Adsorption of Lactic Acid onto Three Ionic Liquid-Modified Porous Polymers

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ABSTRACT: Three ionic liquid (IL)-modified porous polymers were synthesized and used for the adsorption of lactic acid. The experimental adsorption kinetics and equilibrium data from the IL-modified polymers were obtained. The kinetic study revealed a low temperature to be advantageous to the adsorption process. The dependence of the level of lactic acid adsorption on the amount of polymer, initial lactic acid concentration, and pH was examined at equilibrium. The maximum efficiency was obtained using the maximum adsorbent dose. A comparison of lactic acid adsorption at different pH revealed anion exchange to be the main interaction between the lactic acid and polymers, not molecular adsorption. The amounts adsorbed were fitted to the Langmuir, Freundlich, and Temkin equations. The equilibrium data for modified polymers (imidazole modified polymer, methylimidazole modified polymer, and ethylimidazole modified polymer) were best represented by the Langmuir and Freundlich isotherm with R^2 values of 0.99. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1306–1313, 2013

INTRODUCTION

Some short chain organic acids can be removed from raw solutions using a range of purification methods, such as extraction, electrodialysis, reactive distillation, and adsorption.[1–4] Adsorption or ion exchange is a reliable technology,[5] and several studies have successfully adsorbed organic acids using polymeric ion exchange polymers. For example, Kulprathipanja and Oroshar[6] reported the absorption of lactic acid from a fermentation broth using strong, moderate, or weak basic anion exchange polymers. Some commercially available ionic polymers, such as Amberlite IRA-400 and IRA-67, etc., have been studied.[5,7] On the other hand, the low compressive strength and capacity of the polymers have limited their further applicability.[4] Therefore, new materials are needed to overcome these shortages.

Recently, some new ionic liquid (IL) modified porous polymers have been synthesized as sorbents for a range of separation processes.[8–11] These IL-modified materials have been applied effectively because of their unique properties, such as polarity and low volatility associated with ionic interactions, as well as controllable adsorption performance according to the functional groups on their surfaces.[12] These materials adsorb analytes through ion exchange, hydrogen bonding, π–π interactions, Van der Waals interactions, or hydrophobic interaction, etc. Therefore, lactic acid can be ionized in aqueous solutions and

anion-exchanged with imidazolium groups, as shown Scheme 1. The entire lactic acid molecule also can be adsorbed on porous sites of the polymer defined using the following equation,

$$[R - IM^+][Cl^-] + [H^+][A^-] \leftrightarrow [R - IM^+][H^+][Cl^-][A^-] \quad (1)$$
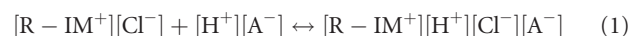
In eq. (1), $[R\text{-}IM^+]$ $[Cl^-]$ is the IL-modified polymer and $[H^+][A^-]$ is the acid. This study examined which scheme is the major of the two adsorption models.

Lactic acid is one of the most important organic acids produced by lactic acid bacteria. The acid was first discovered by the Swedish scientist, Scheele, in 1780 from sour milk. Currently, it is used widely in the food, pharmaceuticals, and chemical industries.[13–17] Lactic acid can be manufactured by both chemical synthesis and microbial fermentation. Although high purity lactic acid can be obtained by chemical synthesis, the process is far more expensive than fermentation. Microbial fermentation has significant advantages over chemical synthesis because it can use cheap raw materials, such as whey, molasses, starch waste, beet, cane sugar, and other carbohydrate rich materials.[18–22] Consequently, fermentation processes are used widely in lactic acid production. Nevertheless, a large number of impurities are also produced during the biological process. Therefore, more attention on the technology for purifying lactic acid is needed.
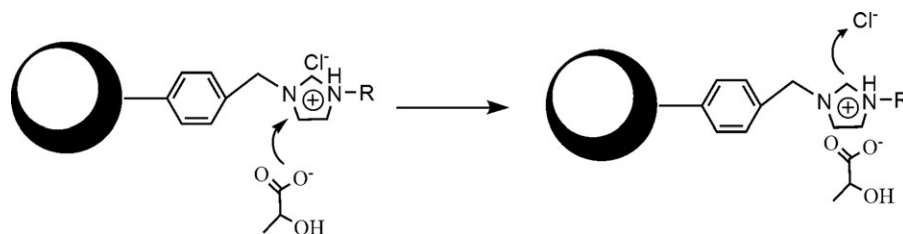
Scheme 1. Proposed scheme for the anion exchange mechanism on porous polymers.

