Decolourization of azo dyes using magnesium–palladium system

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Abstract

Magnesium–palladium system was found to efficiently decolourize reactive black 5, sunset yellow FCF and tartrazine dyes. There is complete loss of visible range absorption peaks and extent of colour removal exceeded 95% within 24 h of reaction. There is appearance of new peak(s) in the UV region and/or gradual and significant shift of the λ_{max} in the UV range during 1–24 h of reaction of dyes with Mg/Pd system. LC–MS analyses following the reaction of dyes with magnesium palladium system suggest reductive cleavage of azo bonds and formation of amines as the end products. Kinetic analyses of dye decolourization indicate that the reaction follows first order kinetics. Agreement between the experimental and predicted Michaelis–Menten plots for the decolourization of reactive black 5, sunset yellow FCF and tartrazine dyes by Mg^0/Pd^{4+} system, suggests the correctness of Michaelis–Menten model for the prediction of dye decolourization rates by Mg^0/Pd^{4+} system. Our investigations reveal that Mg^0/K_2PdCl_6 system is more effective in decolourizing dyes as compared to Mg^0/Pd^0–alumina or Mg^0 alone. Results obtained from reuse experiments suggest that Pd^0 pellets have the potential for recycling which will make the treatment process cost effective. Mg^0/Pd^{4+} system was found to be efficient in decolourizing mixture of drimarene, remazol and procion dyes as well as raw effluent generated by textile dye manufacturing company.
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1. Introduction

Water pollution due to discharge of coloured effluents from textile dye manufacturing and textile dyeing mills is one of the major environmental concerns in the world today. Strong colour imparted by the dyes to the receiving aquatic ecosystems poses aesthetic problem and serious ecological problems such as inhibition of benthic photosynthesis and carcinogenicity. Therefore a number of techniques aimed at preferential removal dyes from wastewater have been developed [1,2]. Among these are physico-chemical methods for decolourization of azo dyes, which include adsorption of rifafix red 3 BN and reactive red 241 on activated carbon; electrochemical coagulation of reactive blue-19, acid red 266 and disperse yellow 218; TiO₂-UV mediated photocatalytic decolourization of reactive orange 4,

enhancement of biodegradability of acid red 151 by ozonation and degradation of methyl red using Fenton's reagent [3–8]. However, the above listed physico-chemical methods for removal of colour have several shortcomings such as high cost, limited applicability and/or generation of chemical sludge that presents disposal problem. Therefore treatment methods based on the biological methods are considered as an alternative option since they are cost effective and ecofriendly. However several of the textile dyes such as water-soluble azo reactive dyes (constituting the largest class of textile dyes) are resistant to aerobic biodegradation and hence conventional aerobic treatment methods cannot be employed. On the other hand dyes such as reactive black 5, direct brown 2 and acid orange 7 have been reported to be amenable to anaerobic biotransformation and decolourization [9,10]. Despite numerous research efforts, anaerobic biotransformation processes have not been applicable for biological decolourization and detoxification of textile industry discharges due to the below listed limitations:

- Isolation of anaerobic microorganisms capable of decolourizing dyes has proved to be tedious task.

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- The enzyme systems in anaerobic bacteria, namely, azoreductases that are induced in response to the presence of dyes are highly specific and attack only one type of dye or dyes that are structurally similar. Therefore these bacteria cannot be applied to textile mill effluents, which most often contain mixture of dyes rather than one specific dye.
- Azoreductases are highly oxygen sensitive and function only under strict anaerobic conditions.

Thus it is evident that research must be directed towards sequential anaerobic/aerobic process [11,12] or identification of sequential biological–chemical processes that meet the following criteria: (i) non-specific with respect to their application to various types of water soluble reactive dyes and (ii) result in complete removal and decolourization of dyes under natural environmental conditions.
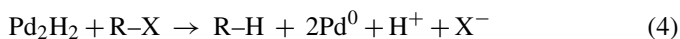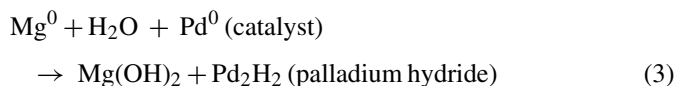
In our previous investigations we have exploited bioadsorption using fungal (*Aspergillus foetidus*) biomass for removal of water-soluble textile dyes, namely the drimarene and procion dyes [13–15]. Key parameters related to fungal mediated bioseparation process were optimized. However mere application of bioadsorption process will result only in the phase separation of the dyes without significant degradation. Therefore an environmentally benign dye destruction/degradation technique is required as a follow-up process. In the present investigations we have examined the potential of zero-valent metal-based system, Mg/Pd for its ability to decolourize textile and food dyes. The ultimate goal is to develop a sequential biological–chemical method for rapid removal and degradation of dyes. Bioadsorption will facilitate rapid uptake and concentration of dye molecules on the surface of the sorbent, fungal biomass. The dye molecules can be subsequently desorbed form the fungal biomass by treatment with sodium hydroxide and subjected to Mg/Pd catalyzed reductive decolourization process. The end products formed may be subjected to aerobic biodegradation process.

Abiotic reductive dechlorination catalyzed by zero-valent metal-based systems has generated huge interest for the possible application of this reaction to degrade persistent organic compounds. The reaction is initiated by the ionization (corrosion) of zero-valent metals such as iron or magnesium as shown in reactions (1) and (2), respectively, with the corresponding redox potentials:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad E_0 = -0.44\,V \qquad (1)$$

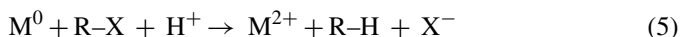$$Mg^0 \rightarrow Mg^{2+} + 2e^- \qquad E_0 = -2.2\,V \qquad (2)$$
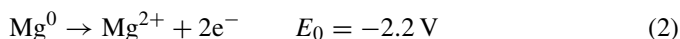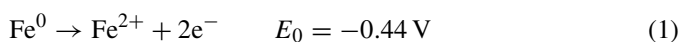
In the next step, electrons derived from the metal are captured by protons to generate nascent hydrogen, which in the presence of hydrogenating metal catalyst such as palladium yields palladium hydride. The metal hydride in turn reacts (via aromatic nucleophilic substitution) rapidly with target compounds to produce the corresponding reduced products. The hydrogenation reactions represented below in Eqs. (3)–(5) are presumed to occur at the interface of ionizing metal surface and deposited palladium or on the surface of Pd^0 particulates floating in the reaction phase [16]. Alternatively, electrons may be donated directly to the functional groups of target compounds:

$$Mg^0 + H_2O + Pd^0 \,(catalyst)$$
$$\rightarrow Mg(OH)_2 + Pd_2H_2 \,(palladium\ hydride) \qquad (3)$$

$$Pd_2H_2 + R\text{–}X \rightarrow R\text{–}H + 2Pd^0 + H^+ + X^- \qquad (4)$$

Thus the overall reaction is:

$$M^0 + R\text{–}X + H^+ \rightarrow M^{2+} + R\text{–}H + X^- \qquad (5)$$

There have been several applications of zero-valent iron for the reduction/removal of relevant functional groups such as azo, chloro and nitro. For example zero-valent iron (Fe^0) has been successfully used under anaerobic condition to degrade *p*-chlorophenol, azo dyes, chlorinated pesticides, polychlorinated biphenyls, 2,4,6 trinitrotoluene [TNT], hexahydro-1,3,5-trinitro 1,3,5-triazine [RDX], nitroaromatics, heavy metals [16–27]. Although Fe^0 has been applied extensively for remediation of several pollutants, the major drawbacks are slow reaction rates, rapid passivation of the metal and requirement for strict anaerobic conditions. In comparison, magnesium metal (Mg^0) exhibits superior performance and has been used in combination with palladium, an excellent hydrogenation catalyst for the successful and rapid dechlorination of DDT, pentachlorophenol, and phenol [28–30]. The major advantageous features of the magnesium-based system are: high negative reduction potential of Mg^{2+}/Mg^0 (−2.2 V) as compared to Fe^{2+}/Fe^0 (−0.44 V, respectively); high solubility of magnesium hydroxide, reduced passivation of metal as compared to iron and no requirement for creating anaerobic conditions. However to the best of our knowledge Mg^0/Pd has not been explored for decolourization and degradation of textile dyes. In the present investigations we have evaluated two forms of palladium, namely, K_2PdCl_6 and Pd^0–alumina pellets in combination with Mg^0 for reductive transformation and total decolourization of reactive black 5, sunset yellow FCF and tartrazine dyes using lab scale systems. Reactive black 5 is one of the most commonly used recalcitrant dyes in textile industries whereas sunset yellow FCF and tartrazine are food colouring agents. All of the above dyes are important chromophoric pollutants in aquatic and soil environments.

