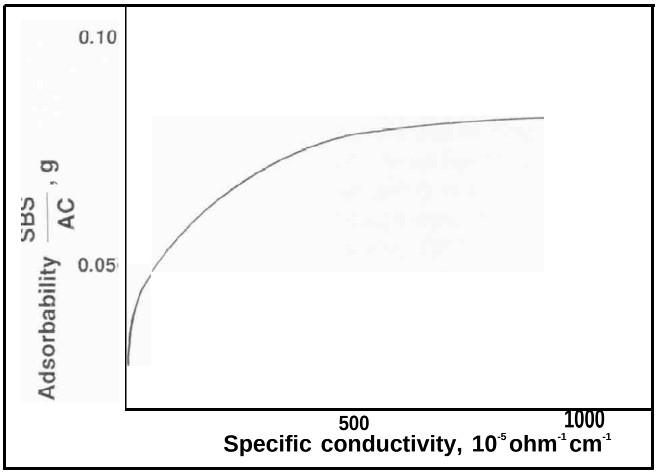

Fig. 2—Relationship between the specific conductivity of nickel sulfate bath **and the** *adsorbability of higher concentrations of SBS onto AC.*

the concentration of nickel sulfate. A larger concentration of electrolyte has greater ionic strength, as measured by conductivity, resulting in increased flocculation and charge shielding of an organic pollutant in solution and, consequently, higher adsorbability onto AC. Therefore, the adsorbability of SBS onto AC increased with the concentration of nickel sulfate from 0.05 to 30.0 g/L, or even to the concentration of a Watts bath. Consequently, one may see from Fig. 2 that the adsorbability of SBS onto AC was relative to the specific conductivities of the nickel sulfate solutions. Higher specific conductivity of the nickel sulfate bath resulted in higher adsorbability of SBS onto AC.

In order to ascertain the effect of pH on adsorbability, buffer phosphate electrolytes were studied. As shown in Table 1, with the addition of these electrolytes, pH values decreased from 11.3 ($Na_3PO_4 \cdot 12H_20$ bath) to 4.8 ($NaH_2P0_4 \cdot H_20$ bath), resulting in higher adsorbability of the SBS pollutant onto AC, regardless of the small difference in their conductivities.

Insoluble Concentrated Electrolyte

Although the presence of an electrolyte will increase the adsorbability of organic pollutants onto AC, most electrolytes in wastewater operation are removed before carbon adsorption. After clarification of the heavy metal ion precipitation, the wastewater contains nickel ions in concentration below one ppm, too small an amount to increase the adsorbability of an organic pollutant onto AC. To overcome this deficiency, it is desirable to develop a more effective BOD treatment. Therefore, in this work, insoluble IX and IXM were mixed with AC in the carbon adsorption system to study their effectiveness on the adsorbability of an organic pollutant onto AC. It was not expected that organic materials would be adsorbed by IX alone, but that some improvement might be seen in combination with AC.

In IX or IXM, the distance of the counter ion to the nearest framework-oxygen is much too long for bonding.[8] Adamson concluded that the exchange phase may be treated as essentially a concentrated electrolyte solution.[5] With the advantages of both insoluble and electrolytic characteristics, these two materials should be valuable to the system of adsorption of organic pollutants onto AC and are termed “insoluble concentrated electrolyte” in this work.

Some IX were used to adsorb organic materials in water; for example, Anderson and Maier concluded that the strong base resin was able to remove organic compounds from water, especially when the charge of IX is opposite to that of the adsorbate.[9,10] As shown in Table 2, the strong basic exchanger [d] had a charge opposite to the SBS and the ability to remove the SBS from water. Therefore, the adsorbability of SBS onto AC was increased partly because of the adsorption by the strong basic exchanger. Similarly, with the opposite charge of the strong acid cation exchanger resin,[c] cetyl pyridinium chloride (CPC) was almost completely removed during BOD treatment by both AC and this resin.

