New Modified Poly(ethylene terephthalate) (MPET)-Based Adsorbent for Heavy Metal Ions

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ABSTRACT: Modified poly(ethylene terephthalate) (MPET) samples of both powder and fiber types, which contain sodium 5-sulfodimethyl isophthalate as the third comonomer component, were explored as an adsorbent for the elimination of heavy metal ions, e.g., Cr^{3+}, Pb^{2+}, and Cd^{2+}, in wastewater. The ions were preferentially adsorbed on finer particles at a lower temperature and pH 4 and were exothermically chemisorbed onto the MPETs via an ionic interaction. It was also found that among the ions Cr^{3+} is the most preferentially adsorbed, followed by Pb^{2+} and Cd^{2+} ions and the adsorption capability of MPETs increased considerably with the presence of phenol. The separation factor indicated that the MPET fiber wastes may possibly be reutilized as an economical adsorbent for heavy metal ions in wastewater. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 773–778, 1997

Key words: modified poly(ethylene terephthalate); adsorption; wastewater purification; heavy metal ions

INTRODUCTION

During last few decades, the progress of industrialization has deteriorated the global environment. Consequently, environmental pollution has become one of the major serious problems threatening our daily life. In particular, the presence of heavy metal ions in wastewater may be detrimental to human beings and all living bodies. Many methods have thus been proposed for the removal of heavy metal ions, such as chemical precipitation, activated carbon adsorption, membrane filtration, and ion exchange.[1] The ion exchange method is generally known to be one of the most effective processes. However, it is often unsuitable for the mass removal of heavy metal ions due to the high process cost. Many efforts have consequently been expended to find more effective and economical methods, although anything of importance has not yet been commercialized.

A modified poly(ethylene terephthalate) (MPET) was initially developed for the purpose of manufacturing cation dyeable polyester fibers. In contrast to regular PET, which is condensed from terephthalic acid and ethylene glycol, MPET has a third monomer component of sodium 5-sulfodimethyl isophthalate of which the sodium ion can be replaced with a cation dye molecule or another ionizable element. We noticed that this type of ion-exchange function could commonly be found from ion-exchange chelating resins or fibers.[2] By utilizing such peculiar characteristics of the MPET, it was tempting to explore a possible application as a new and cheap adsorbent material for wastewater purification and precious metal recovery.

In this study, we investigated the adsorption behavior of various heavy metal ions onto the MPET powder and MPET fiber acting as adsorbents, which may be able to ensure more economical removal of heavy metal ions from wastewater. This new approach may also suggest an additional advantage of the reduction of industrial wastes by reutilizing synthetic MPET waste fibers for the purification of wastewater and the recovery of precious metals.

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Table I Characteristics of MPET Samples

Sample code	MPET10	MPET16
Comonomer content	10 wt %	16 wt %
Particle size	0.297–0.355 mm	0.297–0.355 mm
Density	1.33	1.27
Moisture content	20%	25%
Sodium content	0.50 mmol/g	0.56 mmol/g
Intrinsic viscosity	0.394 dL/g	0.319 dL/g

EXPERIMENTAL

Materials

Two types of MPET chips containing 10 wt % (coded as MPET10) and 16 wt % (coded as MPET16) sodium 5-sulfodimethyl isophthalate as a comonomer were supplied from Sun Kyung Industries Co. The MPET fiber wastes, of which the comonomer content is confidential, were used for comparison and for the feasibility test as a practical adsorbent for a continuous wastewater treatment.

The MPET chips were ground into powder, refluxed with ethanol, and then the impurities were scoured off. After drying at 50°C, the powder was kept in a desiccator. A binary mixture of phenol and tetrachloroethane (60 : 40 by weight) was used for measuring the intrinsic viscosity of the MPET chips. The sodium ion content in the MPET was determined with an atomic absorption spectrophotometer (AAS) (Hitachi Z 6100).[3] The characteristics of the MPET samples are listed in Table I.

