

ORIGINAL ARTICLE

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa www.sciencedirect.com



Preparation of unsaturated polyester Ce(IV) phosphate by plastic waste bottles and its application for removal of Malachite green dye from water samples

Asif Ali Khan^{a,*}, Rais Ahmad^b, Anish Khan^a, Pijush Kanti Mondal^b

^a Analytical and Polymer Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, UP, India

^b Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, UP, India

Received 11 March 2010; accepted 14 October 2010 Available online 20 October 2010

KEYWORDS

Polyethyleneterephthalate; Composite; Characterization; Isotherm; Kinetics; Desorption Abstract In this paper, recycling of polyethyleneterephthalate (PET), a non-biodegradable plastic, was carried out by preparing unsaturated polyester Ce(IV) phosphate (USPECe(IV)P) composite cation exchanger. Various samples of USPECe(IV)P was prepared by mixing different volume ratios of unsaturated polyester in an inorganic Ce(IV) phosphate gel and characterized by TGA/DTA, XRD, SEM, Fourier transform infra-red spectroscopy (FTIR) instrumental methods. The composite has been employed as adsorbents for the removal of Malachite green dye from waste water. The nature of possible adsorbent and dye interaction was examined by the FTIR technique. The adsorption of MG was found to be maximum (98%) at pH 8. The extent of removal of MG was found to be dependent on adsorbent dose, temperature and time. The equilibrium data for adsorption was best represented by the Friendlich isotherm. Thermodynamic parameters (ΔH^0 and ΔG^0) suggest an endothermic and spontaneous process. Kinetic studies show better applicability of an intraparticle diffusion kinetic model.

© 2011 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +91 9897767450. E-mail address: asifkhan42003@Yahoo.com (A.A. Khan).

 $1878\text{-}5352 \ensuremath{\,\odot}$ 2011 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

Peer review under responsibility of King Saud University. doi:10.1016/j.arabjc.2010.10.012



Production and hosting by Elsevier

1. Introduction

Recent development in composite materials offers several outstanding properties as compared to conventional materials. Synthesis of a polymeric inorganic composite received a great deal of attention because it provided new material with special mechanical, chemical, electrochemical, and optical as well as magnetic properties (Chujo, 1996; Sanchez and Ribot, 1994; Judeinstein and Sanchez, 1996). These type of composite materials prepared with electrical conducting polymers have emerged as fascinating materials. Due to a wide range of other desirable properties such as environmental stabilities, ease of fabrication, light weight mechanical properties and so on. Electrical conducting organic-inorganic cation-exchange composite materials are also an advanced class of materials (Fisher et al., 2005) used in various chromatographic studies as well as in making an ion-selective membrane electrode (Khan et al., 2005; Khan and Inamuddin, 2006; Khan et al., 2007, 2008). Synthesis of organic-inorganic composite materials using post consumer waste plastics also created interest for scientists and engineers, because large amount of disposable plastic waste bottles posing environmental problems since they are not biodegradable (Avila and Duarteb, 2003). Recycled polyethylene terephthalate (PET) from post consumer plastic bottles was used for the synthesis of a polymer mortar composite by Mahdi et al. (2007). Encouraging results received the interest to generate organic-inorganic cation-exchange materials using recycled PET from plastic waste bottles. The prepared composite material was used for the separation of heavy metal from water and making an ion-selective electrode (Khan and Khan, 2008).

Dves are widely used in textile, plastic, food, dveing, paper. printing, pharmaceutical and cosmetic industries. Textile processing industries now a days are widespread sectors in developing countries. Among the various processes in the textile industry, the dyeing process uses a large volume of water for dyeing, fixing and washing processes. Thus, the wastewater generated from the textile processing industries contains suspended solids, high amount of dissolved solids, un-reacted dyestuffs (color) and other auxiliary chemicals that are used in the various stages of dyeing and processing. These dyes color the water and make penetration of sunlight to the lower layers impossible and hence are affecting aquatic life. Many of these are toxic or even carcinogenic (McKay et al., 1981). Polluted water not only damages plants and animals, but also harms the environment. Discharge of these into water bodies would pollute the water and, by their toxicity, make it unfit for aquatic life.