In contrast to the strong basic exchanger, the adsorbabilities of the four pollutants on cationic IX and IXM were almost negligible; thus, cationic IX and IXM showed the special effectiveness of the insoluble concentrated electrolyte on carbon adsorption. As shown in Tables 1, 3, 4 and 5, with the electrolyte effect of IX or IXM, the adsorbabilities of the studied pollutants onto AC were increasingly obvious in treated baths.

The model of insoluble concentrated electrolyte could be further explained by the ionic strengths of IX and IXM solutions. As measured by specific conductivity, the conductivity of water did not increase after the addition of H+, Ni^{++}, or Ca^{++} forms of IX and IXM. There was no real dissociation, so no free ions from IX or IXM to increase the value of specific conductivity of the water, but the presence of these IX or IXM in water had the effect of a dissolved electrolyte and increased the adsorbability of organic pollutants onto AC. From the data of Table 1, the effectiveness of 0.5 g/L of a strong acid cation exchange resin’ on the adsorbability of SBS onto AC was equal to the dissolved electrolyte effect of about 0.10 to 0.20 g/L $NiSO_4 \cdot 6H_20$. The operating capacity of insoluble concentrated electrolyte is about equal to the equivalent amount of soluble electrolyte.

Similarly, in the IX-free bath, as shown in Table 1, the effectiveness of a strong cation exchange resin’ on the adsorbability of SBS onto AC was also increased at lower pH values.

Table 2
Amenability to Adsorption of Organic Compounds with IX Containing Opposite Charge*

		Adsorbability $\left(\frac{\text{Adsorbate}}{\text{Ac}}, \text{g}\right)$		
Bath	**Adsorbate concentration**	**IX-free**	**0.5 g/L IX**	**Ix**
SBS in water	**high**	**0.021**	**0.049**	**IRA 400**
	low	**0.010**	**0.020**	
CPC in water	**high**	**0.111**	**0.148**	**#l**
	low	**0.045**	**0.051**	

***The adsorbabilities of SBS onto IRA 400 is 0.068 g SBS/g IRA 400 at higher concentration of 0.018 g SBS/g IRA 400 at lower concentration of SBS.**

Table 3
Amenability to Adsorption of Organic Compounds with #1 Resin

Bath	Avg. adsorbate concentration, g/L	Adsorbability ($\frac{\text{Adsorbate}}{\text{AC}}$, g) IX-free	0.5 g/L IX
SVS in water	1.5	0.023	0.043
	0.5	0.011	0.019
SVS in 0.10 g/L Ni*	1.5	0.042	0.049
	0.5	0.021	0.024
SDS in water	1.5	0.055	0.069
	0.5	0.021	0,028
SDS in 0.10 g/L Ni	1.5	0.063	0.073
	0.5	0.032	0.032
Phenol in water	1.5	0.045	0.082
	0.5	0.020	0.035
Phenol in 0.10 g/L Ni	1.5	0.047	0.060
	0.5	0.022	0.027

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*Ni = $NiS0_4 . 6H_20$

Table 4
Amenability to Adsorption of SBS and SDS with #4 and IRA-120 Resins

Bath	Adsorbate concentration	Adsorbability ($\frac{\text{Adsorbate}}{\text{AC}}$, g) 0.5 g/L IX	Ix
SBS in water	high	0.059	IRA-120
	low	0.041	
SBS in water	high	0.043	IRA-120
	low	0.018	
SBS in 0.10 g/L Ni*	high	0.052	IRA-120
	low	0.022	
SDS in water	high	0.064	IRA-120
	low	0.029	
SDS in 0,10 g/L Ni	high	0.069	IRA-120
	low	0.034	

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*Ni = $NiSO_4 . 6H_20$

Table 5
Amenability to Adsorption of Sodium Benzene Sulfonate with R-1010 IXM

Bath	Adsorbate concentration	Adsorbability y ($\frac{\text{Adsorbate, SBS}}{\text{AC}}$ g) 0.5 g/L IXM
SBS inwater	high	0.044
	low	0.019
SBS in 0.10 g/L Ni*	high	0.043
	low	0.019
SBS in water”	high	0.043
	low	0.018