2. Materials and methods

2.1. Source of chemicals

Mg^0 granules (∼20 mesh), K_2PdCl_6 (hexachloropalladate (IV) dipotassium), Pd^0–alumina (0.5% w/w) pellets, tartrazine and sunset yellow were purchased from Sigma–Aldrich Chemical Company. Reactive black 5, drimarene red, remazol brown and drimarene navy dyes were procured from local companies. Molecular structures of selected dyes are shown in Table 4. Acetone and glacial acetic acid were purchased from Merck Ltd., Mumbai, India. Methanol was purchased from J.T. Baker, USA. All dyes used were 90% pure. All other chemicals were of analytical grade and >98% pure.

2.2. Time dependent spectral profiles of dyes reacted with Mg^0/Pd^{4+} and Mg^0/Pd^0 systems

To 4 ml of 100 mg l^{-1} of dye [reactive black (110.7 μM), tartrazine (187.3 μM) or sunset yellow FCF (221 μM)] solution, 2.5 mg of Mg^0 ml^{-1} and 0.25 mg ml^{-1} of K$_2$PdCl$_6$ or 12 mg ml^{-1} of Pd^0–alumina (0.5% w/w) were added. Reactions were conducted in the presence of 87 mM acetic acid or in the absence of acid. Reaction samples were maintained on an incubator shaker set to 100 RPM and 30 °C. At designated time points (1 and 24 h) the entire reaction mixture was centrifuged to settle solids and the clear supernatant was analyzed for residual dye concentration by UV–visible absorption spectroscopy (details of the instrument given under support information). Reaction solutions were diluted four-fold prior to recording spectra.

2.3. Comparison of the dye decolourization efficiency using Pd^0–alumina pellets and K$_2$PdCl$_6$ salt

The reaction mixtures (4 ml) consisted of 10 mg Mg^0, 48 mg of Pd^0–alumina pellet or 1 mg K$_2$PdCl$_6$ (equivalent elemental weight of Pd in each compound was ~0.24 mg Pd), 100 mg l^{-1} of reactive black 5 or tartrazine or sunset yellow FCF dyes and 87 mM acetic acid. Reaction mixtures were incubated on an incubator shaker at 100 rpm and 30 °C. At the end of 1 h of reaction the samples were analyzed for residual dye concentration using UV–visible absorption spectroscopy.

2.4. Effect of varying concentrations of Pd^{4+} on the kinetics of dye decolourization at a fixed Mg^0 concentration

To 120 ml of 100 mg l^{-1} reactive dye solutions (reactive black 5, tartrazine and sunset yellow FCF) 600 mg (5 mg ml^{-1}) of Mg^0 was added followed by the dosing of chosen concentrations (5–17.5 μg ml^{-1}) of K$_2$PdCl$_6$ from stock solutions. The reaction mixture contained in a 250 ml of capped bottle was stirred continuously on a magnetic stirrer at 30 °C. Reaction was initiated by the addition of 87 mM acetic acid. Aliquots were withdrawn at various time points and analyzed to obtain kinetic profiles of dye decolourization. Decrease in the intensity of absorbance at the visible range λ$_{max}$ of the three dyes (i.e. 599 nm for reactive black 5, 427 nm for tartrazine and 483 nm for sunset yellow FCF) was taken as an indication of decolourization due to transformation of dyes. Control experiments were conducted under similar conditions as test except that only Mg^0 was included in the reaction mixture or both magnesium and palladium were excluded.

2.5. Effect of varying concentrations of Pd^0–alumnia on the kinetics of dye decolourization at a fixed Mg^0 concentration

To 105 ml of 100 mg l^{-1} reactive dye solutions (reactive black 5, tartrazine and sunset yellow FCF) 525 mg (5 mg ml^{-1}) of Mg^0 was added followed by the dosing of varying concentrations (0.95–1.9 mg ml^{-1}) of Pd^0 immobilized on alumina pellet. Other experimental conditions for this kinetic study were similar to those described for Mg^0–Pd^{4+} system.

2.6. Rates of decolourization by Mg^0/Pd^{4+} as a function of varying concentrations of dye

To 120 ml of 25 or 50 or 100 or 150 or 200 mg l^{-1} reactive dye solutions (reactive black 5, tartrazine and sunset yellow FCF) 600 mg (5 mg ml^{-1}) of Mg^0 and 17.5 μg ml^{-1} of K$_2$PdCl$_6$ were added. All reactions were initiated by the addition of 87 mM acetic acid. Aliquots of the reaction mixture were withdrawn at various time points and analyzed for residual dye concentration. V_{max} (maximal velocity) and K_m (half saturation coefficient) values were computed from the Lineweaver–Burk [31] plots of $1/V$ versus $1/[C]$ for reactive black 5, tartrazine and sunset yellow FCF dyes.

2.7. Decolourization study using mixture of dyes

Mixture contained 20 mg l^{-1} each of reactive black 5, sunset yellow FCF, drimarene red, drimarene navy and remazol brown dyes. To 100 ml of this mixture, Mg^0 (2.5 mg ml^{-1}) and Pd^{4+} (17.5 μg ml^{-1}) were added and reaction was initiated by the addition of acetic acid (87 mM). Aliquots were withdrawn at 1 and 24 h of the reaction and analyzed using UV–visible absorption spectroscopy.

2.8. Decolourization study using raw industrial effluent

A study was conducted using 50 ml of composite industrial effluent generated from combining streams of dye manufacturing, leather tanning and pharmaceutical units of Clariant (India) Ltd. The effluent was collected from the equalization tank and subjected to reaction with Mg^0/Pd^{4+} system (Mg^0 = 20 mg ml^{-1} and Pd^{4+} = 17.5 μg ml^{-1}) in presence of acetic acid (174 mM). Analysis of the treated effluent was done following 1 h of reaction using UV–visible absorption spectroscopy.

2.9. LC–MS study of dyes and their degraded products

The methanolic solution of the native dyes (100 mg l^{-1}) and products formed following reaction with Mg^0/K$_2$PdCl$_6$ were analyzed using LC–MS. The study was carried out in negative ion mode since the dye contained negatively charged (sulphonate) groups.

2.9.1. Instrumentation

The HPLC analyses of the native and Mg^0/Pd^{4+} reacted (24 h reaction time in the presence of 87 mM acetic acid) dyes were performed using Agilent 1100 series system equipped with a degaser G 1379 A, gradient pump G 1311 A, autosampler G 1329 A, UV system G 1314 A and a thermostat G 1330 B for controlling temperature.

2.9.2. Chromatographic conditions

The mobile phase consisted of a mixture of 90% aqueous solution of ammonium acetate (20 mM) and 10% methanol at a flow rate of 0.5 ml min^{-1} with a split 60:40. The stationary phase was an Agilent Zorbax Eclipse column XDB-C8 (150 mm × 4.6 mm × 5 μm). The injection volume was 20 μl.

2.9.3. Mass spectrometry conditions

The mass spectrometry experiments were conducted using Applied Biosystems USA-API 2000 triple quadruple equipped with electron spray ion (ESI) source and atmospheric pressure ionization (API). The mass spectrometer was operated in negative ion full scan mode and mass to charge range was 100–500 m/z. The temperature was set at 300 °C. The following were the conditions used for the three dyes used in our investigations: reactive black 5: declustering potential (DP) of -21 V, focusing potential (FP) of -400 V, entrance potential (EP) of -8 V and ion spray set at a potential of -3500 V; sunset yellow FCF: DP of -10 V, FP of -200 V, EP of -10 V and ion spray set at a potential of -4500 V; tartrazine: DP of -30 V, FP of -400 V, EP of -10 V and ion spray set at a potential of -3000 V.