Some physical and chemical methods such as filtration, sedimentation, degasification ozonation, coagulation, adsorption, photodegradation and ion exchange are available for the treatment of water. Biological treatment methods like aerobic and anaerobic digestions by microorganisms, mostly bacteria are used in the decomposition of wastewaters to stable end products. There are tones and tones of effluents being released every single day and the most effective removal technique is out to be grabbed. Currently sorption process is also proved to be an effective process for the removal of pollutants from wastewaters.

In the following research paper, unsaturated polyester Ce(IV) phosphate (UPECe(IV)P) was synthesized using recycled PET obtained from waste plastic bottles and used as a adsorbent for the removal of Malachite green from waste water. Further studies on dc electrical conductivity will be carried out by doping process in the next paper.

2. Materials and methods

2.1. Reagents

Soft drink waste bottles of PET were obtained in the form of beverage bottles from the City of Aligarh; UP; India. After the removing of caps and labels, the bottles were shredded to sizes of approximately 1.5–3.0 cm. The shredded PET was

washed by tap water and dried at room temperature. The adhesives on the bottles were not purposely removed, most of them still remained. Cerric sulphate and disodiumhydrogenphosphate, zincacetate, maleic and phthalic anhydride, Malachite green [4-[(4-dimethylaminophenyl)-phenyl-methyl]-*N*,*N*-dimethyl-aniline] were obtained from CDH and Qualigens (India Ltd.) and were used as received. All other chemicals used were of analytical reagent grade and supplied by CDH India.



Structure of Malachite green [4-[(4-dimethylaminophenyl)-phenyl-methyl]-*N*,*N*-dimethyl-aniline].

2.2. Instruments

The following instruments were used in the experimental work: a FTIR spectrophotometer (Perkin Elmer, USA, model Spectrum-BX); digital pH-meter (Elico Li-10, India); X-ray diffractometer – Phillips (Holland), model PW 1148/89; UV/Vis spectrophotometer – Elico (India), model EI 301E; a thermal analyzer – V2.2A DuPont 9900; an elemental analyzer – Elementary Vario EL III, Carlo-Erba, model 1108; an electronic balance (digital, Sartorius-21OS, Japan). T70-UV/Vis spectrophotometer (PG Instrument Ltd., UK); scanning electron microscope (LEO 435 VP) and transmission electron microscope (Philips EM-400).

3. Preparation of materials

3.1. Glycolysis experiment

The conversion of polyethylene terephthalate (PET) in the presence of glycol is known as alcoholyses or glycolysis in the presence of a catalyst. One-litre three-necked round bottomed flask (reactor) was used for all glycolysis experiments. In order to ensure that the moisture content in the reactor was as low as possible, the reactor was heated up to 100 °C and held at that temperature for at least 5 min. The reactor was equipped with a thermometer and a reflux condenser. A magnetic stirrer was put in the reactor to ensure proper mixing. The ratio of diethylene glycol to PET used in the glycolysis experiment was 4:1 by weight i.e. the weight of diethylene glycol and PET flakes were 84 and 21 g, respectively. Glycolysis temperature was set at 190 °C and glycolysis time was 2 h and the amount of the catalyst was fixed 0.25% by weight of PET.

3.2. Synthesis of unsaturated polyester (UPE)

After glycolysis, the maleic and phthalic anhydrides were added into the reactor for non-catalyzed melt polyesterification reaction. The reaction was carried out at 190 °C for 8 h, and 0.5% hydroquinone by weight of PET was added to check the back depolymerization. The slurry was allowed to cool at room temperature.

3.3. Preparation of Ce(IV) phosphate

The method of preparation of the inorganic precipitate of Ce(IV) phosphate ion-exchanger was very similar to that of De and Chowdhury (1974) with a slight modification (Khan et al., 2007). A solution of 0.1 M Ce(SO₄)₂·4H₂O prepared in 1 M H₂SO₄ was mixed in different molar solutions of H₃PO₄ and the pH was maintained at 1. Yellowish gel type slurries obtained were kept for 24 h at room temperature.