In this study, three IL-modified porous polymers were prepared using imidazole chloride, methylimidazole chloride, and ethylimidazole chloride as surface modifiers. The lactic acid adsorption characteristics of the three IL-modified porous polymers were examined, taking equilibrium into account. The dependence of lactic acid adsorption on the time, amount of adsorbent, initial lactic acid concentration, temperature, and pH was investigated. The equilibrium isotherms were expressed using the Langmuir, Freundlich, and Temkin models to better understand the mechanism of this adsorption process.

EXPERIMENTAL

Materials

(D,L)-Lactic acid (90%) was purchased from Fluka (Milwaukee, WI), whereas imidazole (99%), 1-methylimidazole (99%), and 2-ethyl-4-methylimidazole (95%) were obtained from Aldrich (Milwaukee, WI). 2,2′-Azobisisobutyronitrile (AIBN) was acquired from Junsei Chemical Co. (Tokyo, Japan). 3-Amino-propyl bromide hydrobromide (97%), 4-(chloromethyl)styrene (90%), divinylbenzene (50%), and polyvinylpyrrolidone (PVP, K 30) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Hydrochloric acid (HCl) (35.0%–37.9%), sodium hydroxide (NaOH) (extra pure), methanol, ethanol, and other organic solvents were supplied by DUKSAN Pure Chemical Co. (Ansan, Korea). Distilled water was filtered using a vacuum pump (Division of Millipore, Waters, Milford, Ireland) and filter (HA-0.45, Division of Millipore, Waters, Milford, Ireland). All solvents used in the experiment were of either HPLC or analytical grade. All samples were filtered through a filter (MFS-25, 0.2 μm TF, Whatman) before being used in the experiments.

Preparation of IL-Modified Porous Polymers and Characteristic Analysis

The three IL-modified porous polymers were synthesized using a similar procedure to that reported in the literature and is divided into two reactions.[8] Scheme 2(A) shows the first reaction. 0.48 g of PVP was dissolved in 100.0 mL of ethanol in a 250.0-mL flask. Subsequently, 5.65 mL of 4-(chloromethyl)styrene (monomer), 16.2 mL of divinylbenzene (crosslinker), 5.0 mL of heptanes (porogen), and 0.22 g of AIBN (initiator) were added under a nitrogen atmosphere with rapid stirring. The emulsion solution was heated to 70°C for 1 day to allow polymerization. After complete polymerization, the porous polymer was filtered and washed three times with ethanol to remove the coagulated and soluble impurities.

Scheme 2(B) shows the second reaction. The porous polymer (2.0 g) and different IL modifiers (2.0 mmol) were added to 35.0 mL of ethanol. After heating for 12 h under reflux, the modified polymers [Imidazole polymer (PIM), methylimidazole polymer (PMIM), ethylimidazole polymer (PEIM)] were cooled to room temperature. The polymers were washed sequentially with toluene, ethanol, and methanol and dried at 60°C.

The synthetic polymers were characterized by Fourier transform infrared (FTIR, Vertex 80V, Bruker, Billerica, MA) spectroscopy and field emission-scanning electron microscopy (FE-SEM, S-4200, Hitachi, Ontario, Canada). The FTIR data was obtained in the range of 400–4000 cm^{-1} with a scan rate of 20 scans min^{-1}. A KBr pellet was prepared as follows. Approximately 100 mg of anhydrous KBr was placed into an agate mortar and ground to a fine powder. Approximately 2 mg of polymers was then mixed with the KBr powders and ground for 5 min. The ground mixtures were placed into a die-set and pressed at 10 MPa for 2 min in a manual hydraulic machine to form a pellet. FE-SEM was performed using at an acceleration voltage of 15 kV (pixel size, 0.5 nm). The brunauer emmett teller (BET) surface area (0.03 g of polymer in N$_2$ atm at −195.85°C) was measured using an ASAP2010 apparatus (Micromeritics, Norcross, GA). The aggregated particle size was determined using an ELS-Z2 (ELS-8000, Otsuka Electronics, Japan) in an ethanol suspension (0.01 g of sample/10 mL of ethanol).