Adsorption of Heavy Metal Ions

The mixture of 0.2 g of the MPET16 or MPET10 and 100 mL of aqueous $CrCl_3$ (pH 4, 1 mmol/L) or $PbCl_2$ (pH 4, 1 mmol/L) solution was placed in a glass stoppered 100-mL Erlenmeyer flask and then shaken in a water bath maintained at temperatures of 25, 35, and 45°C.[4]

The stock solution containing 1000 ppm of $CrCl_3$ or $PbCl_2$ was prepared to study the adsorption behavior, followed by the dilution with twice distilled water to make a 10–90 ppm solution of $CrCl_3$ (pH 4) or a 50–300 ppm solution of $PbCl_2$ (pH 4). The diluted solutions of various concentrations of $CrCl_3$ or $PbCl_2$ were aliquoted to a glass stoppered 100-mL Erlenmeyer flask to which 0.2 g of the MPET16 or MPET10 was added.[5] The mixture was stirred in a shaking water bath under the same temperature conditions as specified previously. We similarly studied the pH effects of the selected solution, adjusted by adding an adequate amount of HCl or NaOH, and the particle size effect on the adsorption isotherms.

From the solutions containing the same concentrations (1 mmol/L, pH 4) of Cr^{3+}, Pb^{2+}, and Cd^{2+} ions, the preferential ion selectivity was studied. The effect of phenol addition on the adsorption behavior was also studied as a function of phenol concentration.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 shows the adsorption behavior of heavy metal ions onto MPET10 and MPET16 at various

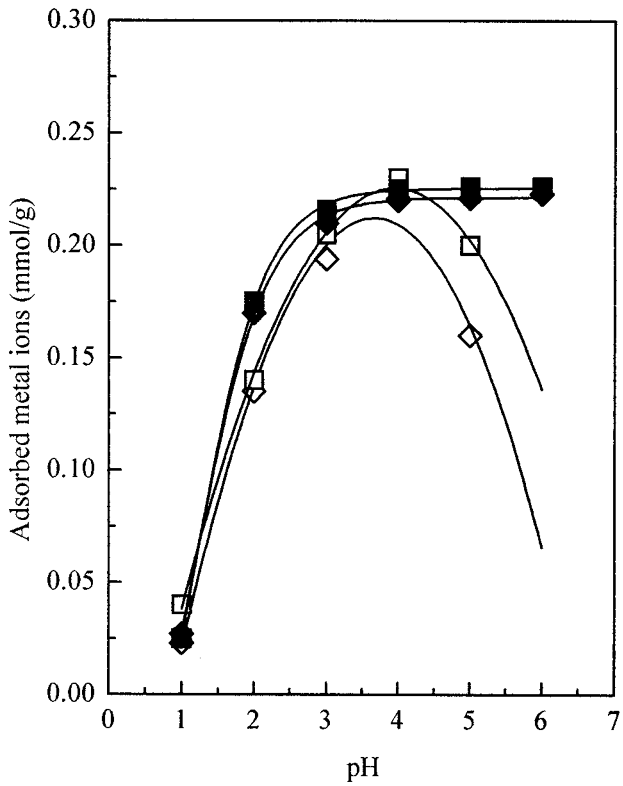

Figure 1 Effect of pH on the adsorptions of Cr^{3+} (blank symbol) and Pb^{2+} (filled symbol) ions onto (□, ■) MPET16 and (◇, ◆) MPET10.

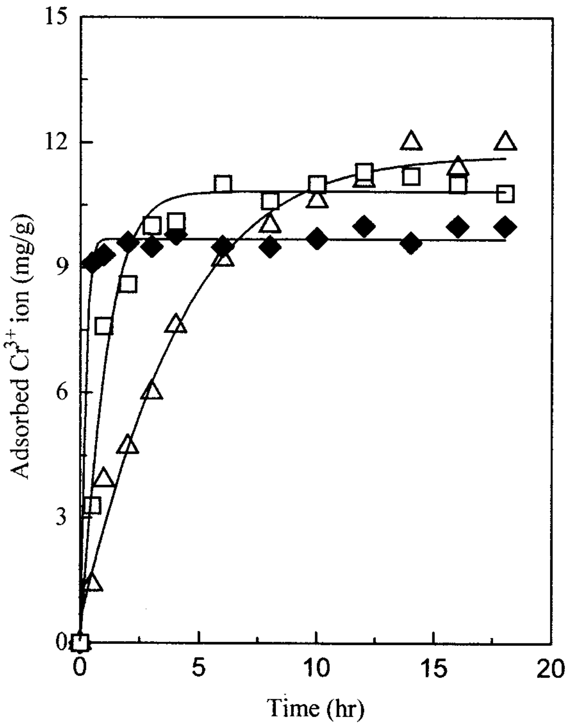

Figure 2 Effect of temperature on the adsorption of a Cr^{3+} ion onto MPET16; (△) 25°C, (□) 35°C, and (♦) 45°C.