3.4. Preparation of unsaturated polyester Ce(IV) phosphate composite cation exchanger

The composite cation-exchanger was prepared by the sol-gel mixing of unsaturated polyester (UPA) and Ce(IV) phosphate inorganic material. In this process when the gels of unsaturated polyester were added to the white inorganic precipitate of cerrium(IV) phosphate with a constant stirring at room temperature, the resultant mixture was turned slowly into white colored slurries. The resultant white colored slurries were kept for 24 h at room temperature.

Now the unsaturated polyester based composite cation-exchanger gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering traces. The washed gels were dried over P_4O_{10} at 30 °C in an oven. The dried products were immersed in DMW to obtain UPECe(IV)P as granules. They were converted to the H⁺ form by keeping it in 1 M HNO₃ solution for 24 h with occasional shaking intermittently replacing the supernatant liquid. The excess acid was removed after several washings with DMW. The material was finally dried at 40 °C and sieving to obtain particles of a particular size range of ~125 µm. Hence a number of unsaturated polyester Ce(IV) phosphate composite cation-exchanger samples were prepared and on the basis of Na⁺ exchange capacity (IEC), a percent of the yield sample S-2 (Table 1) was selected for further studies.

4. Adsorption studies

Adsorption studies were carried out by batch process. In batch process 0.1 g of the adsorbent (unsaturated polyester Ce(IV) phosphate) was placed in a conical flask in which 100 mL solution of MG of the desired concentration (50, 80 and 100 ppm) was added and the mixture was shaken in a temperature controlled shaker incubator for 30 min at 200 rpm. The mixture was then filtered using Whatman filter paper No. 40 and the final concentration of dye was determined in the filtrate by UV–Vis spectrophotometer (Elico, SI-164).

5. Results and discussion

5.1. Characterization

Various samples of organic–inorganic composite unsaturated polyester Ce(IV) phosphate cation-exchange material have been developed by the incorporation of unsaturated polyester into the inorganic matrices of Ce(IV) phosphate. Due to high percentage of yield, better ion-exchange capacity, reproducible behaviour, chemical and thermal stability, sample S-1 (Table 1) was chosen for detailed studies. The exchanger possessed a better Na⁺ ion-exchange capacity (3.62 meg g⁻¹) as compared to an inorganic precipitate of amorphous Ce(IV) phosphate (1.14 meg g⁻¹).

It is clear from the thermogravimetric analysis (TGA) curve (Fig. 1) of the material that up to 85 °C only 5% weight loss was observed, which may be due to the removal of external H₂O molecules present at the surface of the composite (Duval, 1963). Further weight loss of mass approximately 6.5% between 100 and 200 °C may be due to the slight conversion of inorganic phosphate into pyrophosphate. Slow weight loss of mass about 7.5% in between 200 and 700 °C may be due to the slight decomposition of the organic part of the material. A broad peak at ~90 and 550 °C in DTA curve shows that the reaction is exothermic during the change of phase of material.

The X-ray diffraction pattern of this material (S-1 as prepared) recorded in powdered sample exhibited some small

Samples	Mixing volume ratios (mL)		Glycolysis of PET				Polyesterification after glycolysis		Ion-exchange capacity (meg ⁻¹)	
	$\frac{\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}}{\text{in 1 M H}_2\text{SO}_4}$	H ₃ PO ₄	PET (g)	DEG (mL)	Heating time (h)	Heating temperature (°C)	MA (g)	PthA (g)		
S-1	100	100 (2 M)	1	10	4		0.5	0.5	3.62	
S-2	50	50 (2 M)	2	15	4	85	1	1	2.7	
S-3	250	100 (2 M)	3	15	4	85	1	1	2.3	
S-4	100	100 (2 M)	_	-	_	-	_	-	1.14	
S-5	75	75 (2 M)	4	20	4	85	1.5	1.5	1.58	
S-6	75	125 (1 M)	5	25	4	85	2	2	1.69	
S-7	_	-	1	10	4	85	0.5	0.5	0.17	
S-8	125	100 (4 M)	6	30	4	85	2.5	2.5	1.06	

 Table 1
 Conditions of preparation and ion-exchange capacity of unsaturated polyester Ce(IV) phosphate composite cation exchanger

PET = polyethylenetrephthalate.