3. Results and discussion

3.1. Time dependent spectral profile transitions of Mg^0/Pd^{4+} and Mg^0/Pd^0–alumina reacted dyes

Figs. 1(a)–3(b) compare 1 and 24 h spectral profiles of Mg^0/Pd^{4+} reacted dyes in the presence and absence of acid with those of native dyes. Fig. 4(a)–(c) compare 1 and 24 h spectral profiles of Mg^0/Pd^0–alumina reacted dyes in the presence of acid with those of native dyes. It must be pointed out at this juncture that decolourization reaction is negligible for Mg^0/Pd^0–alumina in the absence of acid and therefore all experiments were done only in the presence of acid for this system. The following observations may be summarized for the reaction of dyes with Mg^0/Pd^{4+} or Mg^0/Pd^0–alumina based on the
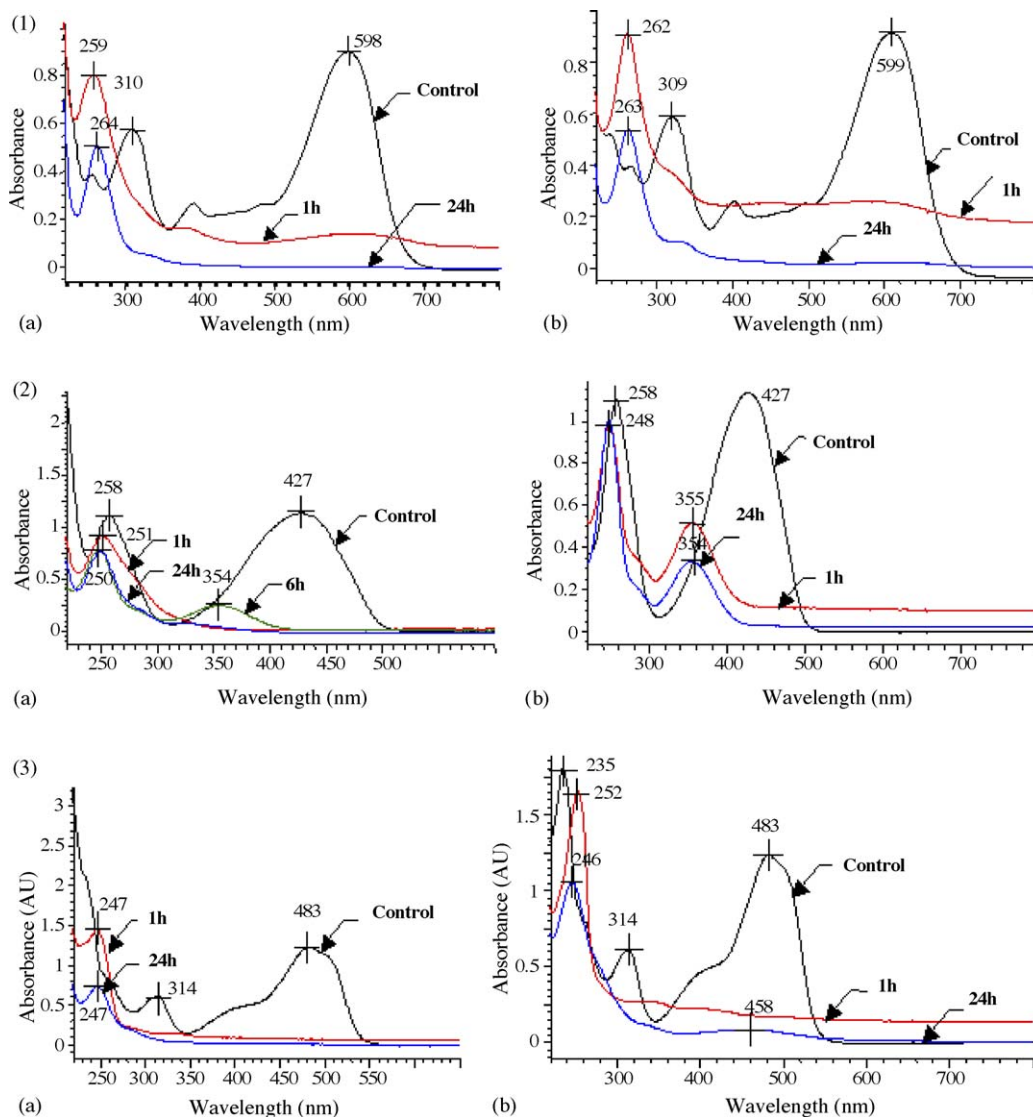
Figs. 1–3. (1) Comparison of time dependent spectral profiles of dyes reacted with Mg^0/Pd^{4+} salt in the presence (87 mM) and absence of acetic acid. Control represents untreated (native) dye. (a) reactive black 5 dye in presence of acid; (b) reactive black 5 dye in absence of acid. (2) (a) tartrazine dye in presence of acid; (b) tartrazine dye in absence of acid. (3) (a) sunset yellow FCF dye in presence of acid; (b) sunset yellow FCF dye in absence of acid. Experimental conditions which were similar for 1 and 24 h treated dyes are given below. *Experimental conditions*: initial concentration of dye was fixed at 100 mg l^{-1}; $Mg^0 = 2.5$ mg ml^{-1}; Pd^{4+} salt = 0.25 mg ml^{-1}; temperature = 30 °C; speed of shaker = 100 rpm, acetic acid = 87 mM or none. All solutions were diluted four-fold prior to taking spectra.
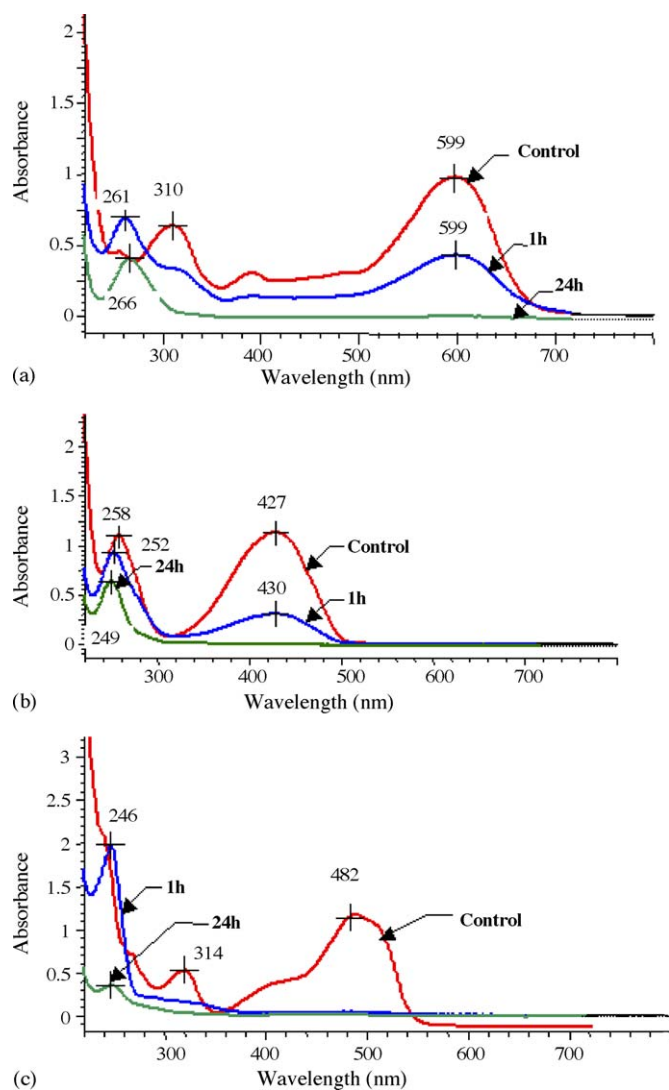
Fig. 4. Comparison of time dependent spectral profiles of dyes reacted with Mg^0/Pd^0–alumina in the presence (87 mM) of acetic acid. (a) Reactive black 5 (110.7 μM); (b) tartrazine (187.26 μM); (c) sunset yellow FCF (221.05 μM). Control represents untreated (native) dye. *Experimental conditions for 1 and 24 h reaction*: initial concentration of dye was fixed at 100 mg l^{-1}; $Mg^0 = 2.5$ mg ml^{-1}; $Pd^0 = 12$ mg ml^{-1}; temperature = 30 °C; speed of shaker = 100 rpm, acetic acid = 87 mM. All samples were diluted four-fold prior to recording spectra.

