Adsorption of 4-nitrophenol onto Amberlite® IRA-900 modified with metallophthalocyanines

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Abstract

The adsorption of 4-nitrophenol using commercially available Amberlite® IRA-900 modified with metal phthalocyanines (MPc) was investigated. The metallophthalocyanines immobilised onto the surface of Amberlite® IRA-900 include Fe (FePcS$_4$), Co (CoPcS$_4$) and Ni (NiPcS$_4$) tetrasulphophthalocyanines, and differently sulphonated phthalocyanine mixtures of Fe (FePcS$_{mix}$), Co (CoPcS$_{mix}$) and Ni (NiPcS$_{mix}$). Adsorption rates were fastest for the modified adsorbents at a loading of 1×10^{-3} g MPc/g Amberlite, at pH 9. The highest amount of 4-NP removal was obtained on FePcS$_{mix}$ modified Amberlite® IRA-900 with $Q_t = 42.9$ mmol g^{-1} and adsorption efficiency of 86%. The recovery efficiency of 4-NP within 150 min was 76%. Using the Langmuir–Hinshelwood kinetic model, the complexes showed an order of 4-nitrophenol adsorption to be as follows: CoPcS$_{mix}$ > NiPcS$_4$ > NiPcS$_{mix}$ > FePcS$_4$ > FePcS$_{mix}$ > CoPcS$_4$. The MPc modified Amberlite® IRA-900 was used repeatedly, following removal of 4-NP by nitric acid, without any significant loss of activity.
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1. Introduction

The presence of phenolic compounds in waste effluent streams is of growing concern, due to their relative toxicity. Nitrophenols are of interest, as they are listed as priority toxic pollutants by the United States Environmental Protection Agency [1]. Their removal from surface water and groundwater is hindered due to their high stability and solubility in water as well as their resistance to traditional water purification methods [2]. Methods that have been developed for the removal of nitrophenols from water include microbial degradation and chemical oxidation. Slow reaction rates, disposal of sludges, and control of temperature and pH are all drawbacks associated with microbial degradation, while chemical oxidation is only economically feasible at high pollutant concentrations [2,3]. We have recently reported on the photodegradation of 4-nitrophenol (4-NP) using metallophthalocyanines (MPcs) as homogeneous photocatalysts. This study resulted in the degradation of the catalyst [4], hence MPc complexes are being employed as het-

erogeneous absorption catalysts in this work. Also it is important to re-use the catalyst hence heterogeneous adsorption is preferred. 4-NP was selected for this study, as it is produced in the highest quantities worldwide and has a higher toxicity compared to the other mononitrophenols [1]. 4-NP is used commercially to manufacture pharmaceutical drugs, pesticides such as nitrofen and parathion, and dyes to darken leather. Consequently the photodegradation of pesticides such as nitrofen and parathion results in the release of 4-NP into the environment [1].

Polymeric adsorbents have been employed for the removal and recovery of phenolic compounds from aqueous solutions [5–9]. They have replaced activated carbon in solid phase extraction due to their regenerability, cost-effectiveness and greater mechanical strength. They are also more varied in functionality, surface area and porosity [10,11]. Most commonly employed polymeric adsorbents include Amberlite® XAD and NDA series [5–9]. The macroreticular adsorbent used in this study is Amberlite® IRA-900. Prior to this work, solid phase extraction of phenols has not been reported for macroreticular adsorbents such as Amberlite® IRA-900. Phenol complexes attach directly to Amberlite® IRA-900 resin by forming hydrogen bonds between the tertiary ammonium groups of the resin (proton acceptors) and the hydroxyl group of the phenolic com-

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pound (proton donor). Attachment is also possible through π–π interactions between the aromatic ring of the phenolic complex and the phenyl ring on the divinylbenzene matrix of Amberlite® IRA-900 [6]. As well as modification of the adsorbent, the phenol derivatives can be modified to improve adsorption efficiency. Phenols are usually converted to less polar phenyl acetates for chromatographic analyses [12–14]. Moreover, acetylation can be carried out in situ in the water samples before the extraction step. Acetylation of 4-NP resulted in 11% efficiency in hexane and 85% efficiency in toluene [13]. Even though derivatization of phenols has resulted in high efficiencies depending on solvents, direct extraction without prior derivatization as presented in this work has advantages.

Porphyrins have been employed for the modification of Amberlite® XAD resins for the extraction of phenol and chlorophenols. Higher recoveries of the phenolic compounds were achieved for the modified resins due to an increase in π–π interactions between the adsorbent and adsorbate [15]. MPcs were employed in this study for the modification of Amberlite® IRA-900. MPcs have a more complex macroporous structure than porphyrins, resulting in increased opportunity for π–π interactions between phenols and the ring structure of MPcs. The MPcs used are iron, cobalt and nickel tetrasulfophthalocyanine (FePcS$_4$, CoPcS$_4$ and NiPcS$_4$, respectively), as well as MPcs containing a mixture of differently sulphonated derivatives (FePcS$_{mix}$, CoPcS$_{mix}$ and NiPcS$_{mix}$, respectively) (Fig. 1a).

The MPcs adsorb onto the surface of Amberlite® IRA-900 through electrostatic interaction between the sulfonato groups of the MPc complex and tertiary ammonium groups of the macroreticular adsorbent [16] (Fig. 1b). The aforementioned MPcs were used since the metal centre has the potential to bind ionically to the phenolate ion of 4-NP in basic media, thus increasing the opportunity for attachment of 4-NP to the modified resin, through axial ligation, thus enhancing 4-NP removal.

The objective of this study is to use the MPc modified Amberlite® IRA-900 resin for the removal and recovery of 4-NP from aqueous solution, and compare the rate of adsorption of 4-NP on bare Amberlite® IRA-900 with rates obtained using modified Amberlite® IRA-900.