DEG = diethyleneglycol.

MA = maleic anhydride.

PthA = phthalic anhydride.



Figure 1 Simultaneous TGA–DTA curves of unsaturated polyester Ce(IV) phosphate as prepared.

peaks in the spectrum, which suggest the semi-crystalline nature of the composite material.

The scanning electron microphotograph (SEM) of unsaturated polyester Ce(IV) phosphate composite, unsaturated polyester and Ce(IV) phosphate are represented in Fig. 2. Small and big flakes are seen in the unsaturated polyester Ce(IV) phosphate composite cation exchange material. Thus the morphology of the material has been changed with the formation of organic inorganic composite material unsaturated polyester Ce(IV) phosphate after adhesion of organic polymer (UPE) with inorganic precipitate Ce(IV) phosphate.

FTIR spectrum of the composite (Fig. 3) shows the twisting and wagging vibration frequencies of the methylene group in the region of 1300–1200 cm⁻¹ (Rao, 1963). The vibration frequency at 1700 cm⁻¹ shows an aromatic ring. A small peak in the region of 1600 cm⁻¹ may be due to the presence of a carbonyl group of the composite. A peak at \sim 3000 cm⁻¹ shows the presence of –CH stretching vibration frequency of a benzene ring in the plane while 600 cm⁻¹ show –CH out of the plane deformation vibration frequency of the benzene ring.

Carbon, hydrogen, oxygen, phosphorus and cerium contents of the material were determined by different methods



Figure 2 SEM photographs of unsaturated polyester Ce(IV) phosphate (a), unsaturated polyester (b) and Ce(IV) phosphate (c).



Figure 3 FTIR spectra of unsaturated polyester Ce(IV) phosphate before (a) and after (b) adsorption of MG dye.

of analysis. The percent composition of C, H, O, P and Ce was found to be 14.58%, 1.30%, 46.36%, 11.58%, 26.16% and a tentative molecular formula of the composite is: $C_{12}H_{10}O_5$ ·Ce(IV)(PO₄)(HPO₄)_{0.5}(H₂O)_{0.5}.

5.2. Nature of the adsorption by FTIR technique

Change in the FTIR spectra after the adsorption of MG on the surface of UPECe(IV)P can be seen in Fig. 3. The vibration frequencies of the methylene group in the region of $1300-1200 \text{ cm}^{-1}$ are not clear due to adsorption of MG in the matrices of composite material. However a sharp band at 1086 cm^{-1} represents C–OH stretching vibrations which also signify the involvement of dye on the surface of UPECe(IV)P.

5.3. Effect of contact time with different concentration

Adsorption studies were carried out to determine the uptake rates of MG on the adsorbent and to get access to the equilibrium times. The evolution of MG removal with time by UPE-Ce(IV)P for different initial MG concentrations was first studied (Fig. 4), indicating that the equilibrium time is in the 30–35 min range for all MG initial concentrations. More then 90% adsorption of Malachite green (MG) was observed on the surface of unsaturated polyester Ce(IV) phosphate [UPE-Ce(IV)P] composite cation exchange material. It may be due to the interaction between the anionic group present in the matrices of the composite cation exchanger and hydrochloric acid in MG.

5.4. Effect of pH

The effect of pH for the adsorption of MG on the UPE-Ce(IV)P from aqueous solution. It was observed that the MG adsorption was highly dependent on the pH of the solution which affected the surface charge of the UPECe(IV)P and the degree of ionization of the adsorbate. It was found that an increase in the solution pH led to an increase in the MG adsorption efficiency. The percent adsorption of MG increased from 71% to 98% by varying the solution pH from



Figure 4 Effect of contact time with different concentration.

2 to 10. At lower pH, more protons were available (excess H^+ ions), thereby decreasing the electrostatic attractions between positively charged dye anions and positively charged adsorption sites of the cation exchanger and therefore ionic repulsion between the positively charged surface and the cationic dye molecules caused a decrease in MG adsorption. The adsorption of MG was found to be maximum (98%) at pH 8, thus all the experiments were performed at pH 8.