spectral profile transitions shown in Figs. 1(a)–4(c): (a) almost complete loss of 300–600 nm range peaks of all the three dyes (except for tartrazine reacted with Mg^0/Pd^{4+} in the absence of acid) following 1–24 h of reaction suggest the destruction of chromophoric groups in the dye molecules. Further, this is an irreversible decolourization process since the colour does not reappear after 24–48 h of incubation of Mg^0/Pd^0–alumina or Mg^0/Pd^{4+} reacted dye solutions (colour reversibility experiment described under support information). In addition, change in pH of the medium to acidic or alkaline conditions does not reverse the decolourization process, (b) there is either appearance of new peak(s) in the UV region and/or gradual and significant shift of the λ_{max} in the UV range by 5–11 nm (red or blue shift) during 1–24 h of reaction. The UV λ_{max} wavelength shift is accom-

Table 1
Comparison of decolourization efficiencies of Mg^0/Pd^{4+} with Mg^0/Pd^0–alumina

Dye	Percent decolourization using Pd^0	Percent decolourization using Pd^{4+}
Reactive black 5	57	85
Tartrazine	74	98
Sunset yellow FCF	90	96

Experimental conditions: dye concentration 100 mg l^{-1}; $Mg^0 = 2.5$ mg ml^{-1}; $Pd^0 = 12$ mg ml^{-1} or $Pd^{4+} = 0.25$ mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; speed = 100 rpm; reaction time = 1 h.

panied by reduction in its optical density, (c) the persistence of peaks in the UV region indicate that the aromatic components of the dye have not been disrupted i.e. dyes have not been degraded totally and (d) appearance of UV region peaks with λ_{max} ranging between 247–265 nm is indicative of the formation of sulfanilic acid as one of the end products following reductive transformation and decolourization of the dyes [32] (also see LC–MS presented in Table 4 which provides evidence for the formation of this product). The main absorbance region for sulfanilic acid is 258–269 nm and that for sulfanilate ion is 249 nm. Cao et al. [17] studied the degradation of acid orange II dye in aqueous phase using Fe^0 system and observed reduction in the visible absorbance of reacted dye that is accompanied by wavelength shifts in UV region.

3.2. Comparison of dye decolourization by K_2PdCl_6 and Pd^0–alumina

Results presented in Table 1 clearly indicate that Pd^{4+} is more efficient in decolourizing dyes as compared to the Pd^0–alumina pellets. In our experiments we noted that the size of Pd^0 particles obtained from reduction of K_2PdCl_6 was much smaller as compared to the commercial Pd^0–alumina pellets. The increased surface area of these small Pd^0 particles may be responsible for efficient hydrogen transfer and dye reduction in comparison to the larger Pd^0–alumina pellets.

3.3. Effect of varying concentrations of Pd^{4+} on the kinetics of reactive black 5 dye decolourization at a fixed Mg^0 concentration

Reductive decolourization of dyes occur on the Mg^0/Pd^0 deposit interface or directly on the surface of Pd^0 particles and one can expect that the amount of palladium would affect the dye degradation reactions. Fig. 5 illustrates the time dependent profiles and linearized kinetic plots (inset in the same figure) for decolourization of 100 mg l^{-1} reactive black 5 dye using fixed concentration of Mg^0 and varying concentrations of Pd^{4+} in the presence of acetic acid. The disappearance of reactive black 5 dye fits the first order kinetic equation as given below:

$$C = C_0 e^{-k_{obs}t} \tag{6}$$

where C is the concentration of dye at any time, t, C_0 the initial concentration of dye and k_{obs} is the pseudo first order rate constant.
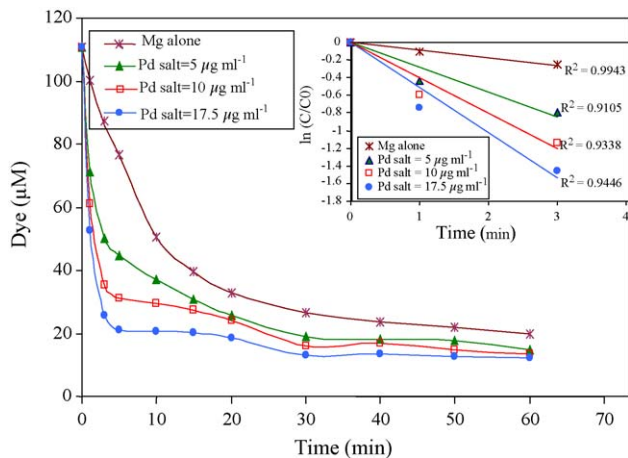
Fig. 5. Comparison of kinetic plots for decolourization of reactive black 5 dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^{4+} salt at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, C and C_0 represent the concentrations of dye at time zero and t, respectively. *Experimental conditions:* dye concentration = 100 mg l^{-1} (110.7 μM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 120 ml.

Results illustrate that increase in Pd^{4+} concentration enhances the extent and rate of decolourization. The first order rates constants for decolourization of reactive black 5 dye were estimated to be 0.28, 0.40 and 0.51 min^{-1} using 5, 10 and 17.5 μg ml^{-1} of Pd^{4+}, respectively. For 3.5-fold increase in Pd^{4+} concentration (5–17.5 μg) the rate constant value enhanced by ~two-fold.

3.4. Effect of varying concentrations of Pd^0–alumnia on the kinetics of reactive black 5 dye decolourization at a fixed Mg^0 concentration

We also decided to investigate the decolourization of reactive black 5 dye using Mg^0/Pd^0–alumina pellet since this form of palladium can be recycled. We observed very insignificant rates of dye removal by the above bimetallic system in the absence of acid. Addition of small concentration of acid enhanced dye degradation rate. Fig. 6 shows time dependent profiles and linearized kinetic plots (inset in the same figure) for the decolourization of reactive black 5 dye using varying concentrations of Pd^0–alumina at a fixed concentration of reactive black 5 dye and Mg^0 in the presence of acid. The first order rate constants were calculated to be 0.074, 0.084 and 0.098 min^{-1} for 0.95, 1.4 and 1.9 mg ml^{-1} of Pd^0, respectively. Nam and Tratnyek [18] studied the reduction of azo dyes in an anaerobic batch system using Fe^0 and reported that the dyes were reduced by first order kinetics. In our investigations the rate constant increases ~1.2–1.3-fold for every 0.45 mg ml^{-1} increase in Pd^0 in the reaction mixture.

3.5. Reuse efficiency of Mg^0/Pd^0–alumina using reactive black 5 dye

The reuse efficiency of Mg^0/Pd^0 pellets was observed using 100 mg l^{-1} of reactive black 5 dye each time (experiment described under support information). Nearly 85% of the colour
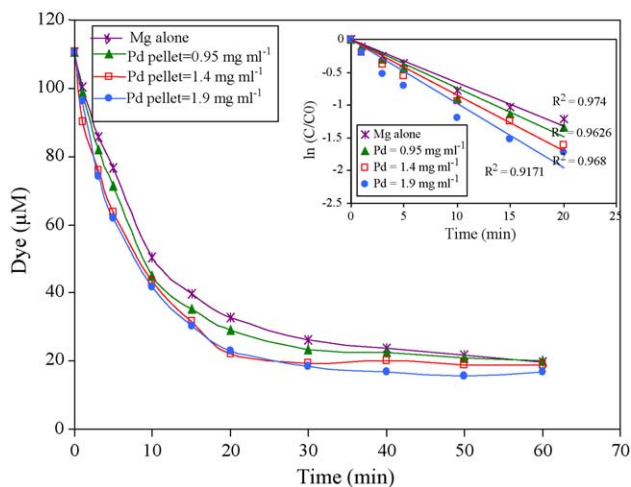

Fig. 6. Comparison of kinetic plots for decolourization of reactive black 5 dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^0 (pellets) at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, C and C_0 represent the concentrations of dye at time 0 and t, respectively. *Experimental conditions*: dye concentration = 100 mg l^{-1} (110.7 μM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 105 ml.

disappeared with every use of Pd^0 pellets and fresh dosing of Mg^0 in each trial. Results obtained from reuse experiments suggest that Pd^0 pellets have the potential for recycling which will make the treatment process cost effective.