pHs. It is obvious from the figure that adsorption is weak under strong acidic conditions because the adsorption is interrupted by the protonation of sodium sulfite groups in the MPETs. With the increase of pH, the adsorption of Pb^{2+} ion increased rapidly up to the equilibrium values, 0.225 mmol/g for MPET16 and 0.223 mmol/g for MPET10. However, in the case of the Cr^{3+} ion, the adsorption decreased above pH 4. This may be attributed to the competition between the precipitation of chromium hydroxide at high pHs and the concurrent adsorption of the Cr^{3+} ion onto the MPETs.[6,7] It may be noted that the adsorption occurred in the Langmuir mode, and a somewhat higher equilibrium value of adsorption was found for MPET16 containing a higher amount of sodium sulfite groups than for MPET10.

Effect of Temperature

The adsorption behaviors of Cr^{3+} and Pb^{2+} ions onto MPET16 are shown in Figures 2 and 3, respectively, as a function of temperatures ranging from 25 to 45°C. Both ions show temperature dependent adsorption behavior in that the equilibration occurs faster and the maximum adsorption concentrations decrease with the temperature rise. It may be expected that at higher temperatures the ions can be adsorbed and concurrently desorbed more actively on the adsorption sites. The kinetic constants (k), calculated from the data for Figures 2 and 3, are related with the temperature by the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

From the plots of ln k versus $1/T$ the apparent activation energies were estimated to be 73.1 kJ/mol for Cr^{3+} ions and 80.7 kJ/mol for Pb^{2+} ions. The high activation energies obviously imply that the adsorption of these metal ions onto MPET is highly influenced by temperature.[8]

Heat of Adsorption

Figures 4 and 5 present the Langmuir-type adsorption isotherms of Cr^{3+} and Pb^{2+} ions, respectively. The adsorption isotherms can be analyzed with eq. (2),

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{kQC_e} \tag{2}$$

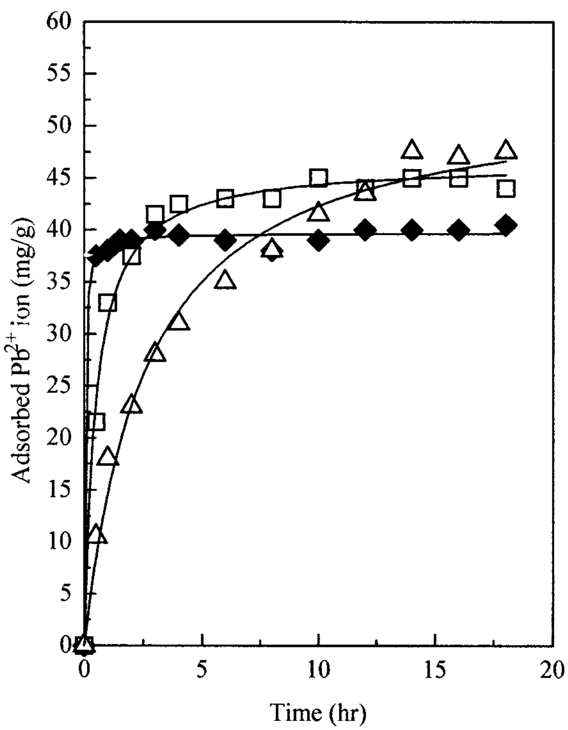

Figure 3 Effect of pH on the adsorption of a Pb^{2+} ion onto MPET16; (△) 25°C, (□) 35°C, and (♦) 45°C.