5.5. Effect of temperature and thermodynamic parameters

The effect of temperature on adsorption of MG on the UPE-Ce(IV)P was investigated by varying the adsorption temperature at 20–40 °C. The thermodynamic parameters such as standard enthalpy (ΔH^0), standard entropy (ΔS^0) and standard free energy (ΔG^0) were calculated by using the following equations (Wang and Zhu, 2007):

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{1}$$

where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_d is the distribution coefficient which can be calculated as:

$$K_d = \frac{C_{Ae}}{C_e} \tag{2}$$

where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration.

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plots of ln K_d versus 1/T and ΔG^0 can be calculated using the relation below:

$$\Delta G^0 = -RT\ln K_d \tag{3}$$

The calculated values of ΔH^0 , ΔS^0 and ΔG^0 are listed in Table 2. The positive value of ΔH^0 indicates the endothermic nature of the adsorption interaction. The positive value of ΔS^0 showed the increased disorder at the solid/solution interface during the adsorption of MG on the UPECe(IV)P. The positive values of ΔS^0 show the randomness at the solid–solution interface. The negative value of ΔG^0 indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of MG onto the UPECe(IV)P.

Table 2	Thermodynamic pa	rameters for a	dsorption.
Temperat	ture (°C) ΔG^0 (kJ mol	$^{-1}$) ΔH^0 (kJ mo	ΔS^0 (kJ mol ⁻¹)
20	-2.66	48.195	0.165
30	-1.13	48.195	0.165
40	-0.86	48.195	0.165

5.6. Adsorption isotherms

Langmuir isotherm (Langmuir, 1918) is based on an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent and the monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{4}$$

where C_e is the equilibrium concentration of adsorbate (mg/L); q_e the adsorption capacity (mg/g); b and q_m are the Langmuir constants. The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e . The coefficient b in Langmuir equation is a measure of the stability of the complex formed between dye and adsorbent under specified experimental conditions.

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter (R_L) , which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant. The value of R_L calculated from different initial concentrations is reported in Table 3. The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Ahmad and Mondal, 2009). The R_L for MG is 0.476. The values are in between 0 and 1 showing favourable adsorption on UPECe(IV)P.

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The wellknown linear form of Freundlich isotherm (Freundlich, 1906) is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants with n giving an indication of how favourable the adsorption process. K_f (mg/g) is the adsorption capacity of the adsorbent which

can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto UPECe(IV) for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu, 1998). A value for 1/n below one indicates a normal Langmuir isotherm. While 1/nabove one is indicative of cooperative adsorption (Fytianos et al., 2000). The plot of $\log q_e$ versus $\log C_e$ (Fig. 5) gave a straight line with slope of 1/n whereas K_f was calculated from the intercept value.

Table 3 summarizes all the constants, correlation coefficients, R^2 values obtained for the two isotherm model for adsorption of MG on the UPECe(IV)P. The Freundlich model yielded the best fit at, as the R^2 values were relatively high close to unity.

5.7. Adsorption kinetics

Kinetics of adsorption are quite significant as it decides the residence time of adsorbate at solid–solution interface and helps in determining the rate of adsorption process. The adsorption of dyes from the liquid to solid phase can be considered as a reversible reaction with equilibrium established between the two phases. The kinetics of adsorption of MG on the UPE-Ce(IV)P was studied by applying three different kinetic models. The linear form of pseudo first-order equation given by Langergren and Svenska (1998) is shown by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e and q_t are the amounts of MG adsorbed (mg/g) at equilibrium and at time t (h), respectively, and k_1 is the rate constant adsorption (1/h). Values of k_1 were obtained from the slopes of the linear plots of $\ln(q_e - q_t)$ versus t.



Figure 5 Freundlich plot for the adsorption of MG on unsaturated polyester Ce(IV) phosphate.