2. Experimental

2.1. Materials

4-Nitrophenol was obtained from BDH Chemical Co., UK. Amberlite® IRA-900 ion-exchange resin was purchased from Aldrich and used as received. Acetonitrile, for immobilisation of the MPc complexes onto Amberlite® IRA-900, was purchased from Aldrich. FePcS$_4$, CoPcS$_4$ and NiPcS$_4$ were synthesized, purified and characterized according to the Weber and Busch method [17]. Briefly, the method involves heating a metal salt, 4-sulfophthalic acid, urea and a catalyst (ammonium molybdate) in nitrobenzene. The crude product is purified by washing with methanol and further treatment with HCl, NaCl and NaOH [17]. FePcS$_{mix}$, CoPcS$_{mix}$ and NiPcS$_{mix}$ complexes were synthesized from FePc, CoPc and NiPc respectively, using fuming sulphuric acid (30% SO$_3$) according to the established procedure [18]. MPc complexes were either purchased from Aldrich or synthesized, purified and characterized using literature methods [19]. Phosphate buffers were prepared using reagent grade potassium dihydrogen orthophosphate (ACE Chemicals) and dipotassium phosphate (PAL Chemicals). All analyses were performed in ultra-pure water (Milli-Q Water System, Millipore Corp., Bedford, MA, USA) at $25 \pm 1\,°C$. All studies were monitored using a Cary 500 UV–vis/NIR spectrophotometer. The MPcS$_{mix}$ complexes were characterized using Quad-Gradient Agilent 1100 series high performance liquid chromatography (HPLC) fitted with an analytical Prodigy 5 μ ODS (150 mm × 4.6 mm) column. The mobile phase consisted of 70:30 water:acetonitrile mixture.

2.2. Equipment and procedures

2.2.1. Immobilisation of metallophthalocyanines

The Amberlite® IRA-900 resins modified with the various metallophthalocyanines (referred to as MPc-Amb) were prepared according to the reported literature procedure [20] as follows: the MPcs were mixed with the resin in a 40 mL solution of 1:1 CH$_3$CN:H$_2$O. The solutions were left under gentle stirring and monitored spectrophotometrically. The change in absorbance values of the MPc solution before and after immobilisation was measured in order to calculate the amount of MPc attached to the surface of the resin. The MPc loadings are represented as "g MPc/g Amb". After immobilisation of the MPc complexes, the modified resin was filtered and washed with a 3:1 H$_2$O:CH$_3$CN solution, followed by large amounts of deionised water. The resin was finally dried at $65\,°C$ overnight. Diffuse reflectance spectra were obtained for the solid MPc-Amb resins,
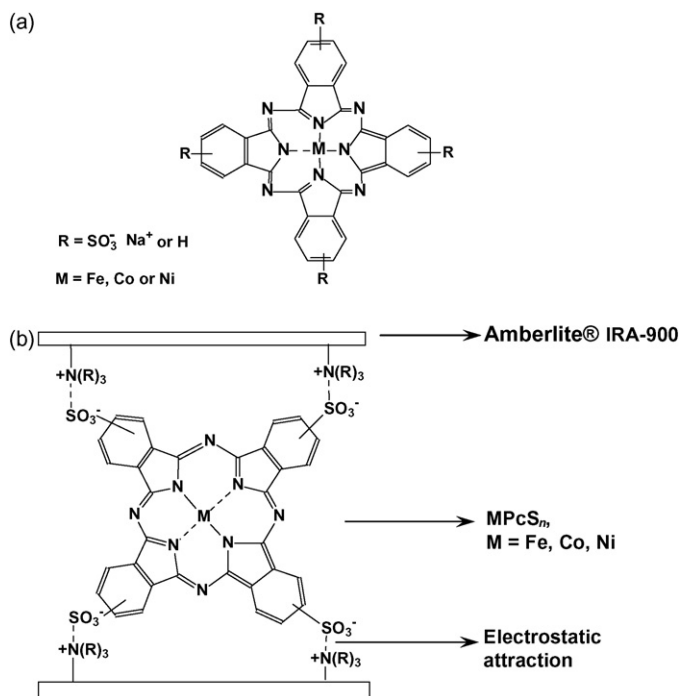

Fig. 1. (a) Molecular structure of MPcS$_n$ complexes; (b) schematic representation of the tetrasulphonated MPcs immobilised onto Amberlite® IRA-900.

using UV–vis–NIR spectrophotometry. 4-NP was then adsorbed from solution onto MPc-Amb. The adsorption process was monitored spectroscopically. The decrease in the intensity of the UV–vis spectral peaks of 4-NP with time was used as an indication of the adsorption process. Studies were also conducted where 4-NP was adsorbed directly onto Amberlite® IRA-900 prior to modification with MPc complexes.

2.2.2. Optimisation studies

Optimisation studies were carried out using varying loadings of FePcS$_4$ on Amberlite® IRA-900, while the concentration of 4-NP was kept constant at 1×10^{-4} mol L^{-1}. The concentration of 4-NP used in this study is considerably higher than the daily maximum effluent limit of 1.1×10^{-6} mol L^{-1} [1] and the permissible amount of 4-NP in drinking water of 2 mg L^{-1} and 1.4×10^{-7} mol L^{-1} [21]. The optimum loading of FePcS$_4$ was determined by comparing the initial rates of 4-NP adsorption onto the modified surface of the adsorbent. The initial rates were determined over the first 10 min of adsorption, from the linear plots of absorbance versus time. Following establishment of the optimum FePcS$_4$ loading, MPc-Amb resins were prepared at this loading for the rest of the MPc complexes, and the rate of adsorption of 4-NP was compared for all modified adsorbents, using the mass balance relationship in Eq. (1) [5,8]:

$$Q_t = V_L \frac{(C_0 - C_t)}{W} \tag{1}$$

where Q_t is the amount of 4-NP adsorbed onto the resin (mmol g^{-1}) after time t, C_0 and C_t are the initial and final (after a known time) concentrations of 4-NP (mmol L^{-1}), respectively, V_L is the volume of aqueous solution (L) and W is the mass of dry adsorbent (g). V_L, C_0 and W were maintained at 5×10^{-3} L, 1×10^{-4} mol L^{-1} and 0.010 g, respectively, for all analyses. The time "t" at which Q was determined was 30 min for all analyses. Adsorption efficiency was calculated from the ratio of Q_t calculated for total adsorption of 4-NP to the Q_t obtained experimentally.

The rate of adsorption of 4-NP was determined at different pH values in order to establish the pH at which the fastest adsorption of 4-NP is achieved. The pH of each buffered solution was measured using the WTW pH 330/SET-1 pH meter.

The 1×10^{-4} mol L^{-1} 4-NP solution was prepared in pH 9 buffer, as 4-NP is very soluble at this pH (solubility = 1.73 mol L^{-1}, calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris) and the predominant species in solution is the phenolate ion of 4-NP. Adsorption rates were monitored spectroscopically, where ε (λ_{max}) for 4-NP was determined graphically to be 1.7×10^4 L mol^{-1} cm^{-1} in pH 9 buffer.