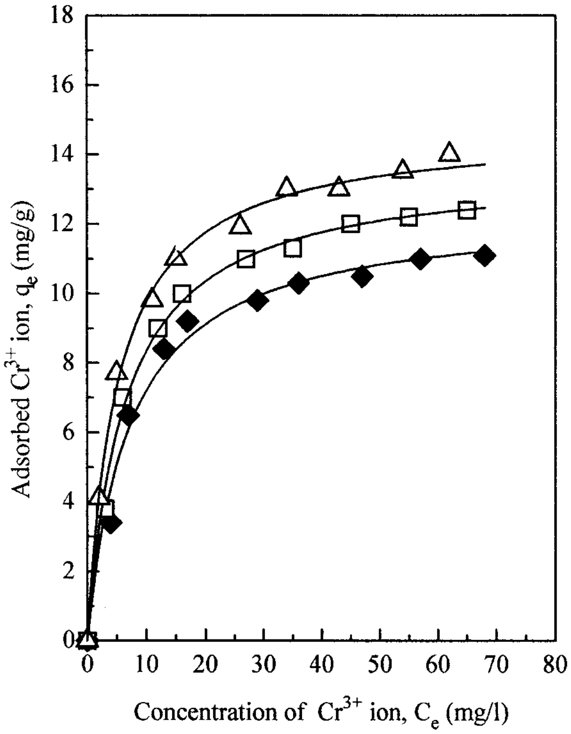

Figure 4 Adsorption isotherms of a Cr^{3+} ion onto MPET16; (△) 25°C, (□) 35°C, and (◆) 45°C.

where C_e is the residual liquid phase concentration at equilibrium, k is a constant related to the intensity of adsorption, q_e is the amount of adsorbate per unit amount of adsorbent for a given concentration, and Q is the solid phase concentration corresponding to complete coverage of available sites.

The slope and the intercept can then be derived from the linear plot of $1/q_e$ versus $1/C_e$, and the ratio of the slope/intercept yields the k value of which logarithms can be plotted as a function of the reciprocal of the temperature (Fig. 6). It is therefore possible to calculate the heat of adsorption using eq. (3),

$$\ln k = \ln k' - \frac{\Delta H}{RT} \quad (3)$$

where k' is a constant related with the adsorption entropy and ΔH is the heat of adsorption. The calculated heats of adsorption, that is, −29.2 kJ/mol for the Cr^{3+} ion and −67.1 kJ/mol for the Pb^{2+} ion, are above −25 kJ/mol, which means that the adsorption is an exothermic chemisorption.[9–11]

Adsorption Selectivity

Table II shows the adsorption selectivity onto the MPETs in the solution containing two or three different kinds of equimolar heavy metal ions. It is apparent that Cr^{3+} ions are most effectively adsorbed onto MPET, followed by Pb^{2+} and Cd^{2+} ions. Although the order of the adsorption affinities for various ions is not unique to any particular adsorbent, it generally increased with increasing atomic valence and atomic number.[12] As can be seen from the order of Pb^{2+} and Cd^{2+} ions, the higher atomic number activated a preferential adsorption of heavy metal ions when the atomic valence was the same. This tendency is in good agreement with other literature results.[13,14]

Effect of Phenol

In the dyeing industry, some carriers of phenol type have been commonly used for improving the dyeability of polyester fabrics. It is widely accepted that the carriers swell the fiber so that the diffusion of dye molecules into the fiber structure can be done more easily.[15] If this is the case, it may be expected that the presence of phenol could also help the diffusion of heavy metal ions inside the MPETs. Figure 7, indeed, shows that the adsorption of the Cr^{3+} ion increases by about 28% for MPET16 and by about 33% for MPET10. This result appears to suggest that numerous adsorp-

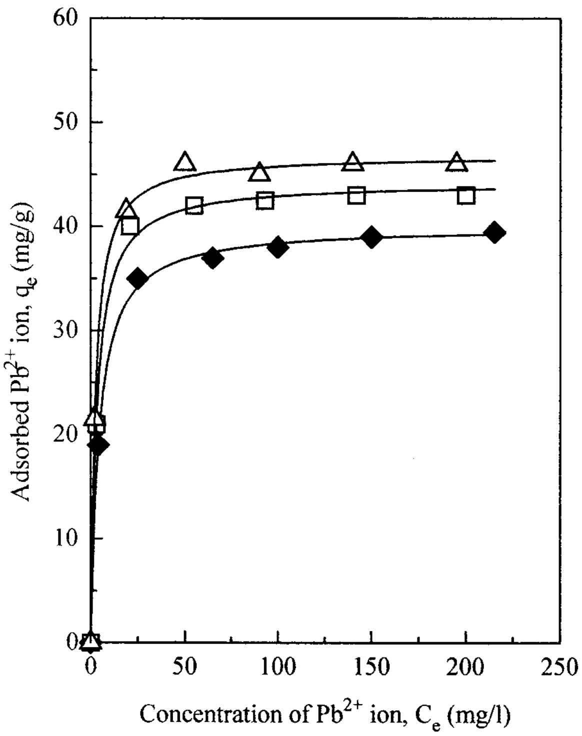

Figure 5 Adsorption isotherms of a Pb^{2+} ion onto MPET16; (△) 25°C, (□) 35°C, and (◆) 45°C.