Adsorption

Five standard lactic acid solutions (0.5, 2.5, 10.0, 20.0, and 50.0 mg mL^{-1} in distilled water) were prepared. Mixtures of a known amount of IL-modified polymer and 1.0 mL of the lactic acid solution were prepared in a sample vial (5 mL). The sample vial was heated (if necessary) on a thermostated plate and stirred with a magnetic bar (0.5 cm). The pH of the lactic acid solution was adjusted with HCl and NaOH solutions. When the adsorption process was complete, the lactic acid in the aqueous phase sample was analyzed by gas chromatography coupled with flame ionization detection (GC-FID, Yong Lin, GC-6100, Korea).

GC Analysis of Lactic Acid

GC-FID analysis of lactic acid was performed using a DB-FFAP capillary column (30 m × 0.320 mm × 0.25 μm) (Agilent Technologies). Ultra-high purity helium (purity 99.999%) was used as a carrier gas at a flow rate of 1.80 mL min^{-1}. The oven temperature was programmed as follows: initial temperature of 80°C (held at the temperature for 3 min) increased to 150°C at 8°C min^{-1}, and held at that temperature for 4 min. The total time for a single GC run was 15 min. The FID and the injector temperatures were 250°C and 150°C, respectively. The injection was performed in split mode at a rate of 42: 1.
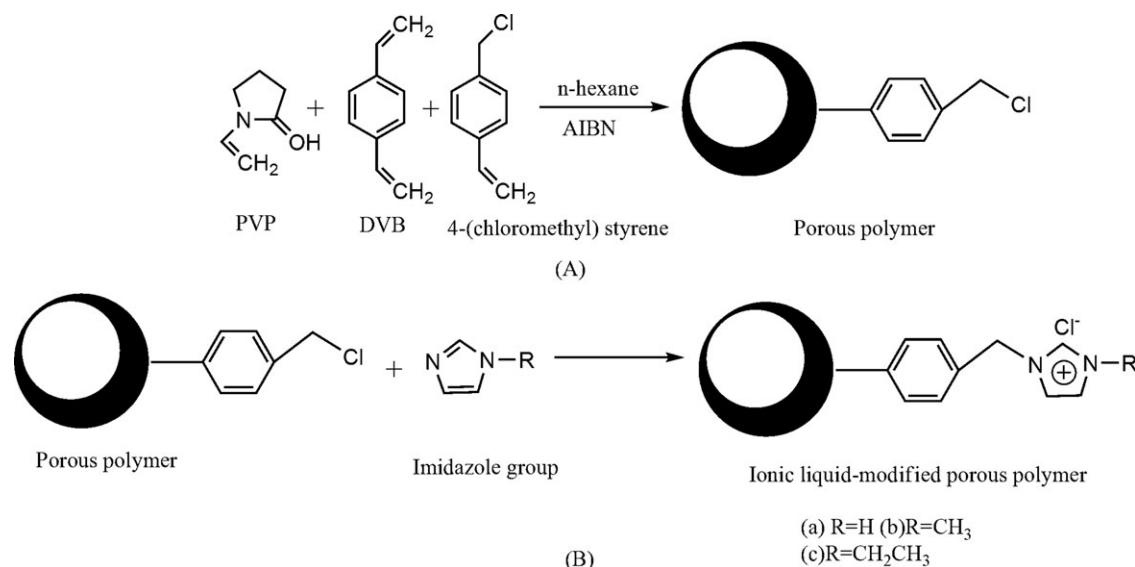
Scheme 2. Preparation scheme of the IL-modified porous polymer.

RESULTS AND DISCUSSION

Characterization of the Synthesized Polymers

Figure 1 shows the FTIR spectra of the three polymers. The peak at 1593 cm^{-1} was assigned to the imidazole group immobilized on the polymers.[23,24] The FTIR spectra indicated the presence of two absorption bands (v_{as} (benzene ring)) at 690 and 760 cm^{-1}. The peak at 2880–3000 cm^{-1} was assigned to C—H groups. Therefore, the band absorbance of PMIM or PEIM, which have one more alkyl group, was higher than PIM.[25,26]