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*Ni = $NiSO_4 \cdot 6H_20$
**With reused R-1010 IXM

Practical Operations

In order to demonstrate that operation of the insoluble concentrated electrolyte is practical, as shown in Table 6, the effectiveness of spent and reused IX on adsorbability was also studied. Although resins were equilibrated with nickel or calcium ions, they still had the same effectiveness as that of their fresh, unused types. Besides, the reused exchangers also gave the same performance on the adsorbabilities of organic pollutants onto AC as their fresh forms. These applications of both spent and reused resins showed this work to be very practical.

The main drawback for the reused resin was the time necessary to separate it from AC before reuse. To overcome this, IXM was introduced. in addition to the advantage of insoluble concentrated electrolyte characteristic, the membrane film’ was easily separated from the carbon adsorption system. As shown in Table 5, the reused film also had the same effectiveness on adsorbability as fresh film. Therefore, this IXM offers greater flexibility of operation because it is economically practical.

No regenerate liquid is needed, other than water, for the reused IX and IXM, and waste is not produced. After separation from the AC by decanting, the IX and IXM were washed with water. The IXM was introduced to reduce the laborious nature of this process.

In addition to the treatment in nickel wastewater, as shown in Tables 3 and 6, these studies were also conducted for phenol, a typical organic pollutant in other industrial wastewater.