3.6. Decolourization studies on reactive black 5 dye using Mg^0 alone

We decided to also investigate the decolourization ability of Mg^0 in the absence of hydrogenating agents like Pd (experiment as described under support information). Our results indicate that reaction follows first order kinetics and rates of decolourization of reactive black 5 dye as well as the extent of dye removal is increased by the addition of acid (nearly 80% decolourization is achieved in the presence of acid within 1 h of reaction as compared to only 30% decolourization in the absence of acid). Comparison of time dependent profiles for decolourization of reactive black 5 dye using Mg^0 alone and Mg^0/Pd^{4+} (Fig. 5) or Mg^0/Pd^0 (Fig. 6) clearly suggests the superior performance of Mg^0/Pd^{4+} bimetallic system. Rate constant for decolourization is enhanced five-fold for Mg^0/Pd^{4+} (5 mg/17.5 μg ml^{-1}) when compared to those obtained using Mg^0 alone (5 mg ml^{-1}) or Mg^0/Pd^0 (5 mg/1.9 mg ml^{-1}). Clearly the coordinate complex salt of palladium is more reactive towards the dye molecules.

3.7. Effect of varying concentrations of Pd^{4+} on the kinetics of sunset yellow FCF dye decolourization at a fixed Mg^0 concentration

Fig. 7 illustrates time dependent profiles and linearized kinetic plots (inset in the same figure) for the decolourization of 100 mg l^{-1} of sunset yellow FCF with increasing concentrations of Pd^{4+} at a fixed concentration of Mg^0. The first order rate constant values were calculated to be 0.239, 0.328, 0.592 min^{-1} for
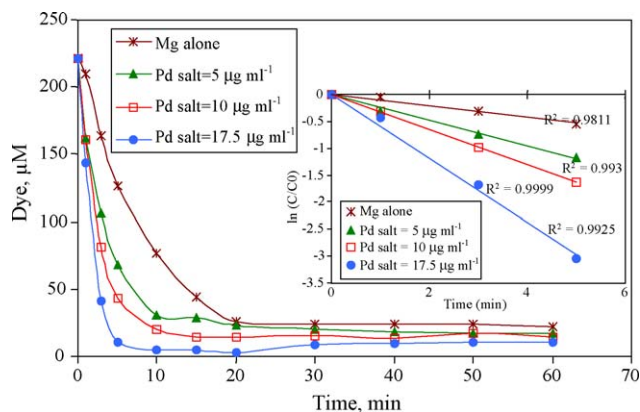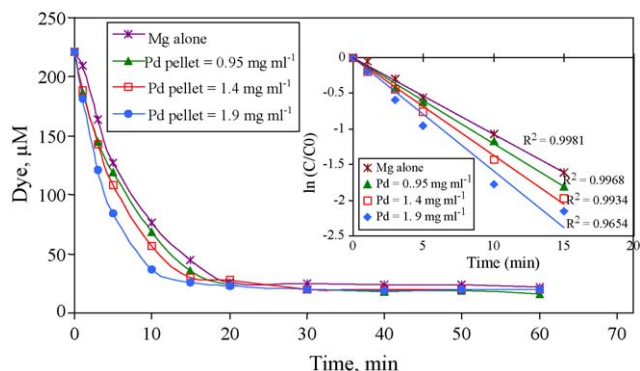
Fig. 7. Comparison of kinetic plots of decolourization of sunset yellow FCF dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^{4+} salt at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, C and C_0 represent the concentrations of dye at time 0 and t, respectively *Experimental conditions:* dye concentration = 100 mg l^{-1} (221 µM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 120 ml.

100 mg l^{-1} dye using 5, 10 and 17.5 µg ml^{-1}, of Pd^{4+}, respectively. The results indicate nearly 2.5-fold increase in the rate constant for 3.5-fold increase in the Pd^{4+} salt concentration. These results corroborate with those obtained with reactive black 5 dye.

3.8. Effect of varying concentrations of Pd^0–alumnia on the kinetics of sunset yellow FCF dye decolonization at a fixed Mg^0 concentration

Fig. 8 compares time dependent profiles and linearized kinetic plots (inset in the same figure) for the decolourization of sunset yellow FCF dye using Mg^0/Pd^0 in the presence of acid. The rates were assessed using varying concentration of Pd^0–alumina at a fixed concentration of sunset yellow FCF dye and Mg^0. The first order rate constants were calculated to be 0.120, 0.136 and 0.158 min^{-1} for 0.95, 1.4 and 1.9 mg ml^{-1} of Pd^0, respectively. The rate constant increases ∼1.3-fold for two–fold increase in Pd^0 concentration.

Fig. 8. Comparison of kinetic plots for decolourization of sunset yellow FCF dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^0 (pellets) at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, C and C_0 represent the concentrations of dye at time 0 and t, respectively *Experimental conditions*: dye concentration = 100 mg l^{-1} (221 µM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 105 ml.
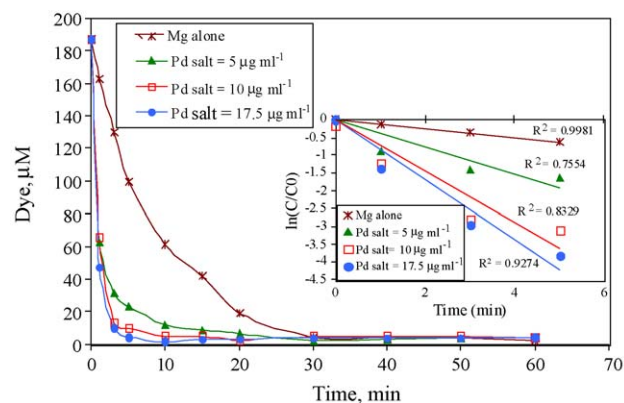

Fig. 9. Comparison of kinetic plots of decolourization of tartrazine dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^{4+} salt at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, C and C_0 represent the concentrations of dye at time 0 and t, respectively. *Experimental conditions*: dye concentration = 100 mg l^{-1} (187.3 µM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 120 ml.

3.9. Decolourization studies on sunset yellow FCF dye using Mg^0 alone

Comparison of kinetic plots for decolourization of sunset yellow FCF dye using Mg^0 alone with Mg^0/Pd^{4+} and Mg^0/Pd^0 are shown in Figs. 7 and 8, respectively. The rate constant obtained using Mg^0/Pd^{4+} (5 mg/17.5 µg ml^{-1}) was four-fold and six-fold higher in comparison to those obtained with Mg^0/Pd^0 (5 mg/1.9 mg ml^{-1}) and Mg^0 alone (5 mg ml^{-1}), respectively. These results demonstrate the superior performance of Mg^0/Pd^{4+} in relation to Mg^0 alone and Mg^0/Pd^0.

3.10. Effect of varying concentrations of Pd^{4+} on the kinetics of tartrazine dye decolourization at a fixed Mg^0 concentration

Fig. 9 illustrates time dependent profiles and linearized kinetic plots (inset in the same figure) for the decolourization of 100 mg l^{-1} tartrazine dye using increasing concentrations of Pd^{4+} at fixed concentration of Mg^0. The first order rate constants were calculated to be 0.381, 0.718 and 0.843 min^{-1} for 100 mg l^{-1} dye using 5, 10 and 17.5 µg ml^{-1} of Pd^{4+}, respectively. There is ∼two-fold increase in the rate constant with the higher concentrations of Pd^{4+}.