2.2.3. Regeneration studies

Regeneration of the modified adsorbent, following adsorption of 4-NP on MPc-Amb was carried out using the optimum loading of FePcS$_4$ and NiPcS$_4$ (as examples) on the macroreticular resin. A 5 mL solution of 1×10^{-4} mol L^{-1} 4-NP was added to a known amount of MPcS$_4$-Amb and left to stir overnight in order to reach equilibrium. The adsorption process was moni-

tored spectroscopically to determine the concentration of 4-NP adsorbed onto the MPcS$_4$-Amb, by recording the decrease in the intensity of solution absorption spectra of 4-NP. Adsorption was carried out until there was no change in the spectra of 4-NP solution, then the resin was removed from the solution and washed with deionised water. Then, 1×10^{-3} mol L^{-1} nitric acid solution (5 mL) was used to remove 4-NP from the surface of the resin to regenerate the adsorbent and recycle the MPc-Amb. The MPc-Amb adsorbent was washed three times with deionised water after removal of 4-NP with HNO$_3$. The rate of adsorption of fresh solution of 4-NP after regeneration of the MPc-Amb adsorbent was then calculated.

3. Results and discussion

3.1. Characterization of MPc complexes immobilised onto Amberlite® IRA-900

The component fractions in an MPcS$_{mix}$ preparation are known to possess different degrees of sulphonation. The composition of the prepared MPcS$_{mix}$ complexes may vary from batch to batch. For the studies presented in this work, the same batch of each complex was employed. In an attempt to characterise the mixture in these complexes HPLC was employed (Fig. 2). It is expected that the most highly sulphonated (most soluble) species would be the first to be eluted from the chromatographic column, and so give the lowest retention time and that the monosulphonated fractions give the highest retention times. For the three MPcS$_{mix}$ samples, the HPLC signals with the lowest retention times (~1.3 min) are assigned to the tetrasulphonated fractions, using tetrasulphonated phthalocyanines (MTSPc) as a reference (Fig. 2). Thus, NiPcS$_{mix}$ mainly consisted of NiPcS$_4$, with minute amounts of the less sulphonated derivatives. Whereas FePcS$_{mix}$ contained very little of FePcS$_4$ and CoPcS$_{mix}$ consisted of mainly two components with an almost equal amount of CoPcS$_4$ in the mixture. Sulphonation [18] by the reaction of MPc complexes with fuming sulphuric acid (containing SO$_3$) gives a variable mixture of differently sulphonated metallophthalocyanine complexes (MPc(SO$_3^-$)$_n$) where M = metal ion, n a mixture of 1, 2, 3, or 4 sulpho groups, which is represented as MPcS$_{mix}$ in this paper). Thus, the second HPLC peaks for CoPcS$_{mix}$, NiPcS$_{mix}$ and FePcS$_{mix}$ at about 4 min are due to less sulfonated derivatives (less than 4 sulpho groups). The parameters reported in this work for a mixture of differently sulfonated derivatives will be an average of the mixture. The spectroscopic characterisation of the MPcS$_4$ was consistent with literature.

The resin used in this work is Amebrlite® IRA-900 ion-exchange resin, which is a strongly basic, macroreticular resin of moderately high porosity with benzyltrialkylammonium functionality. The solvent mixture of acetonitrile:water employed in this study was chosen so as to ensure that sulphonated MPc complexes are in monomeric state in solution, since these complexes are notoriously aggregated in aqueous media and organic solvents break the aggregates. The concentration of MPc immobilised onto the resin was calculated by measuring the decrease
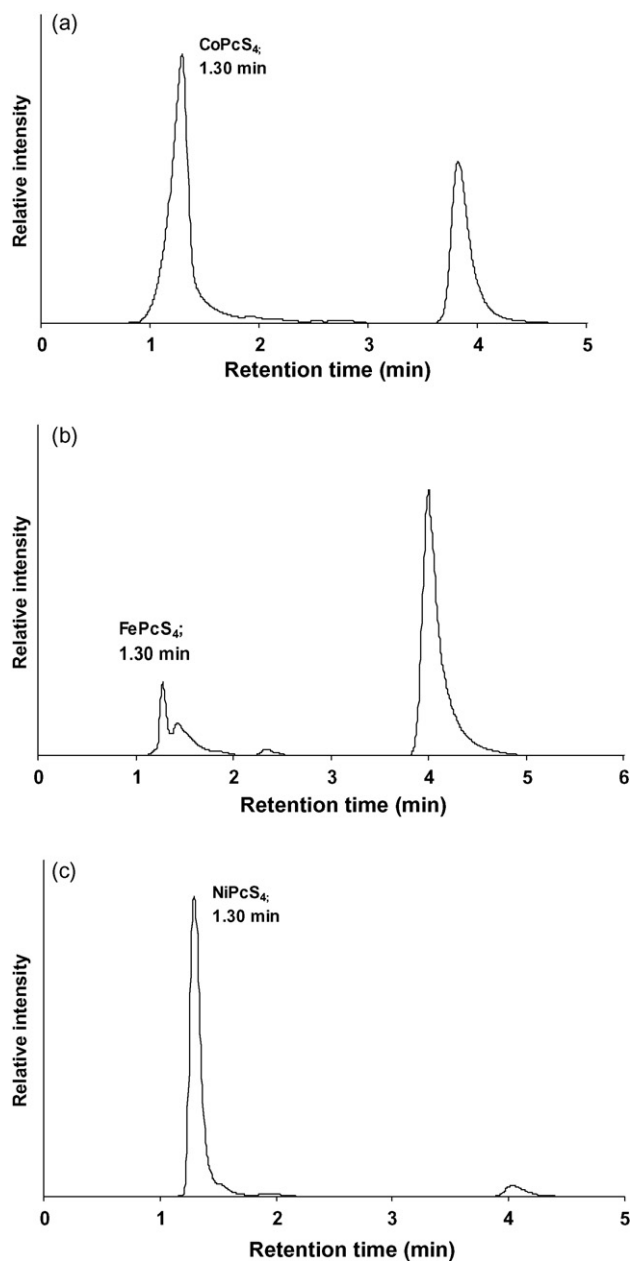
Fig. 2. HPLC traces of (a) $CoPcS_{mix}$, (b) $FePcS_{mix}$ and (c) $NiPcS_{mix}$.