FESEM of PIM, PMIM, and PEIM (Figure 2) showed that a special porous structure had formed, and the pores of PIM, PMIM, and PEIM were similar. The surface area (44.25 m^2 g^{-1} for PIM, 42.31 m^2 g^{-1} for PMIM, and 39.74 m^2 g^{-1} for PEIM), the pore volume (0.098 cm^3 g^{-1} for PIM, 0.101 cm^3 g^{-1} for PMIM, and 0.123 cm^3 g^{-1} for PEIM), and pore size (207.4 Å for PIM, 210.1 Å for PMIM, and 223.6 Å for PEIM) were determined by BET. After modification, the long carbon chain
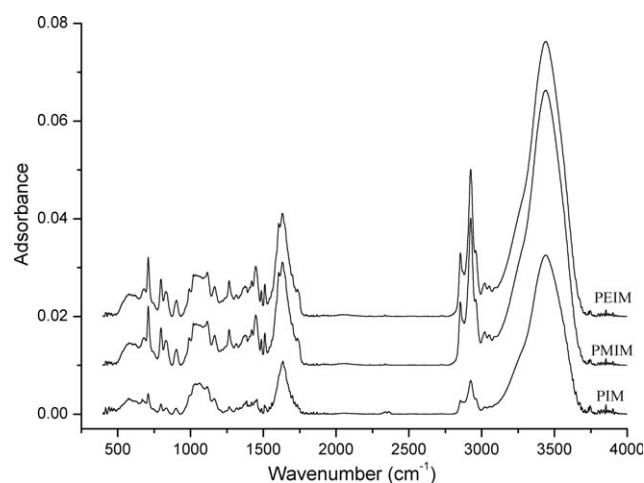

Figure 1. FTIR spectra of all IL-modified porous polymers.

decreased the surface area and increased the pore size. The porous structure of PIM exhibited the largest surface area and minimum pore size of the three polymers.

Adsorption Kinetics

An analysis of the adsorption data is important for developing kinetic equations that can be used for design purposes. The amounts of lactic adsorbed on all sorbents were calculated using the following equation:

$$Q = \frac{(C_0 - C)V}{m} \tag{2}$$

where Q (mg g^{-1}) is the amount adsorbed at any time, C_0 (mg mL^{-1}) is the initial concentration, C (mg mL^{-1}) is the unadsorbed concentration at any time, V (mL) is the volume of the sample solution, and m (g) is the mass of the sorbent.

Effect of Adsorbents. Figure 3 shows the adsorption kinetics of lactic acid on activated carbon and the synthesized IL-modified polymers from 0 to 8 h at an initial lactic acid concentration of 10.0 mg mL^{-1} at pH 2.3 and 20°C. The amount of each adsorbent was 0.02 g. The particle sizes of PIM, PMIM, and PEIM were 602.3, 720.4, and 848.8 nm, respectively, as determined by particle size analysis. Under the given conditions, the amounts of lactic acid adsorbed by the adsorbents increased rapidly in the initial stages (2 h), and then increased at a slower rate, finally reaching saturation at equilibrium. A comparison with activated carbon as a popular adsorbent (Figure 3) revealed both PIM and PEIM to be more suitable for the adsorption of lactic acid.

According to a previous study, when the initial lactic acid concentration was 9 mg mL^{-1}, the amount of lactic acid adsorbed on the anion exchanger, IR A-92, was ~10 mg g^{-1}.[27] The amounts of lactic acid adsorbed on these synthesized materials were much higher than on IR A-92. This is because a large number of [Cl$^-$] anions on the surface of the
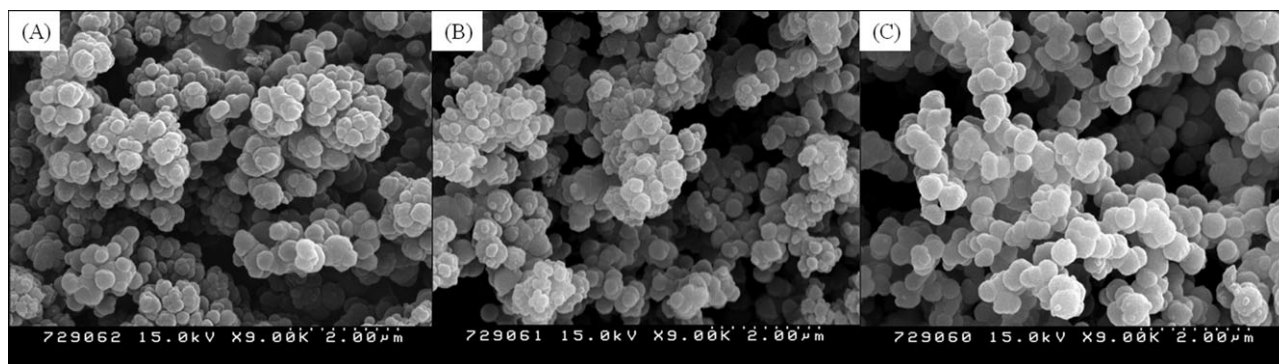
Figure 2. SEM images of PIM (A), PMIM (B), and PEIM (C).