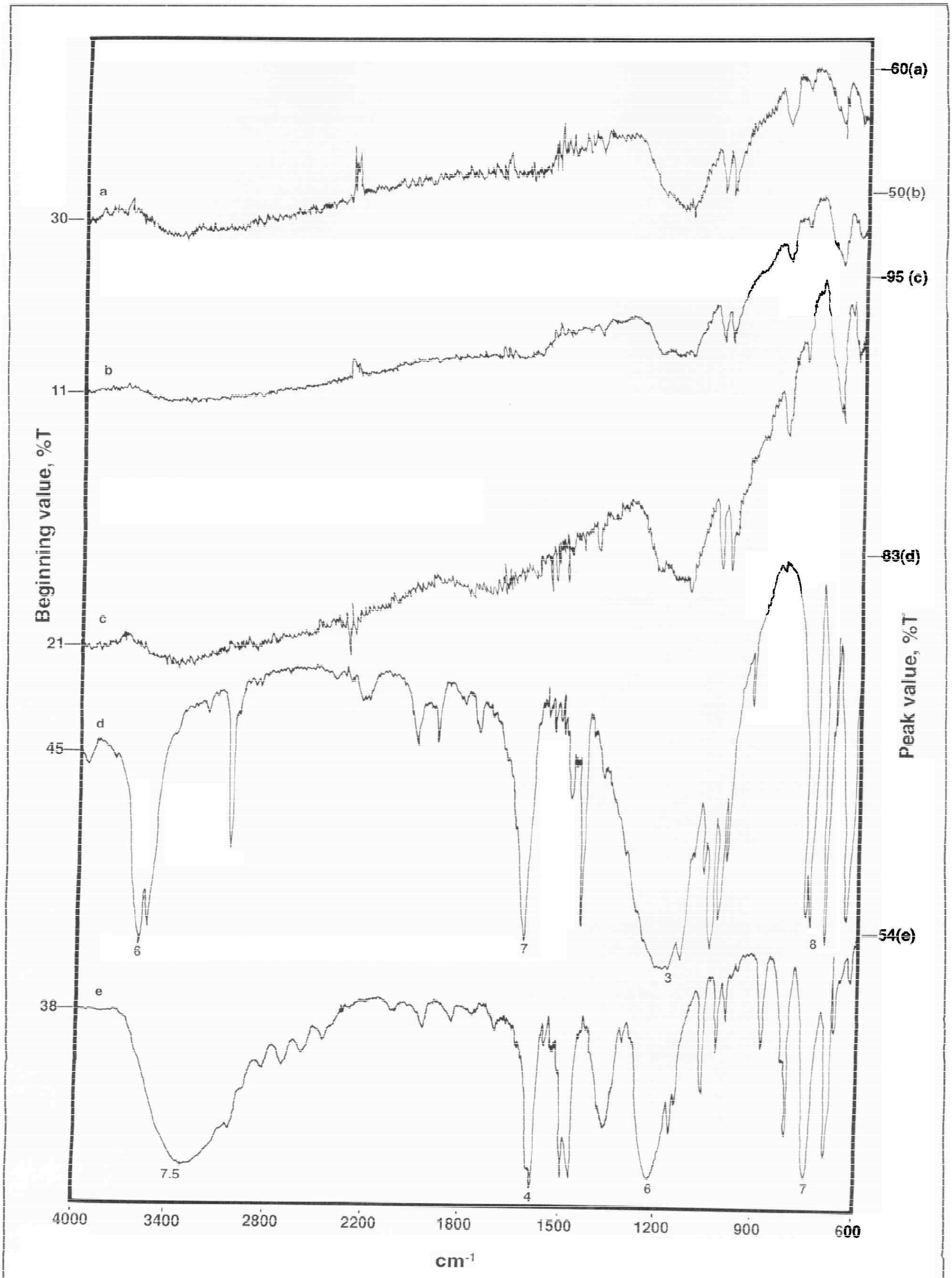


Fig. 3—Infrared spectra of (a) #1 resin; (b) SBS, 2 g/L, adsorbed on # 1 resin; (c)phenol, 2 g/L, adsorbed on #1 resin; (d) SBS: (e) phenol. (Note: Because space limitations, the beginning point of each spectrum is plotted on the left, with maxima noted on the right. Minima for SBS and phenol are noted adjacent to those points for perspective.)

Table 6
Amenability to Adsorption of Organic Compounds with Both Spent and Reused #1 Resins

		Adsorbability	
Bath	Adsorbate concentration	$\left(\frac{\text{Adsorbate, g}}{\text{AC}}\right)$ 0.5 g/L #1	Ix
SBS inwater	high	0.043	in the Ni^{++} form
	low	0.018	
SBS in water	high	0.044	in the Ca^{++} form
	low	0.019	
Phenol in water	high	0.060	in the Ni^{++} form
	low	0.027	
Phenol in water	high	0.060	in the Ca^{++} form
	low	0.028	
SBS in water	high	0.040	1st reuse
	low	0.017	
SBS in water	high	0.041	2nd reuse
	low	0.016	
SBS in water	high	0.041	3rd reuse
	low	0.017	