Fig. 3. Electronic spectral changes with time of $CoPcS_{mix}$ in 1:1 $CH_3CN:H_2O$ mixture during its immobilisation onto Amberlite® IRA-900 resin. Starting concentration of $CoPcS_{mix} = 2.5 \times 10^{-5}$ mol L^{-1}. Mass of Amberlite® IRA-900 = 1.0 g. (i) 0 min and (ii) 15 min of immobilisation.

in absorbance of the Q band following adsorption to a known amount of resin. Fig. 3 shows the decrease in absorbance of $CoPcS_{mix}$ due to its immobilisation onto the resin.

The diffuse reflectance UV–vis spectra, Fig. 4, for the six modified Amberlite® IRA-900 adsorbents were obtained in order to verify immobilisation of the MPcs and qualitatively determine the relationship between the monomeric and dimeric species of each MPc on attachment to the resin. The broadness of the Q bands is due to Davydov splitting, a phenomenon that hinders good resolution of the Q band [22]. In general, dimerisation or aggregation is apparent from the presence of a high-energy band near 620 nm (for NiPc and CoPc derivatives) and near 640 (for FePc derivatives). The low-energy band at 670 nm or higher is due to the monomeric species [23,24].
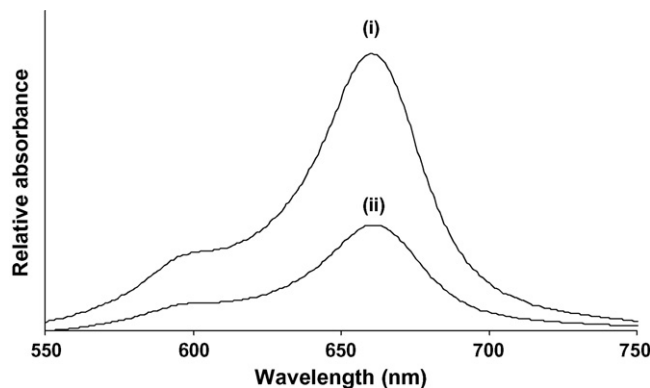
Fig. 4(a) shows that $FePcS_4$ is immobilised onto the Amberlite® IRA-900 resin is aggregated as evidenced by a peak at 641 nm, with a small amount present in the monomeric form. $FePcS_{mix}$ adsorbed in its monomeric form, with the broadness of the Q band being due to Davydov splitting. Both the nickel and cobalt sulphonated phthalocyanine complexes in Fig. 4b and c respectively, are immobilised in the monomeric form, with a small degree of aggregation occurring in all cases. The similarities in the reflectance spectra of $NiPcS_{mix}$ and $NiPcS_4$ are not surprising considering the HPLC results discussed above. $CoPcS_{mix}$ and $CoPcS_4$ also have similar reflectance spectra even though the HPLC traces showed the latter not to be the only component.

The effect of increasing the amount of $FePcS_4$ loaded onto Amberlite® IRA-900 was determined using diffuse reflectance (Fig. 5). On increasing the amount of immobilised $FePcS_4$ there is a broadening of the monomer peak accompanied by increase in its intensity relative to the dimer.

3.2. Optimisation studies

3.2.1. Optimisation of MPc loading on Amberlite® IRA-900

$FePcS_4$ was employed as an example for these studies. Fig. 6 shows the electronic spectral changes observed during the adsorption of 4-NP onto $FePcS_4$-Amb. Similar spectral changes were observed on other MPc-Amb resins and on bare Amberlite® IRA-900. The adsorption of 1×10^{-4} mol L^{-1} 4-NP onto bare Amberlite® IRA-900 was compared with that obtained when the same concentration of 4-NP was adsorbed onto $FePcS_4$-Amb adsorbent. The rates were 2.78×10^{-6} and 4.09×10^{-6} mol L^{-1} min^{-1}, respectively for bare Amberlite® IRA-900 and $FePcS_4$-Amb, showing an almost two-fold improvement for 4-NP adsorbed on MPc modified Amberlite® IRA-900.

The optimum loading of the MPc complexes onto Amberlite® IRA-900 was established by determining the rate of 4-NP adsorption with various loadings of $FePcS_4$ (Fig. 7a). Rate studies were not carried out on resins modified with loadings greater than 3×10^{-2} g $FePcS_4$/g Amb, as the immobilisation of $FePcS_4$ became time-consuming, i.e. 3–4 days. A loading
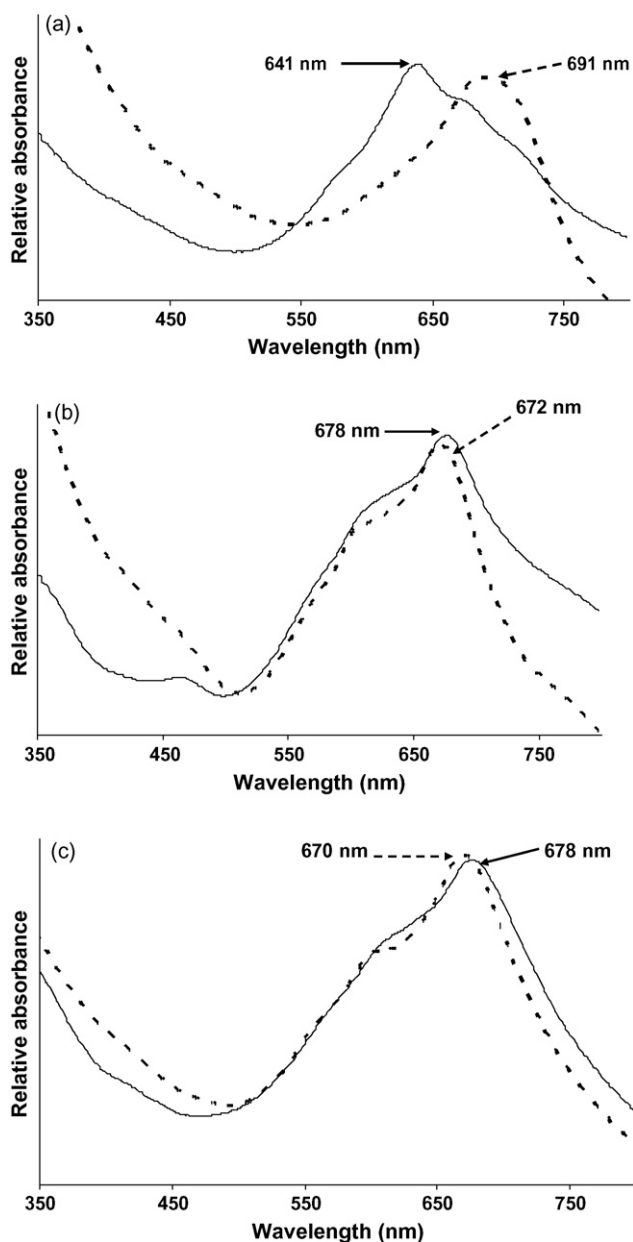
Fig. 5. Diffuse reflectance spectra of FePcS$_4$-Amb showing the effect of increasing the amount of immobilised FePcS$_4$: (a) 1×10^{-5} and (b) 3×10^{-5} mol FePcS$_4$/g Amb.