polymers were exchanged by the anions of lactic acid.[28] Some studies considered that the vacant surface sites of adsorbents are available for adsorption during the initial stages. After a certain time, the remaining vacant surface sites were difficult to occupy due to the repulsive forces between the solute molecules on the solid and bulk phases.[5,29] PIM showed better lactic acid adsorption than the others because of its larger surface area.

Effect of Temperature. The adsorbents of PIM, PMIM, and PEIM were tested at 20, 25, 30, and 80°C over an 8 h period. The initial lactic acid concentration was 10.0 mg mL^{-1}, and the pH was 2.3. Figure 4 shows the related adsorption kinetics curves of the IL-modified polymers. In Figure 4, although the temperature increased, the time to reach equilibrium barely changed. Aksu and Kabasakal[30] reported that the adsorption equilibrium time was not affected significantly by changes in temperature. On the other hand, the effect of temperature on the amount of lactic acid adsorbed by the IL-modified polymers at the equilibrium time was significant. The amount of lactic acid adsorbed by the adsorbents decreased with increasing temperature. This might be due to the reversible adsorption process, where a higher temperature enhanced the mobility of lactic acid ions from the adsorbent surface toward the initial

solution. Other studies showed that the adsorbate molecules adsorbed on the surface have greater vibrational energy when the temperature is increased. Therefore, more adsorbate molecules have sufficient energy to overcome the adsorptive forces with the adsorbent and remain in the initial solution.[31] The results also showed that the adsorption process is exothermic, and a low temperature condition is advantageous in the process.

Adsorption Equilibrium

The adsorption equilibrium data is a basic requirement for the design of adsorption systems for engineering applications. The adsorption equilibrium is also an important analysis factor for design purposes. The amounts of lactic adsorbed on all the sorbents in the equilibrium results were calculated using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (3)$$

where Q_e (mg g^{-1}) is the amount adsorbed at equilibrium and C_e (mg mL^{-1}) is the unadsorbed concentration at equilibrium.
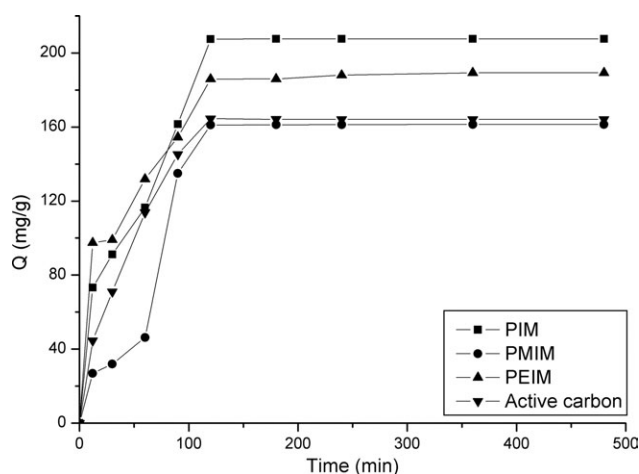

Figure 3. Adsorption kinetics curves of lactic acid at an initial lactic acid concentration of 10 mg mL^{-1} and 20°C (initial pH: 2.3, m: 0.02 g).
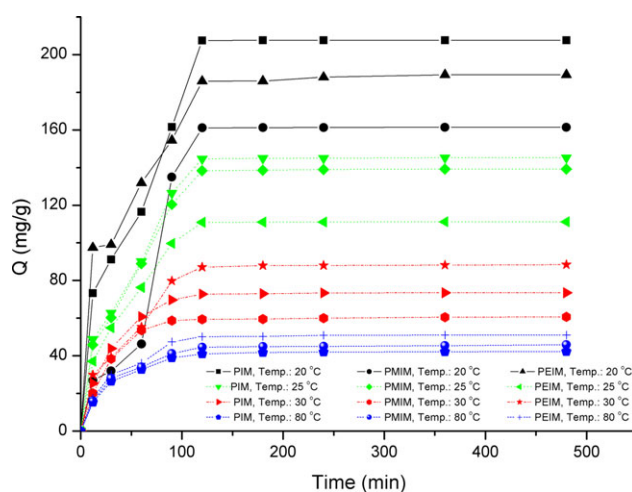