Table 3	Langmuir and Freundlich constant for the adsorption of MG.							
Dye	Langmuir constan	Langmuir constant				Freundlich constant		
	$q_m ({ m mg/g})$	b (L/mg)	R^2	R_L	$K_f (mg/g)$	п	R^2	
MG	1.01	0.022	0.97	0.476	44.85	1.006	0.99	

On the other hand, the linear form of pseudo-second-order equation (Ho and McKay, 2000) based on equilibrium adsorption is expressed as:

$$\frac{t}{qt} = \frac{1}{k_2 q^2 e} + \frac{1}{qe}t\tag{8}$$

where k_2 (g/mg h) is the rate constant of second-order adsorption. If second-order kinetic is applicable, the plot of t/q_t versus t should show a linear relationship. Values of q_e and k_2 can then be determined from the slope and the intercept of the plot. This procedure is more likely to predict the behaviour over the whole range of adsorption.

The kinetic parameter for intraparticle diffusion was determined using the following equation (Weber and Morris, 1963):

$$q_t = k_{int} t^{1/2} + C (9)$$

where *C* was the intercept and k_{int} was the intraparticle diffusion rate constant (mg/g min^{-1/2}). The plot may present multilinearity, indicating that three steps take place. Fig. 6 shows the first, sharper portion was attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion was the rate limiting step (Ayyappan et al., 2005) and the third portion was attributed to the final equilibrium stage.

Table 4 summarizes the rate constants and correlation coefficients, R^2 of the three kinetic models for this adsorption process. The correlation coefficients, R^2 values were obtained from the three kinetic models. The intraparticle diffusion model yielded the best fit at, as the R^2 values were relatively high (0.98) close to unity.

5.8. Desorption studies

Desorption studies help to elucidate the nature of adsorption recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye on the adsorbent is weakly bonded. Sodium hydroxide and sulphuric acid (1 M) did not show any desorption but a weak acid, like acetic acid (5 M) solubilized about 65.23% of pure MG from the spent adsorbent (Fig. 7). Desorption of dye in acetic acid indicates that Malachite green



Figure 6 Representation of the kinetic data by intraparticle diffusion.

Table 4 Kinetic parameters on the adsorption of MG ontounsaturated polyester Ce(IV) phosphate.

	Malachite green
Pseudo-first-order equation	
$q_e (mg/g)$	72.27
$k_1 (\times 10^2 \mathrm{min}^{-1})$	0.0539
R^2	0.8576
Pseudo-second-order equation	
$q_e (\mathrm{mg/g})$	136.986
k_2 (g/mg min)	0.0005
R^2	0.931
Intraparticle diffusion equation	
$k_{int} (\mathrm{mg/g min}^{1/2})$	17.077
С	0.1364
R^2	0.9804



Figure 7 Desorption studies of MG adsorbed unsaturated polyester Ce(IV) phosphate by using 5 M acetic acid as an eluent.

dye is adsorbed onto UPECE(IV) through chemisorptions mechanism and very little desorption of the dye in acid or base confirms the strong affinity of dye on the UPECe(IV)P.

6. Conclusion

In the present study recycling of non-biodegradable post consumer waste plastic bottles of polyethylene terephthalate (PET) is carried out by preparing organic-inorganic composite cation exchanger, unsaturated polyester Ce(IV) phosphate, having excellent cation exchange capacity $(3.62 \text{ meg g}^{-1})$ as compared to inorganic precipitate of amorphous Ce(IV) phosphate $(1.14 \text{ meg g}^{-1})$ having double environmental pollution remediation. The present investigation showed that the adsorption process was very fast, and it reached equilibrium in 30 min of contact, which is much faster than that of the other adsorbents for the removal of dye from waste water. The adsorption studies indicate that Freundlich model is better obeyed. Thermodynamic parameters (ΔH^0 and ΔG^0) suggest that adsorption process is endothermic and spontaneous. The kinetics data are best fitted in intraparticle diffusion rate equation as is evident from the value of regression coefficients (R^2) . The maximum efficiency of UPECe(IV)P has been demonstrated by eluting MG from UPECe(IV)P and it has been found that 65% MG could be recovered when 5 M acetic acid was used as eluent. It is concluded that UPECe(IV)P is an effective cation exchanger and can be utilized for the removal and recovery of MG from wastewater.