adsorption rate reaches a maximum after pH 9, which correlates with the pH at which 4-NP is highly soluble. The reason for increased adsorption with increase in pH is due to the predominance of deprotonated form (phenolate ion) of 4-NP at high pH. Thus, pH does affect the rate of 4-NP adsorption. The solution pH may also have an influence on the rate of degradation of 4-NP in that it may affect the surface properties of Amberlite® IRA-900 and/or cause protonation/deprotonation of the MPc modifiers. However, the spectra of the adsorbed FePcS$_4$ complexes did not change with pH following use for at different pHs for Fig. 7b, thus showing that the MPc complexes are not affected by protonation. Protonation of MPc complexes results in splitting of spectra and shifting to the red [23], and this was not observed. The optimum pH in Fig. 7b was 9, hence this pH was employed for all subsequent studies.

3.3. Comparison of 4-NP adsorption rates on MPc-modified Amberlite® IRA-900

The rate and amount of 4-NP adsorption was compared for all MPc complexes with a loading of 1×10^{-3} g MPc/g Amb (Fig. 8). It is evident from Fig. 8a that the initial rate of 4-NP adsorption is faster for the MPcS$_4$ complexes than

Fig. 4. Diffuse reflectance spectra of (a) FePcS, (b) NiPcS and (c) CoPcS complexes after immobilisation onto Amberlite® IRA-900: (—) MPcS$_4$; (- - -) MPcS$_{mix}$.

of 1×10^{-3} g FePcS$_4$/g Amb gave the highest rate of adsorption compared with the other loadings in Fig. 7a. This loading was then employed for further studies and for all the MPc complexes under investigation. There was a decrease in the rate of 4-NP adsorption going from 1×10^{-3} to 1×10^{-2} g FePcS$_4$/g Amb, followed by a rise in adsorption rate of 4-NP after the latter loading. The increase in 4-NP adsorption rate after the loading of 1×10^{-2} g FePcS$_4$/g Amb may be accounted for by the formation of more than one layer on the resin.

3.2.2. pH optimisation

The dependence of the rate of 4-NP adsorption on pH was determined by varying the pH of the 4-NP solution and maintaining its concentration at 1×10^{-4} mol L^{-1} (Fig. 7b). The
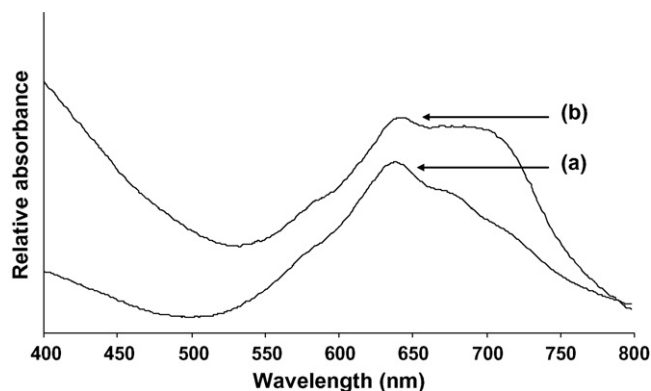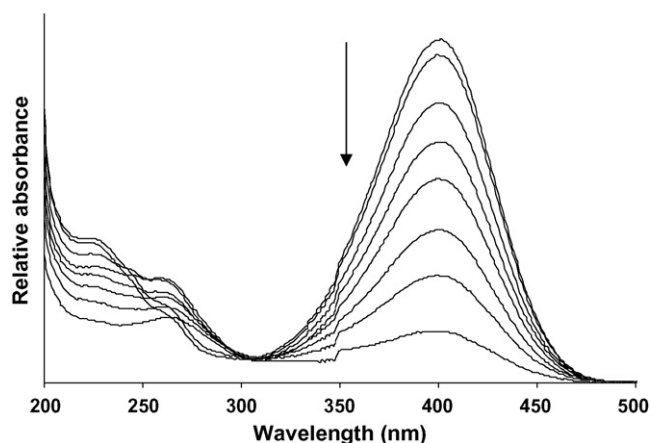

Fig. 6. Electronic spectra showing adsorption of 1×10^{-4} mol L^{-1} 4-NP onto 1×10^{-5} mol FePcS$_4$/g Amb. Adsorption time was 30 min pH = 9.
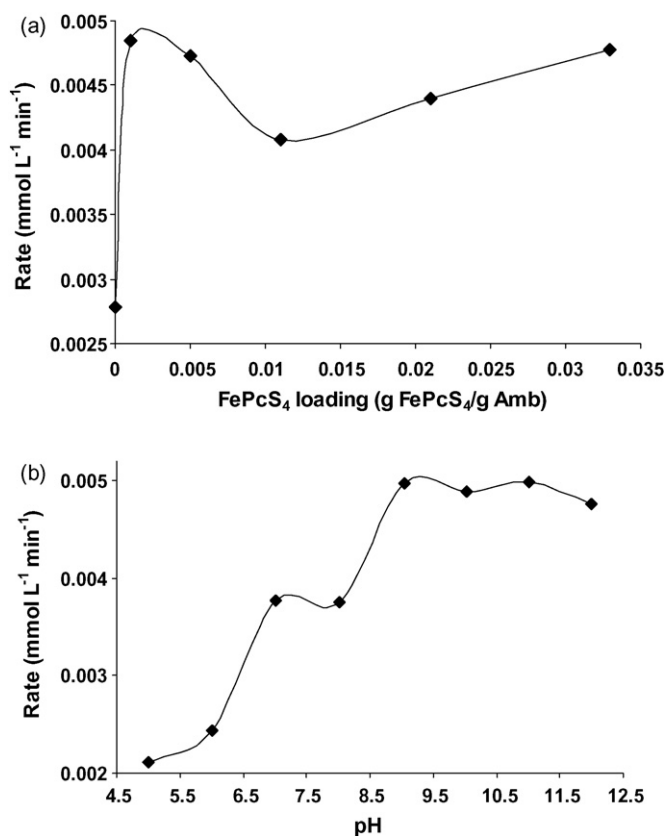
Fig. 7. (a) Plot of initial adsorption rate vs. FePcS$_4$ loading to determine the optimum amount of FePcS$_4$ immobilised onto Amberlite® IRA-900 for the adsorption of 1×10^{-4} mol L^{-1} 4-NP; pH = 9. (b) Plot of initial adsorption rate vs. pH, for the adsorption of 1×10^{-4} mol L^{-1} 4-NP onto 1×10^{-3} g FePcS$_4$/g Amb.