Figure 4. Adsorption kinetics curves of lactic acid at an initial lactic acid concentration of 10 mg mL^{-1} and at different temperatures (initial pH: 2.3, m: 0.02 g). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
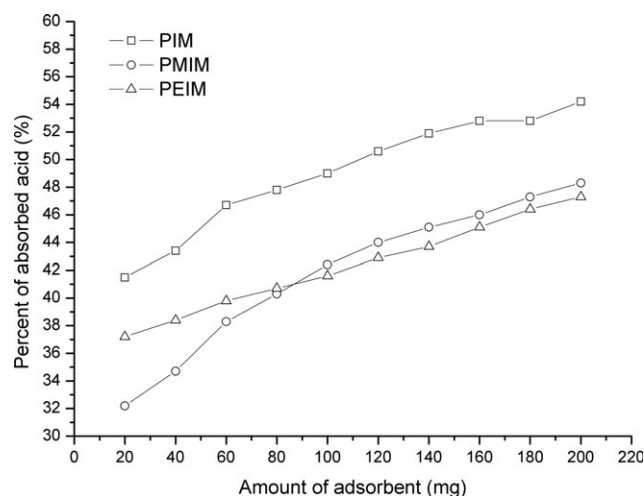
Figure 5. Effect of the amount of adsorbents on the adsorption of lactic acid.

The percentage of acid adsorbed (Ad%) at equilibrium was calculated as follows:

$$Ad\% = \frac{100 * (C_0 - C_e)}{C_o}\%\qquad(4)$$

Effect of Amount of Polymers. The effect of the adsorbent dose on the extent of solute adsorption was examined by varying the dose from 0.02 to 0.20 g at an initial solute concentration of 10 mg mL^{-1} at room temperature for 2 h. The amount of solute adsorbed increased with increasing dose (Figure 5). The maximum adsorption capacity at the maximum PIM, PMIM, and PEMIM dose of 0.20 g was 54.2%, 48.3%, and 47.3%, respectively, at an initial lactic acid of 10.0 mg mL^{-1}. For the three adsorbents, the adsorption efficiency increased with increasing adsorbent dose (Figure 5). The increase in sorption can be attributed to the increase in external surface area, and anions on the adsorbent surface, which means an increase in the number of available sites and [Cl$^-$]. More adsorptive sites and exchange anions are beneficial to the sorption reaction between adsorbates and adsorbents.[32]
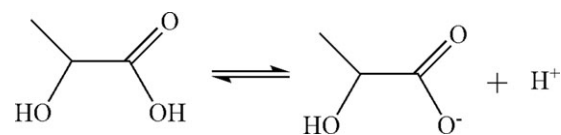
Scheme 3. Disassociation equilibrium of lactic acid in solution.

Effect of the Initial Lactic Acid Concentration. The effects of the initial concentration (10.0, 20.0, and 30.0 mg mL^{-1}) were examined for the three adsorbents at the equilibrium time. The adsorbed efficiency for each adsorbent decreased with increasing initial acid concentration from 10.0 to 30.0 mg mL^{-1} (Table I). The adsorption efficiency decreased with increasing initial lactic acid concentration from 41.5% to 12.0% for PIM, from 32.2% to 3.5% for PMIM, and from 37.2% to 4.7% for PEIM. Uslu and coworkers[5] explained this by the saturation of accessible exchangeable sites for lactic acid molecules.

In this study, the amount of adsorbed lactic acid (Q_e) did not always increase when the initial lactic acid concentration was increased. Normally, lactic acid in solution includes the disassociation equilibrium, as shown in Scheme 3. The adsorption of lactic acid on these IL-modified polymers might not only have occurred through the simple adsorption of molecules on these polymer porous sites but also through an ion exchange procedure, as shown Scheme 1. Therefore, the amount of lactic acid anions in the initial solution, as well as the amount of acid anions that exchanged with the polymers decreased with increasing initial lactic acid concentration. The equilibrium amount of lactic acid adsorbed on these sorbents was affected by molecular adsorption and anion exchange. For these reasons, the effect of the lactic acid form in solution on the adsorption of lactic acid was examined.