Acknowledgements

The authors are thankful to the Chairman, Department of Applied Chemistry, Z.H. College of Engineering and Technology, A.M.U. (Aligarh) India for providing research facilities, and also to the Council of Scientific and Industrial Research of India (CSIR) for financial supports.

References

- Ahmad, R., Mondal, P.K., 2009. Application of acid treated almond peel for removal and recovery of brilliant green from industrial wastewater by column operation. Sep. Sci. Technol. 44, 1638–1655.
- Avila, A.F., Duarteb, M.V., 2003. A mechanical analysis on recycled PET/HDPE composites. Polym. Degrad. Stab. 80, 373–382.
- Ayyappan, R., Sophia, A. Carmalin, Swaminathan, K., Sandhya, S., 2005. Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes. Process Biochem. 40, 1293–1299. Chujo, Y., 1996. Curr. Opin. Solid State Mater. Sci. 1, 806.
- De, A.K., Chowdhury, K., 1974. Studies on thorium phosphate ionexchanger: synthesis, properties and ion-exchange behaviour of thorium phosphate. J. Chromatogr. 101, 63–72.
- Duval, C., 1963. Inorganic Thermo Gravimetric Analysis. Elsevier, Amsterdam, p. 315.
- Fisher, A.S., Goodal, P.S., Hinds, M.W., Penny, D.M., 2005. J. Anal. Atom. Spectrom. 20, 1398.
- Freundlich, H.M.F., 1906. Over the adsorption in solution. J. Phys. Chem. 57, 385–470.
- Fytianos, K., Voudrias, E., Kokkalis, E., 2000. Sorption–desorption behavior of 2,4-dichloriphenol by marine sediments. Chemosphere 40, 3–6.

- Haghseresht, F., Lu, G., 1998. Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. Energy Fuels 12, 1100–1107.
- Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res. 34, 735–742.
- Judeinstein, P., Sanchez, C., 1996. J. Mater. Chem. 6, 511.
- Khan, A.A., Inamuddin, 2006. Sens. Actuators B; Chem. 120, 10.
- Khan, A.A., Khan, A., 2008. In: Sorial, Georj A., Hong, Ghua (Eds.). In: Proceedings from the Fourth International Conference on Environment Science and Technology, vol. II. American Science Press, Houston, USA, pp. 45–52.
- Khan, A.A., Inamuddin, Alam, M.M., 2005. React. Funct. Polym. 63, 19.
- Khan, A.A., Khan, A., Inamuddin, 2007. Talanta 73, 850.
- Khan, A.A., Inamuddin, Akhtar, T., 2008. Organic–inorganic composite cation exchanger; poly-o-toluidine Zr(IV) phosphate based ion-selective membrane electrode for the potentiometric determination of mercury. Anal. Sci. (Jpn. Soc. Anal. Sci.) 24, 881–887.
- Langergren, S., Svenska, B.K., 1998. Zur theorie der sogenannten adsorption geloester stoffe. Veternskapsakad Handlingar 24 (4), 1–39.
- Langmuir, L., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1402.
- Mahdi, F., Khan, A.A., Abbas, H., 2007. Physiochemical properties of polymer mortar composites using resins derived from postconsumer PET bottles. Cem. Concr. Compos. 29, 241–248.
- McKay, G., Allen, S.I., McConvey, I.F., Otterburn, M.S., 1981. Transport process in the sorption of colored ions by peat particles. J. Colloid Interface Sci. 80 (2), 323–339.
- Rao, C.N.R., 1963. Chemical Applications of Infrared Spectroscopy. Academic Press, New York.
- Sanchez, C., Ribot, F., 1994. New J. Chem. 16, 1007.
- Wang, S., Zhu, Z.H., 2007. Effects of acidic treatment of activated carbons on dye adsorption. Dyes Pigments 75, 306–314.
- Weber Jr., W.J., Morris, J.C., 1963. Kinetics of sorption of carbon from solution. J. Saint. Eng. Div. Am. Soc. Civil Eng. 89, SA2– SA31.