the corresponding MPcS$_{mix}$ complexes. The FePc complexes gave the fastest rate (Fig. 8a) and highest amount (Fig. 8b) of adsorbed 4-NP compared with the other MPcs, with the highest rate of adsorption being obtained for FePcS$_4$, and the highest amount of adsorption obtained for FePcS$_{mix}$ after 30 min ($Q_t = 42.9$ mmol g^{-1}; % adsorption efficiency = 86%). CoPcS$_{mix}$ gave both the lowest amount and rate of adsorption of 4-NP 34.5 mmol g^{-1}; % adsorption efficiency = 69%. Percentage adsorption efficiencies obtained for adsorption of 4-NP onto Amberlyst A-21 resin (instead of Amberlite® IRA-900 used in this work) which consists of functional tertiary amino groups, were relatively high (100% for 4-NP in toluene and 87% for 4-NP in dichloromethane) [25] without the MPc catalyst. These values were reported in organic media while in this work an aqueous medium is employed which is more desirable for real application. The reported 86% adsorption efficiency was obtained only after 30 min, the value improved with adsorption time.

3.4. Regeneration of resin

These studies were carried out in order to determine whether the resin modified with adsorbed MPc could be re-used repeatedly for removal of 4-NP. It has been reported that Amberlite® XAD-7, a weakly polar polymeric ion-exchange resin, could be
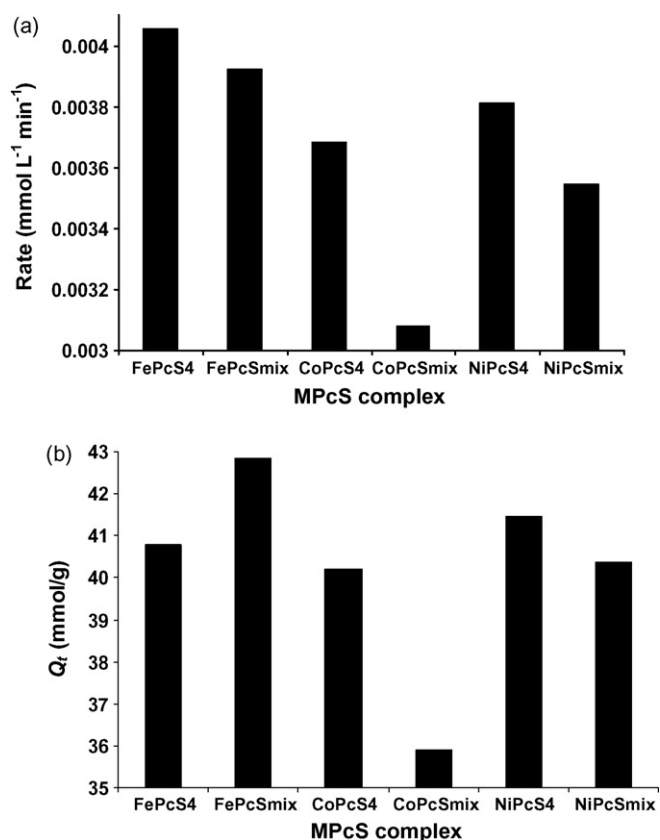

Fig. 8. Plots of (a) initial adsorption rate of 4-NP adsorption and (b) Q_t (time = 30 min) for each MPc complex used to modify Amberlite® IRA-900. [4-NP] = 1×10^{-4} mol L^{-1}; pH = 9.

regenerated using ethanol as the regenerant for the removal of 4-NP [9]. However, the use of ethanol as a regenerant was unsuccessful in this work. Its ineffectiveness may be due to differences in the interaction of 4-NP with Amberlite® XAD-7 compared with modified Amberlite® IRA-900.

The phenolate ion of 4-NP is relatively stable in solution due to the presence of a *para* nitro group which results in electron delocalization [26] and the formation of a corresponding quinonoid complex [27]. The equilibrium that exists between the phenolate ion and the neutral 4-NP species is affected by the pH of the solution. As a result, dilute nitric acid (1×10^{-3} mol L^{-1}) was used to regenerate the MPc-modified Amberlite® IRA-900 for re-use in 4-NP adsorption. The nitric acid causes a shift in the equilibrium, favouring the formation of the protonated 4-NP species, resulting in desorption of 4-NP from the surface of the adsorbent.