3.11. Effect of varying concentrations of Pd^0–alumnia on the kinetics of tartrazine dye decolourization at a fixed Mg^0 concentration

Fig. 10 depicts time dependent profiles and linearized kinetic plots (inset in the same figure) for the decolourization of 100 mg l^{-1} tartrazine dye using increasing concentrations of Pd^0 at fixed concentration of Mg^0. The first order rate constants were calculated to be 0.119, 0.130 and 0.16 min^{-1} for 100 mg l^{-1} dye using 0.95, 1.4 and 1.9 mg ml^{-1} of Pd^0, respectively. These results indicate marginal increase in rate constant with every additional 0.5 mg of Pd^0 in the reaction mixture.
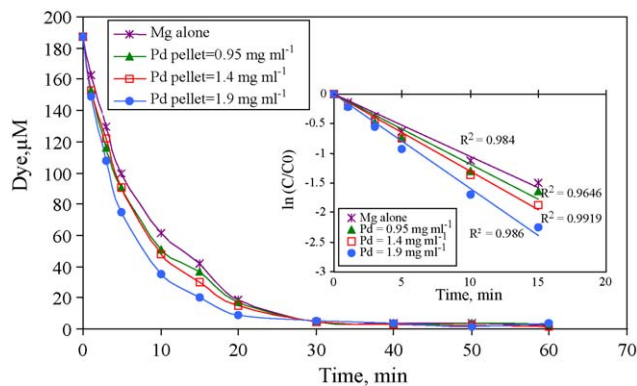
Fig. 10. Comparison of kinetic plots for decolourization of tartrazine dye using 5 mg ml^{-1} of Mg^0 alone or varying concentrations (as indicated) of Pd^0 (pellets) at a fixed concentration (5 mg ml^{-1}) of Mg^0. In the inset figure, *C* and C_0 represent the concentrations of dye at time 0 and *t*, respectively *Experimental conditions:* dye concentration = 100 mg l^{-1} (187.3 μM); Mg^0 = 5 mg ml^{-1}; 87 mM acetic acid; temperature = 30 °C; reaction volume = 105 ml.

3.12. Decolourization studies on tartrazine dye using Mg^0 alone

Figs. 9 and 10 compare the kinetic plots for decolourization of tartrazine dye using Mg^0 (5 mg ml^{-1}) alone with Mg^0/Pd^{4+} and Mg^0/Pd^0 bimetallic systems, respectively. The rate constant obtained using Mg^0/Pd^{4+} (5 mg/17.5 μg ml^{-1}) was five- and seven-fold higher with respect to those obtained with Mg^0/Pd^0 (5 mg/1.9 mg ml^{-1}) and Mg^0 alone (5 mg ml^{-1}). These results again demonstrate the higher decolourization efficiency of Mg^0/Pd^{4+} in relation to Mg^0 alone and Mg^0/Pd^0 systems.

3.13. Comparison of dye degradation rate constant values

The first order rate constants obtained in our investigation (using Mg^0 alone, Mg^0/Pd^{4+} and Mg^0/Pd^0) are summarized in Table 2. The rate constants are significantly higher for decolourization of all the three dyes by Mg^0/Pd^{4+} thereby suggesting that this bimetallic system is relatively more efficient.

Table 3 summarizes the first order rate constants obtained for monometallic systems. It can be seen that rate constants for Fe^0 (200 mg ml^{-1}) mediated degradation of sunset yellow FCF dye and tartrazine dyes as reported by Nam and Tratnyek [18] are comparable to those obtained using 5 mg ml^{-1} Mg^0 alone in our investigations. The rate constant values are enhanced ~four times if 20 mg ml^{-1} of Mg^0 is used. Clearly, Mg^0 is more efficient in decolourizing the dyes as compared to Fe^0.

3.14. Dye desorption studies from Mg/Pd pellets following reaction cycle

Decolourization of dyes using Mg^0/Pd^{4+} or Mg^0/Pd^0– alumina involves two steps: (a) surface adsorption of dyes onto Pd^0 or Mg^0/Pd^0 interface and (b) catalytic hydrogen transfer to the target compounds and its decolourization. Therefore one can envisage that non-reactive adsorption mechanism may be responsible for the decolourization of dye solutions. In order to verify such a possibility we performed desorption experiments (experimental method discussed under support information). Our results demonstrated that adsorption of dyes is only to an extent of 1–3% and 2–10% using Mg^0/Pd^{4+} and Mg^0/Pd^0 systems, respectively.

Table 2
Comparison of dye degradation rate constants values using various zero-valent metals/bimetallic systems

Dye used and concentration (mg l^{-1})	Metallic system used	Concentration of metal (ml^{-1})	First order rate constant (min^{-1})
Reactive black 5 (100 mg l^{-1})	Mg^0 alone	5 mg	0.08
	Mg^0/Pd^0	5 mg/1.9 mg	0.098
	Mg^0/Pd^{4+}	5 mg/17.5 μg	0.51
Sunset yellow FCF (100 mg l^{-1})	Mg^0 alone	5 mg	0.106
	Mg^0/Pd^0	5 mg/1.9 mg	0.158
	Mg^0/Pd^{4+}	5 mg/17.5 μg	0.592
Tartrazine (100 mg l^{-1})	Mg^0 alone	5 mg	0.12
	Mg^0/Pd^0	5 mg/1.9 mg	0.16
	Mg^0/Pd^{4+}	5 mg/17.5 μg	0.84

Table 3
Comparison of dye degradation rate constants values using various zero-valent metal systems (current work vs. literature data)

Reference	Dye used and concentration	Bimetallic system used	Concentration of catalyst (ml^{-1})	First order rate constant (min^{-1})
Current work[a]	Sunset Yellow FCF (300 μM)	Mg^0 alone	5 mg	0.113
			20 mg	0.445
Current work[a]	Tartrazine (300 μM)	Mg^0 alone	5 mg	0.111
			20 mg	0.460
Nam and Tratnyek (2000)	Sunset yellow FCF (300 μM)	Fe^0 alone	200 mg	0.148
Nam and Tratnyek (2000)	Tartrazine (300 μM)	Fe^0 alone	200 mg	0.116

[a] Rate constants obtained from our investigations.

3.15. Modeling of dye decolourization kinetic data

We attempted to model the kinetic data for decolourization of dye using the Michaelis–Menten equation (which describes the relation between the observed initial velocity of an enzyme catalyzed reaction to the substrate concentration) as given below:

$$V = \frac{V_{max}[C]}{K_m + [C]} \qquad (7)$$

where V is the observed velocity; V_{max} the maximal velocity for a given concentration of the catalytic agent; K_m the half saturation coefficient; $[C]$ is the concentration of the substrate (dye in our investigations).

The rationale for applying the above model is that the decolourization of dye by Mg/Pd system involves the following sequential steps (a) adsorption and binding of the dye molecules leading to the formation of metal–dye complex (equivalent to binding of the substrate to the active site of an enzyme to form ES complex), (b) reductive transformation of dye by the reactive bimetallic surface (equivalent to the enzyme catalyzed transformation of the substrate to product) and (c) dissociation of the reduced product from the reactive metal sites (equivalent to dissociation of enzyme–product complex). Non-reactive adsorption of dye molecules to metal surface is negligible and therefore one can ignore its contribution towards decolourization. Also we assume that the numbers of reactive sites on metal surface are constant during the reaction period. First order rate constant values were calculated from the experimental data obtained for a range of concentrations of the three dyes chosen in our investigations. Based on these rate constant values we calculated the observed rates of decolourization. Linearized (Lineweaver–Burk) plots of $1/V$ versus $1/[C]$ was used to compute the V_{max} and K_m values based on which we predicted the rates of decolourization for a given range of dye concentration. Fig. 11(a)–(c) compare the experimental and predicted Michaelis–Menten plots for the decolourization of reactive black 5, sunset yellow FCF and tartrazine dyes by Mg^0/Pd^{4+} system, respectively. Clearly there is a strong agreement between the experimental and predicted sets of data thereby demonstrating the correctness of Michaelis–Menten model for the prediction of dye decolourization rates by Mg^0/Pd system.