Effect of pH. The pH of the lactic acid solution is an important factor affecting the disassociation equilibrium of lactic acid in solution. Therefore, the effects of the pH of lactic acid solutions on the adsorption were investigated (Table II). At an initial lactic acid concentration of 10.0 mg mL^{-1}, the amount of lactic acid adsorbed and the efficiency of lactic acid for each polymer increased with increasing pH. The adsorption

Table I. Effect of the Initial Lactic Acid Concentration on the Adsorption of Lactic Acid

Adsorbent	Amount of adsorbent (g)	Initial lactic acid concentration C_o (mg mL^{-1})	Equilibrium concentration C_e (mg mL^{-1})	Adsorbed amount Q_e (mg g^{-1})	Percent of absorbed acid (%)
PIM	0.02	10.0	5.8	207.5	41.5
		20.0	13.4	329.0	32.9
		30.0	26.4	179.7	12.0
PMIM	0.02	10.0	6.8	161.1	32.2
		20.0	16.5	173.5	17.4
		30.0	29.0	51.8	3.5
PEIM	0.02	10.0	6.3	185.9	37.2
		20.0	14.0	301.8	30.2
		30.0	28.6	70.2	4.7

Table II. Effect of pH on the Adsorption of Lactic Acid

Adsorbent	Amount of adsorbent (g)	Initial lactic acid concentration C_o (mg mL^{-1})	pH	Equilibrium concentration C_e (mg mL^{-1})	Adsorbed amount Q_e (mg g^{-1})	Percent of absorbed acid (%)
PIM	0.02	10	1.5	9.2	41.95	8.4
			2.3	5.8	207.5	41.5
			3.5	4.7	264.8	53.0
			4.0	0.7	465.5	93.1
			4.5	No data	No data	No data
PMIM	0.02	10	1.5	9.6	20.4	4.3
			2.3	6.8	159.8	32.1
			3.5	5.0	249.6	49.7
			4.0	1.2	440.6	88.7
			4.5	1.1	445.1	89.3
PEIM	0.02	10	1.5	9.7	15.1	3.4
			2.3	6.3	184.8	36.9
			3.5	5.3	234.8	47.0
			4.0	1.3	435.1	87.2
			4.5	1.2	441.0	88.9

Note: 'No data' means that the value is not in the range of GC-FID determination.

efficiency increased with increasing initial lactic acid concentration from 8.4% to 93.1% for PIM, from 4.3% to 89.3% for PMIM, and from 3.4% to 88.9% for PEIM. This shows that the main adsorption process of lactic acid on these IL-modified polymers is lactic anion exchange with the anions of the polymers on the polymer surface. Hamdaoui[33] suggested an ion exchange mode as a partial explanation for the result of lactic acid adsorption on PIM at pH 4.5. Therefore, the amount of lactic acid adsorption increases when the main form of lactic acid in the solution is the disassociated form. The number of negatively charged adsorbent sites increased with increasing pH of the system, which favored anion exchange due to electrostatic repulsion.[33]

Adsorption Isotherms. The Langmuir and Freundlich isotherms were examined to determine the equilibrium characteristics of adsorption. The Langmuir equation can be expressed as follows:

$$Q_e = \frac{K_L \times q_m \times C_e}{1 + K_L + C_e} \quad (5)$$

where K_L and q_m are the adsorbent-phase concentrations of lactic acid and saturation capacity, respectively.

The K_L and q_m values were determined using the following equation to which eq. (5) was transformed.

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \times q_m} \quad (6)$$

The K_L and q_m values were determined from the intercept and slope of the straight line in Figure 6, respectively. The

Freundlich isotherm was used in this study as a second isotherm and is given by the following:

$$Q_e = K_f \times C_e^{\frac{1}{n}} \quad (7)$$

A logarithmic plot linearizes the equation enabling the exponent n and constant K_f to be determined:

$$\log Q_e = \log K_f + \left(\frac{1}{n}\right) \times \log C_e \quad (8)$$

The K_f and $1/n$ values at different concentrations were determined from the slope and intercept of the linear plots of log Q_e and log C_e, respectively. Figure 7 shows a plot of the Freundlich
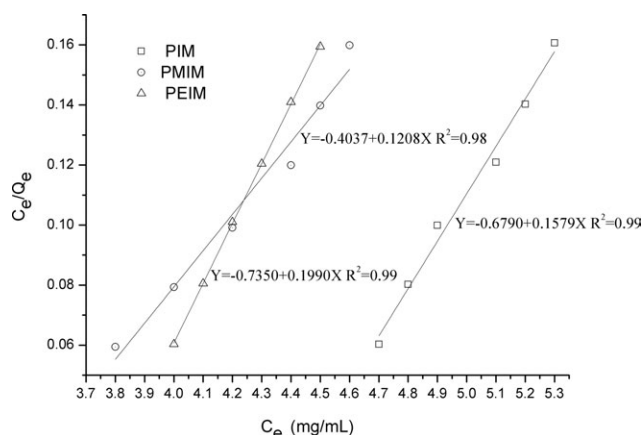