The regenerated FePcS$_4$-Amb was re-used for further adsorption of 1×10^{-4} mol L^{-1} 4-NP. The rate of adsorption of 4-NP after regeneration of the resin increased from 4.85×10^{-6} mol L^{-1} min^{-1} (for original resin) to 6.93×10^{-6} mol L^{-1} min^{-1} (after the first wash) and 6.05×10^{-6} mol L^{-1} min^{-1} (after the second wash). Thus, the rate of 4-NP adsorption was increased by a factor of 1.4 and 1.2 after the first and second washing with nitric acid, respectively, relative to the initial rate of adsorption. The effect of washing of the resin with HNO$_3$ on FePcS$_4$ is shown in Fig. 9. After
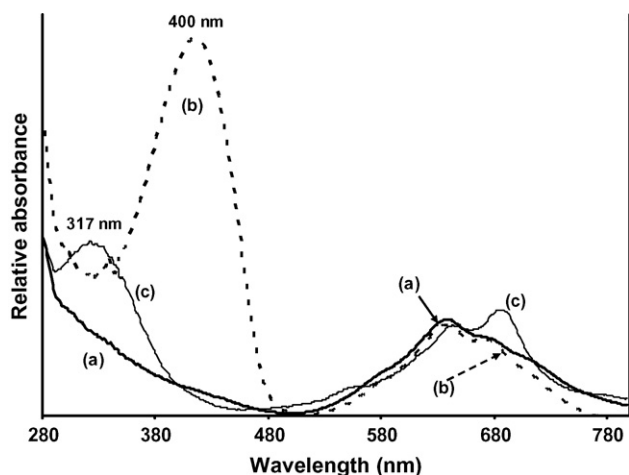
Fig. 9. Diffuse reflectance spectral changes observed for FePcS$_4$-Amb (a) before adsorption of 4-NP, (b) after adsorption of 4-NP and (c) following removal of 4-NP from (b) using dilute HNO$_3$. [4-NP] = 1 × 10^{-4} mol L^{-1}; pH = 9.

washing with HNO$_3$ the FePcS$_4$ becomes more monomeric, as judged by an increase in the intensity of the low energy band. The presence of a monomeric MPc may account for the increase in 4-NP adsorption after the first wash, as the metal centre is more readily available to accept the negatively-charged phenolate ion, thereby increasing the rate of 4-NP adsorption.

It can be seen from Fig. 9 that on washing the resin with nitric acid, a new species (with λ_{max} = 317 nm) with a different spectrum from 4-NP (λ_{max} = 400 nm) was obtained. In order to determine the nature of the new species, we compared the spectra of 4-NP in acidic and basic media (Fig. 10a). The spectra matched those observed in Fig. 9 following washing of 4-NP from MPc-Amb with nitric acid. Thus the new spectrum with λ_{max} = 317 nm in Fig. 9 is due to the acidic form of 4-NP. The formation of the acid form of 4-NP increased with immersion time of resin as shown in Fig. 10b. The absorbance values obtained at 317 nm (Fig. 10b) were used to calculate the percentage 4-NP recovery after 150 min of 4-NP desorption (Fig. 10b, inset). The total amount of 4-NP recovered after removal with 1 × 10^{-3} mol L^{-1} nitric acid (for 150 min) was 76% (7.6 × 10^{-5} mol L^{-1} 4-NP) and this value increased with time. The value is agreeable with the percentage recovery (87%) obtained for 4-NP when a styrene-divinylbenzene copolymer (PS-DVB) was used over an infinite amount of time [28]. A higher percentage recovery (97%) was obtained for the removal of 4-NP from Amberlite XAD-7 using ethanol [9]. The reported recoveries were for resins not modified by MPc catalyst, so direct comparison is not appropriate. However, the recovery of the acid form of 4-NP from the MPc modified catalyst of 78% is high and the fact that the catalytic activity of the catalyst improves on re-cycling the modified resin is an important observation. Also the use of dilute HNO$_3$ to recover 4-NP is favourable, as it is more economically viable. The resin could be re-used repeatedly without considerable loss in adsorption rate for 4-NP and without losing the catalyst. Table 1 shows the first six re-adsorption rates of 4-NP following removal of 4-NP, and shows clearly that the catalytic activity is not lost upon repeated use on NiPcS$_4$ as an example.
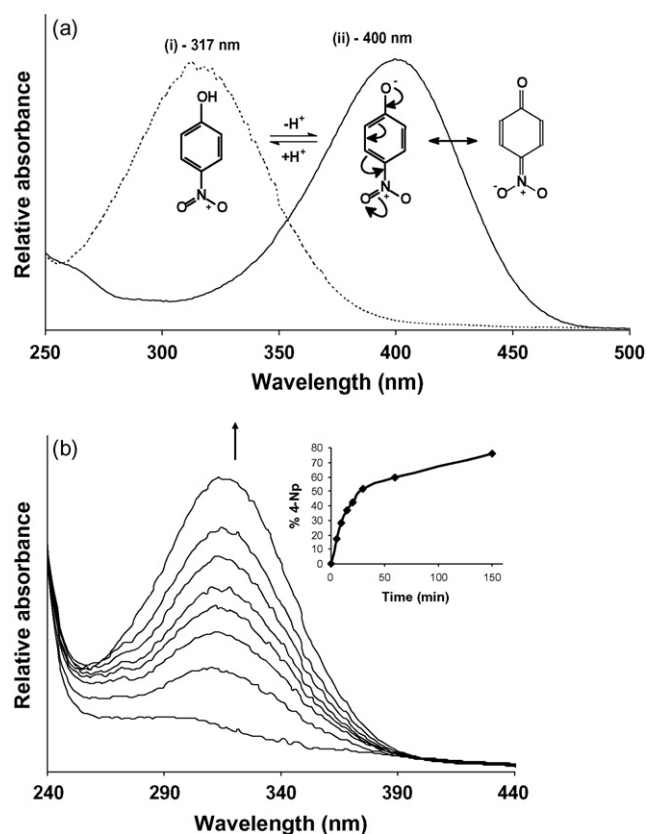

Fig. 10. Electronic absorption spectra (a) of 4-NP in an acidic (i) and basic (ii) medium and (b) observed with time (total = 150 min) on immersion of FePcS$_4$-Amb containing 4-NP in HNO$_3$. Inset: Plot of the percentage 4-NP recovery vs. time following immersion of FePcS$_4$-Amb containing 4-NP in HNO$_3$. [HNO$_3$] = 1 × 10^{-3} mol L^{-1}.