3.16. LC–MS study of dyes and their degraded products

Fig. 12(a) shows the HPLC chromatogram of the native reactive black 5 dye with a broad peak eluting between 1.25–2.5 min and Fig. 12(b) shows the mass spectrum of the same peak. The signals at 705.9, 450.4, 412.6, 401.3 and 352.4 m/z in Fig. 12(b) can be ascribed to: $[M - H - 2H_2SO_4]^-$, $[M - 2H]^{2-}$, $[M - 3H - H_2SO_4 + Na]^{2-}$, $[M - 2H - H_2SO_4]^{2-}$ and $[M - 2H - 2H_2SO_4]^{2-}$, respectively [33]. Fig. 12(c) represents the HPLC elution profile of the reactive black 5 reacted with Mg^0/Pd^{4+} system for 24 h. It can be seen that the broad peak of the parent dye is no more present and instead a new sharp peak eluting at 2.05 min was observed, thereby suggesting the transformation of the dye. Fig. 12(d) shows the mass spectrum

of the product peak eluting at 2.05 min. The two signals at 349 and 280.9 m/z can be ascribed to amine end products, namely, l-2-7-triamino-8-hydroxy, 3-6-naphthalinedisulphonate and 1-sulphonic, 2-(4-aminobenzenesulphonyl) ethanol, the structures of which are shown in Fig. 13. Similarly we carried out LC–MS analyses for native and Mg^0/Pd^{4+} treated sunset yellow FCF and tartrazine dyes. Table 4 depicts the structures of the identified products formed from Mg^0/Pd^{4+} reacted dyes. These results suggest that the decolourization of dyes proceed via the reductive cleavage of azo bonds resulting in the formation of aromatic amines as shown in Fig. 13. Plum et al. [34] and Gosetti et al. [35] reported similar results for the anaerobic biodegradation of reactive black 5 dye and ascorbic acid mediated degradation of sunset yellow FCF, respectively.
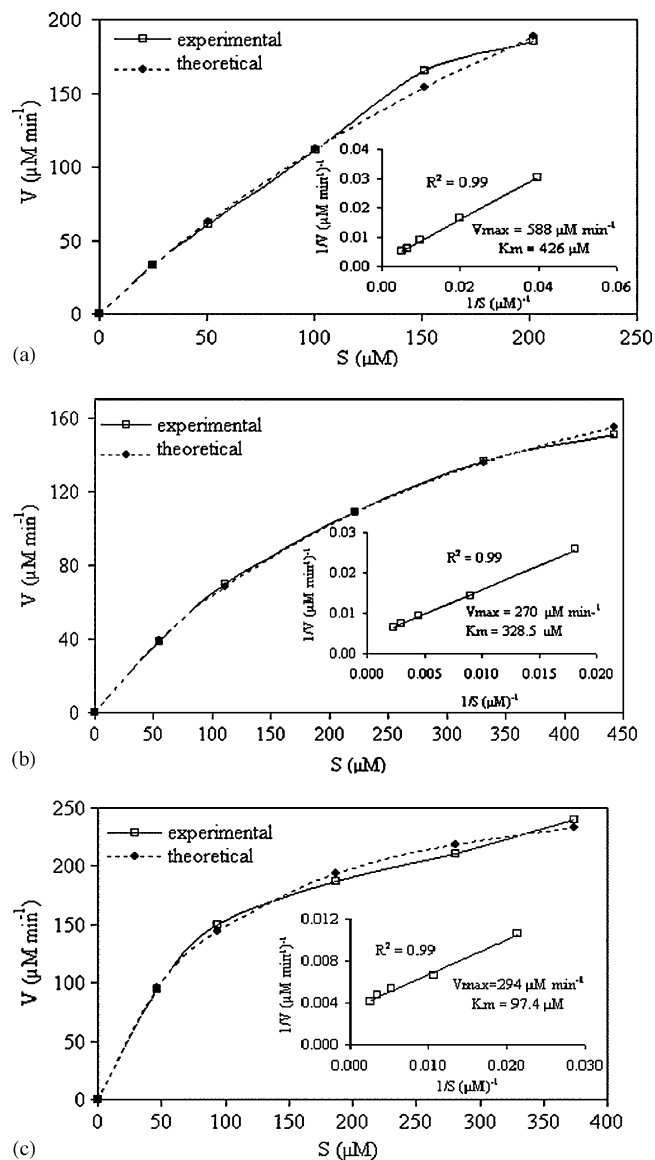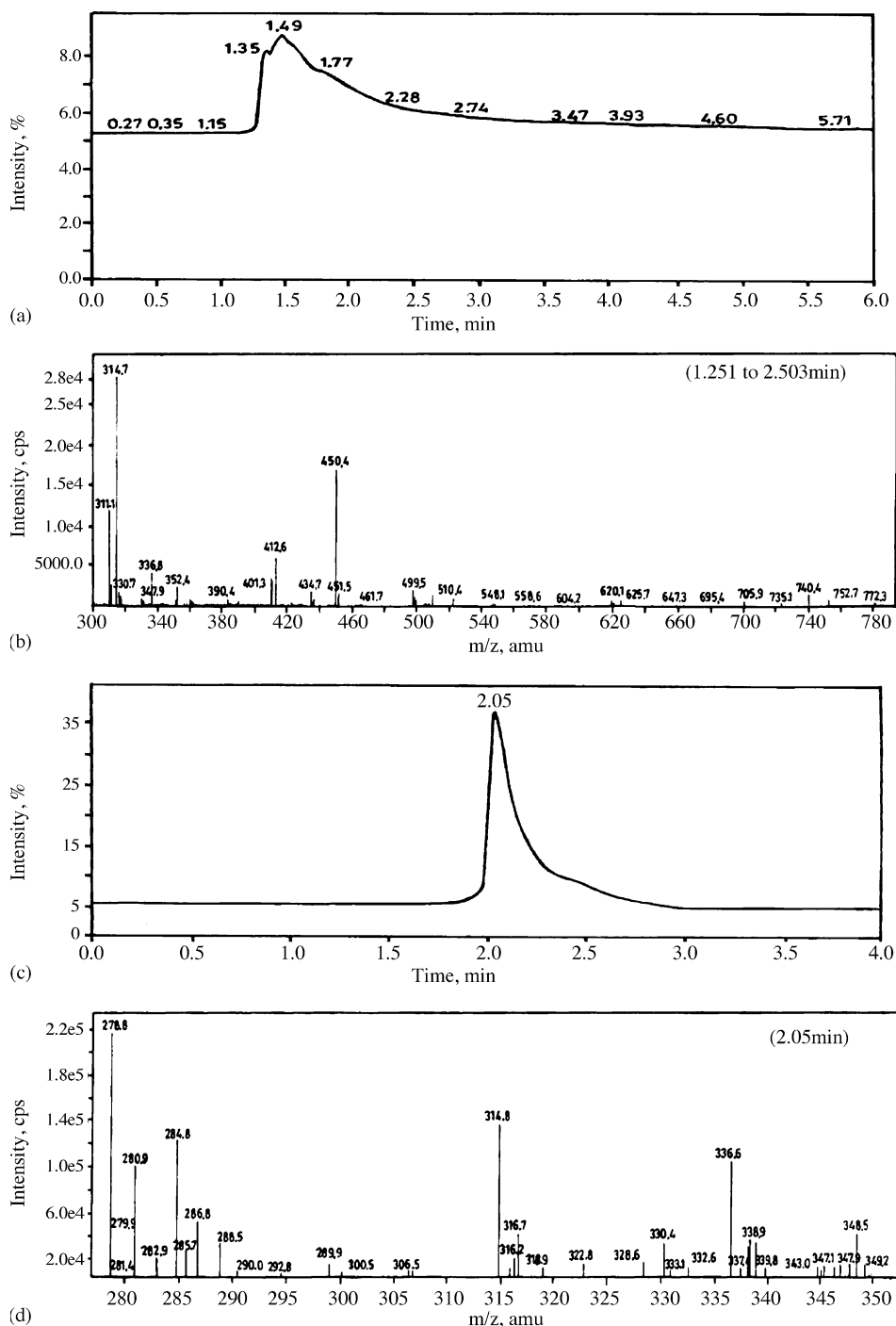

Fig. 11. Comparison of experimental and predicted Michaelis–Menten plots for the decolourization of (a) reactive black 5, (b) sunset yellow FCF and (c) tartrazine using Mg^0/Pd^{4+} system. V_{max} and K_m values were calculated from double reciprocal (Lineweaver–Burk) plots shown as insets in the figures.

Fig. 12. (a) HPLC elution profile of the native reactive black 5 dye, (b) mass spectrum for the peak from 1.251 to 2.503 min, (c) HPLC profile of Mg^0/Pd^{4+} reacted (24 h reaction time in the presence of 87 mM acetic acid) reactive black 5 dye and (d) mass spectrum for the product peak at 2.05 min *Chromatographic conditions*: stationary phase: Agilent Zorbax Eclipse XDB-C8 column (150 mm × 4.6 mm × 5 μm), mobile phase: 90% aqueous solution of ammonium acetate (20 mM) and 10% methanol, flow rate: 0.5 ml min^{-1}, injection volume: 20 μl.