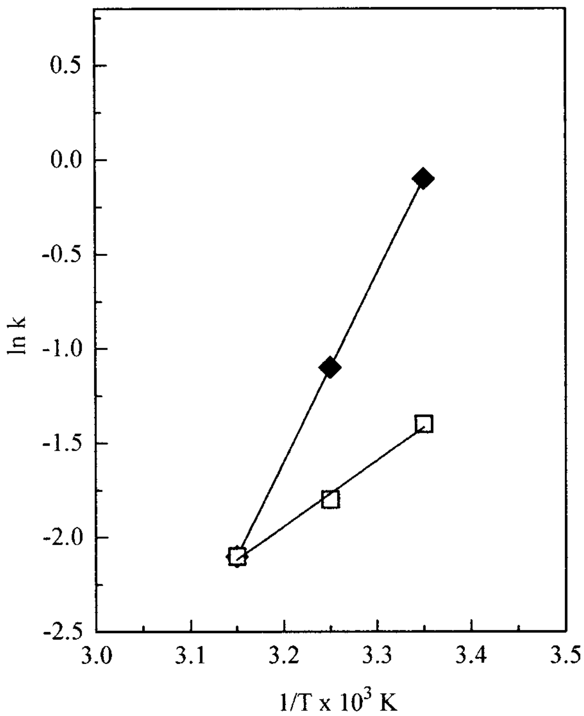

Figure 6 ln k vs. $1/T$ of (◆) Cr^{3+} and (□) Pb^{2+} ions onto MPET16.

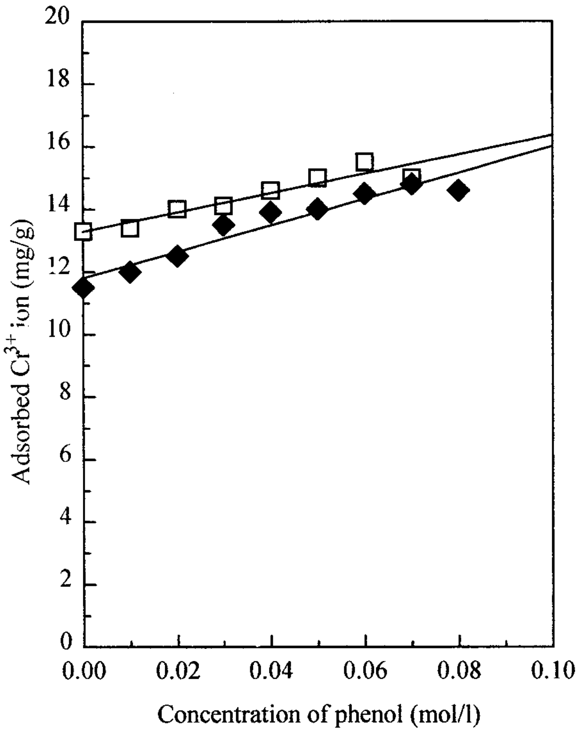

Figure 7 Effect of the phenol addition on the adsorption of a Cr^{3+} ion onto (◆) MPET10 and (□) MPET16.

tion sites remain intact without phenol. However, with the addition of phenol, the intact adsorption sites, the sodium sulfite groups in the MPET chain molecules, can participate in the adsorption process. With this result, it may be possible to conclude that MPET is a useful candidate for an adsorbent of heavy metal ions, especially in wastewater containing phenol species.