3.5. Spectroscopic study of the interaction of 4-NP with MPcs

As mentioned previously, possible methods of attachment of 4-NP to the MPc modified Amberlite® IRA-900 resin include π–π interactions with the resin and MPc, and hydrogen bonding formed between the tertiary ammonium groups of Amberlite® IRA-900 and the hydroxyl group of 4-NP. Hydrogen bonds will be irrelevant in the study, as the predominant species in solution is the deprotonated phenolate ion. Another interaction that is possible is due to the formation of an axial ligand bond between the metal centre of the MPc and phenolate ion. The interaction between the MPc metal centre and 4-NP was determined by

Table 1
Adsorption rates of 1 × 10^{-4} mol L^{-1} 4-NP on 1 × 10^{-6} mol NiPcS$_4$/g Amberlite® IRA-900 resin following regeneration of modified resin

Regeneration number	Adsorption rate (mol L^{-1} min^{-1})
1	3.81 × 10^{-6}
2	3.40 × 10^{-6}
3	3.06 × 10^{-6}
4	3.09 × 10^{-6}
5	3.03 × 10^{-6}
6	3.12 × 10^{-6}
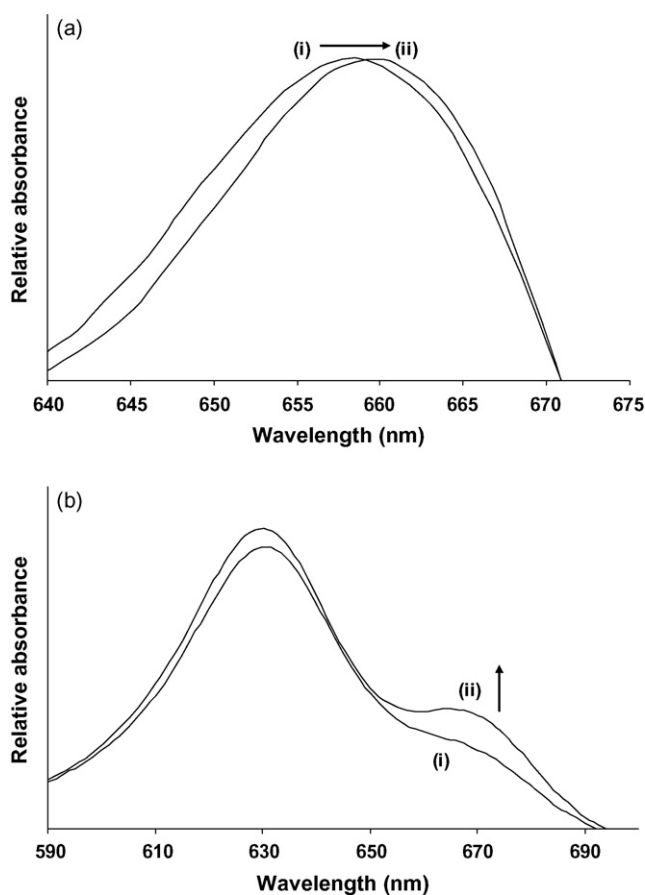
Fig. 11. Spectral changes of (a) $CoPcS_4$ and (b) $FePcS_4$, on addition of 1×10^{-4} mol L^{-1} 4-NP; pH = 9.

adding 4-NP to each MPc in aqueous solution and recording the UV-vis spectra. There was a shift in the wavelength of the Q band for $CoPcS_4$ and $CoPcS_{mix}$ (Fig. 11a). Such small changes are associated with axial ligation in MPc complexes [23]. An increase in the amount of monomeric species was observed for $FePcS_4$ and $FePcS_{mix}$ on addition of 4-NP (Fig. 11b), again suggesting monomerisation due to attachment of axial ligands. There was no change observed for $NiPcS_4$ and $NiPcS_{mix}$ (figure not shown), merely a degradation of the MPc with time. Therefore, it is hypothesized that the metal centres of both the CoPcS and FePcS species attach ionically to unprotonated 4-NP.

3.6. Langmuir–Hinshelwood (L–H) kinetic model

L–H model (Eq. (2)) describes the competitive adsorption of substrates, reaction intermediates and phenol oxidant products [29,30].

$$\frac{1}{\text{rate}} = \frac{1}{k_r} + \frac{1}{k_r K_{ad} C_{sub}^0} \qquad (2)$$

where k_r is the rate constant for the adsorption of 4-NP, C_{sub}^0 is the initial concentration of the substrate (in this case 4-NP). K_{ad}, the adsorption coefficient, represents the equilibrium between the rates of adsorption and desorption [31]. Table 2 shows the kinetic parameters obtained from the plots. A relatively high

Table 2
The LHKM parameter details obtained for the adsorption of 4-NP onto MPc-Amb adsorbents; [4-NP] = 1×10^{-4} mol L^{-1}

Modifier	R^2 value	k_r (min^{-1})	K_{ad} (mol^{-1} L)
$FePcS_4$	0.9952	7.47×10^{-5}	5.25×10^2
$CoPcS_4$	0.9331	5.86×10^{-5}	7.25×10^2
$NiPcS_4$	0.9876	1.36×10^{-4}	3.39×10^2
$FePcS_{mix}$	0.9934	5.88×10^{-5}	7.23×10^2
$CoPcS_{mix}$	0.9283	7.72×10^{-4}	5.76×10^1
$NiPcS_{mix}$	0.9362	9.07×10^{-5}	6.24×10^2
Amberlite® IRA-900	0.9249	3.21×10^{-5}	1.06×10^3

degree of linearity was obtained with R^2 values greater than 0.9 for all adsorbents, therefore the adsorption of 4-NP is dependent on 4-NP concentration. The $MPcS_4$ complexes adsorbed 4-NP in the following order: (according to the k_r values) $CoPcS_{mix} > NiPcS_4 > NiPcS_{mix} > FePcS_4 > FePcS_{mix} > CoPcS_4$. Adsorption rate ($k_r$) was lowest for bare Amberlite® IRA-900. The high k_r for the NiPcS complexes shows that axial ligation is not essential for the adsorption of 4-NP on MPc-Amb. As expected, adsorption was favoured over desorption hence K_{ad} was greater than unity in all cases.

4. Conclusions

The chemically modified polymeric adsorbents, MPc-Amb, were employed for the solid phase extraction of 4-NP from aqueous solution. Faster adsorption rates were achieved for the modified adsorbent at MPc-Amb compared with bare Amberlite® IRA-900, with the fastest rates obtained for $FePcS_4$-Amb at pH 9. The modified resin could be used repeatedly for 4-NP adsorption without significant loss in adsorption rate. MPc-modified Amberlite® IRA-900 can be effectively applied as an adsorbent for the removal and recovery of 4-NP from aqueous solution. The fact that the efficiency of the Amberlite® IRA-900 resin employed in this work improves when an MPc catalyst is employed suggests that the MPc complexes have potential in application for improving the removal of phenols using other resins. The stability of both the resin and the MPc catalyst are also an advantage for real applications.

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