Figure 6. Langmuir isotherm model for lactic acid adsorption on PIM, PMIM, and PEIM.
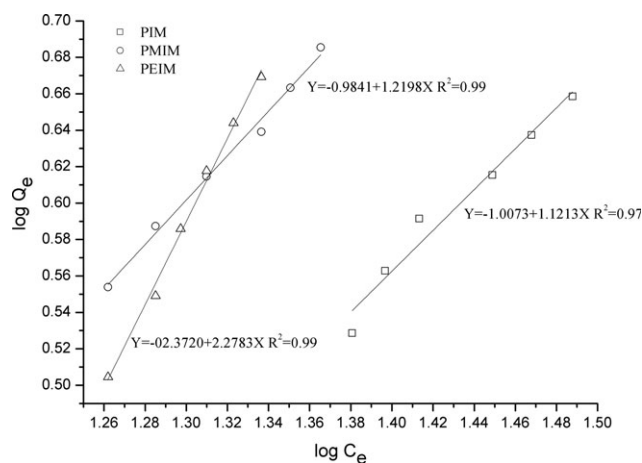
Figure 7. Freundlich isotherm model for lactic acid adsorption on PIM, PMIM, and PEIM.

isotherm for lactic acid adsorption for the three adsorbents. The Temkin isotherm suggests that the heat of adsorption of all molecules in a layer decreases linearly with increasing coverage due to adsorbent–adsorbate interactions. Moreover, adsorption is characterized by a uniform distribution of bonding energies, up to the maximum binding energy. The Temkin isotherm (Figure 8) can be given as

$$Q_e = a \times (\ln A + \ln C_e) \tag{9}$$

The A value is the equilibrium binding constant corresponding to the maximum binding energy, and the constant a is related to the heat of adsorption.

The results show that the Langmuir and Freundlich isotherm fits the experimental data for each polymer with an R^2 value ~0.99. The adsorption equilibrium isotherms for lactic acid on each porous polymer, Q_e, versus the adsorbate liquid concentration at equilibrium, C_e, were fitted to the Langmuir and Freundlich equation. A comparison of the linear correlative coefficients (R^2) of the two models with the Temkin model indicated the Langmuir and Freundlich equation to fit the experimental data better than the Temkin equation.
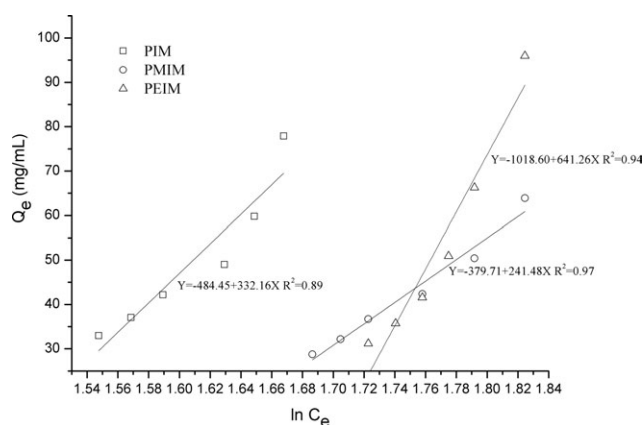

Figure 8. Temkion isotherm model for lactic acid adsorption on PIM, PMIM, and PEIM.

CONCLUSIONS

Three IL-modified porous polymers with a porous surface and large number of functional anions were synthesized. Compared with activated carbon and anion exchanger IR A-92, the synthesized PIM was found to be a more effective adsorbent for the adsorption of lactic acid. The results showed that the adsorption of lactic acid was strongly affected by the surface area of the polymers and the form of lactic acid in solution, and a low temperature condition was advantageous to this process. This type of IL-modified porous polymer highlights the potential for the adsorption of lactic acid from the corresponding fermentation broth.

ACKNOWLEDGMENTS

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