Adsorption on IX and AC

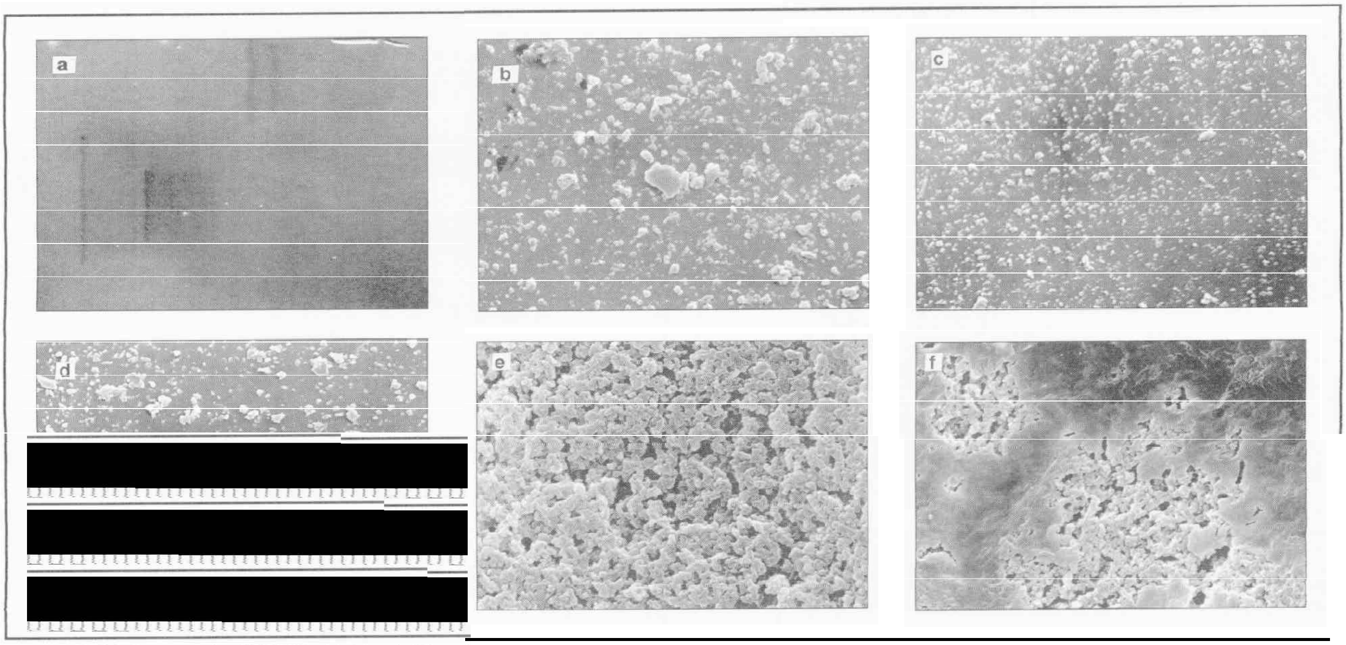
This insoluble concentrated electrolyte model could be further explained by some adsorption phenomena on IX and AC. Infrared spectroscopy can give useful data and provide definitive information on the structure and surface properties of IX. Because the adsorption of pollutants on cationic exchangers was so small compared with the adsorbability results, as shown in Fig. 3, the infrared spectra of a strong acid cation exchange resin[b] after immersion in a solution of 2.0 g/L of pollutant were almost the same as that of a non-immersed resin. Consequently, the main role of IX in the BOD treatment is flocculation and charge shielding.

The adsorption of pollutant on IX was also explained by SEM examination. As shown in Fig. 4, only a very small amount, or even no pollutant was observed on the surface of the washed IX that was separated from a BOD treatment with 2.0 g/L concentration of pollutant. The adsorbed species on the surface of the strong acid cation exchange resin[c] were identified by the X-ray elemental analysis system. The SEM observation could be used to explain the very small change of infrared spectra of the adsorbed IX. Figure 4 also showed that the amount of adsorbed SBS on the surface of a reused strong acid cation exchange resin’ was not obviously increased; that is, the equilibrium adsorption of pollutant on the resin was very small. Therefore, IX could be reused with no more adsorption or deterioration in performance, making the insoluble concentrated electrolyte an economical treatment for organic pollutants.

The determination by X-ray fluorescence and atomic absorption spectrophotometer showed that nickel. ion was adsorbed onto AC. Although the adsorbability of pollutants onto AC was increased by the adsorbed nickel, the increase was too small to affect the results of this study.

Conclusions

Following the flocculating and charge shielding effects of soluble electrolyte on the adsorbability of organic compounds onto AC, an effective carbon adsorption procedure



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Fig, 4—SEM photographs (5000x) of (a) fresh #1 resin; (b) #1 resin after cartbon adsorption with 2 g/L SBS; (c) first reused # 1 resin after carbon adsorption with 2 g/L SBS; (d) second reused #1 resin after carbon adsorption with 2 g/L SBS; (e) fresh #4 resin; (f) #4 resin after carbon adsorption with 2 g/L SBS.

was developed to remove organic pollutants in Watts nickel and other industrial wastewater. Both IX and IXM improved the adsorbabilities of organic pollutants onto AC in the BOD treatment without adverse effect. In addition, both spent and reused IX or IXM also had the same effectiveness on carbon adsorption as their fresh forms; therefore, this treatment is economically advantageous.

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