Feasibility of MPET Fiber Wastes as an Adsorbent

The adsorption of heavy metal ions was further explored for the MPET fiber wastes. Figure 8 clearly shows that the adsorption isotherm of the Cr^{3+} ion onto the MPET fiber wastes is of the Langmuir type, although the equilibrium concentration is much lower than that of the MPET powder. By using eq. (2) it is possible to linearize the adsorption isotherm of Figure 8 so that the kinetic constant k can be calculated from the slope and the intercept of the plot, $1/q_e$ versus $1/C_e$. It is then possible to estimate the separation factor, R, from eq. (4)

$$R = \frac{1}{(1 + kC_0)} \tag{4}$$

where C_0 is the initial concentration of the heavy metal ions. In general, the separation factor with which it is possible to anticipate a breakthrough curve during an adsorption is a measure of the feasibility of an adsorbent for a continuous separation

Table II Selective Adsorption of Heavy Metal Ions onto MPET

	Sample Code (mmol/g × 10^{-2})	
Ion Mixture	MPET10	MPET16
Cr^{3+} + Pb^{2+}	12.89 + 7.37	13.57 + 7.74
Cr^{3+} + Cd^{2+}	16.62 + 1.56	17.05 + 2.02
Pb^{2+} + Cd^{2+}	15.93 + 1.67	16.53 + 2.40
Cr^{3+} + Pb^{2+} + Cd^{2+}	12.56 + 7.30 + 0.56	13.22 + 7.36 + 1.11

process. When the R reads zero or some value between 0 and 1, it is considered to be a very favorable or favorable adsorbent for an industrial application.[16]

Table III lists the R values of the MPET fiber wastes at various concentrations of the Cr^{3+} ion. All the values read between 0 and 1, which is a promising suggestion that the MPET fiber wastes can be reutilized as a favorable practical adsorbent.

Table III Separation Factor, *R*, of MPET Fiber Wastes

Concn (ppm)	2	5	10	20	30
R	0.8	0.6	0.4	0.3	0.2

CONCLUSION

MPET, which contains sodium 5-sulfo-dimethyl isophthalate as the third comonomer component, was explored as an adsorbent for heavy metal ions such as Cr^{3+}, Pb^{2+}, and Cd^{2+}.

The adsorption behavior of the ions onto MPETs of both the powder and fiber type suggests that the higher adsorption can result from the finer particle, the lower temperature, and pH 4.

The calculated activation energy and the heat of adsorption for the adsorption of the above-mentioned ions indicate that the ions are exothermically chemisorbed onto the MPETs via the ionic interaction. It was also found that, among the ions Cr^{3+} is the most preferentially adsorbed, followed by Pb^{2+} and Cd^{2+} ions.

It is noteworthy in this study that the presence of phenol, which generally exists as a carrier in dyeing process of polyester fabrics, considerably increases the adsorption capability of MPETs. The separation factor, indicative of the feasibility of an adsorbent for a continuous treatment process, suggests that the MPET fiber wastes may possibly be reutilized as economical adsorbents for an industrial process for wastewater purification.

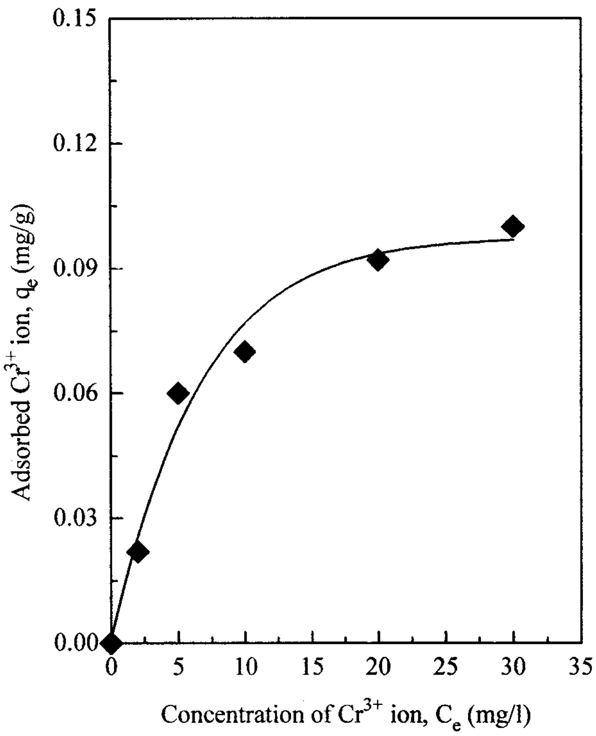

Figure 8 Adsorption isotherm of a Cr^{3+} ion onto MPET fiber wastes.

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