3.17. Decolourization study using mixture of dyes

An attempt was made to examine the efficiency of Mg^0/Pd^{4+} system for the decolourization of solution containing mixture of dyes. Fig. 14 shows the composite spectra of the mixture of dyes obtained following 1 and 24 h of the reaction using Mg^0/Pd^{4+} system. It may be noted that the loss of colour is nearly 80% and 95% following 1 and 24 h of reaction, respectively, thereby

indicating that the bimetallic system is efficient in decolourizing mixture of commercial dyes.

3.18. Decolourization study using raw industrial effluent

Fig. 15 compares UV–visible spectral profiles of untreated (control) and Mg^0/Pd^{4+} treated (1 h reaction time) raw industrial effluent. It may be noted that the bimetallic system achieves
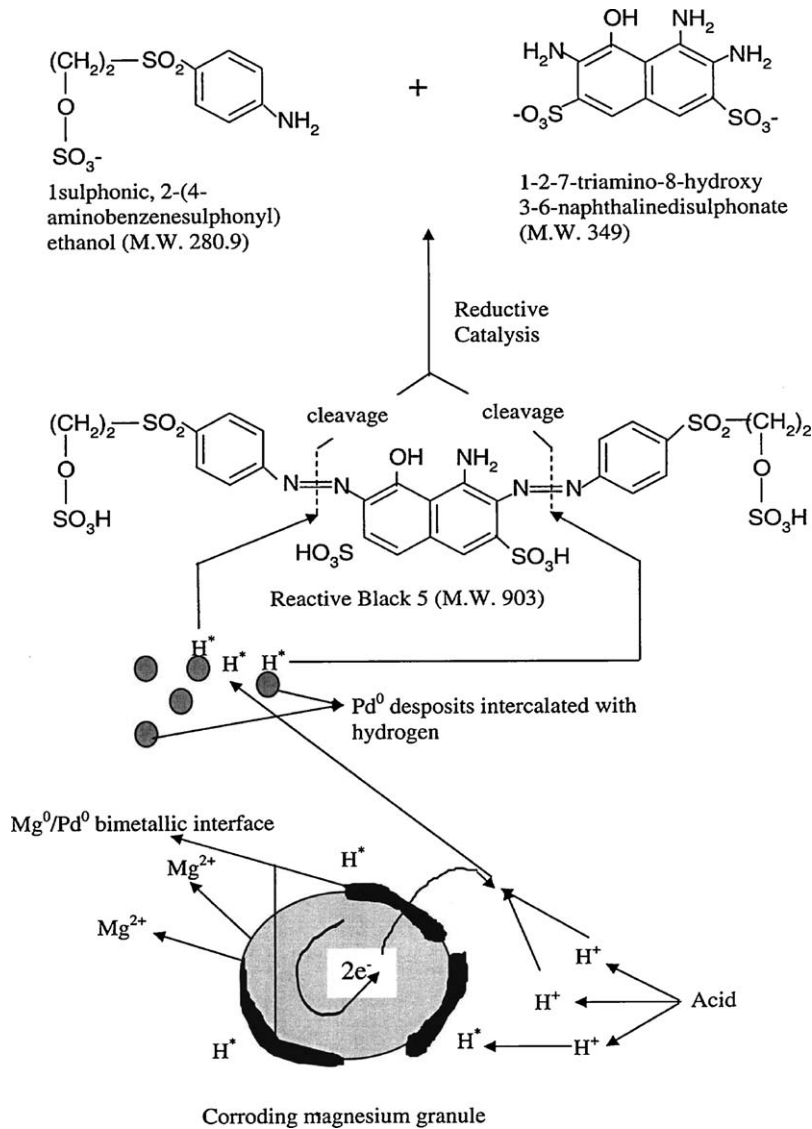
Fig. 13. Decolourization of reactive black 5 dye by magnesium–palladium system through reductive cleavage of azo bonds.
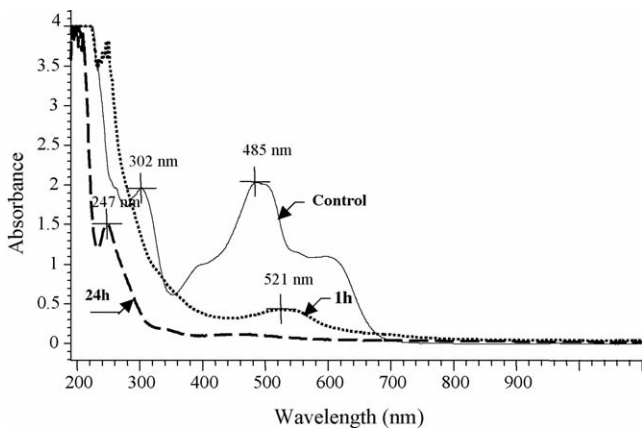

Fig. 14. Spectral profile of mixture of dyes following treatment with Mg^0/Pd^{4+} system. Control represents untreated (native) dye. *Experimental conditions*: Mg^0 = 2.5 mg ml^{-1}; Pd^{4+} = 17.5 μg ml^{-1}; temperature = 30 °C; acetic acid = 87 mM; reaction volume = 50 ml; reaction time = 1 and 24 h; dye mixture contained: 20 mg l^{-1} each of reactive black 5, sunset yellow FCF, drimarene red, drimarene navy and remazol brown dyes.
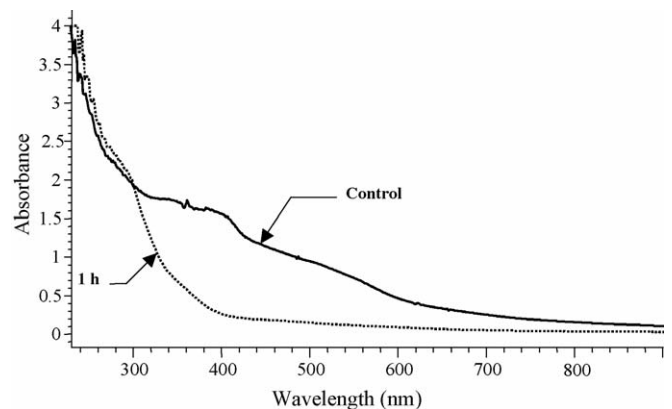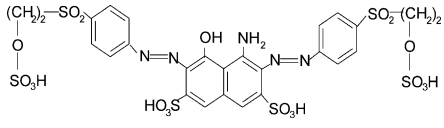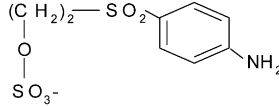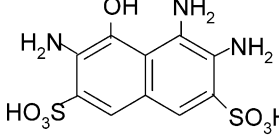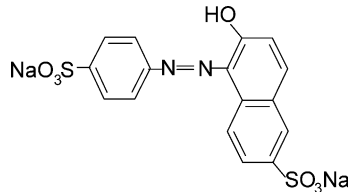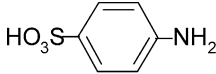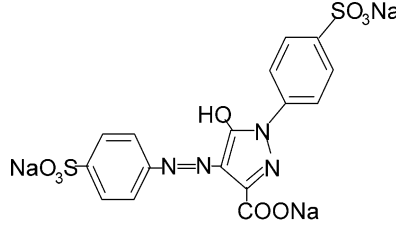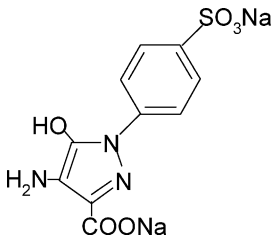

Fig. 15. Spectral profile of industrial effluent following treatment with Mg^0/Pd^{4+} system. Control represents untreated (raw) effluent from the equalization tank of a local dye manufacturing company. Experimental conditions: Mg^0 = 20 mg ml^{-1}; Pd^{4+} = 17.5 μg ml^{-1}; temperature = 30 °C; 174 mM acetic acid; reaction volume = 50 ml; reaction time = 1 h.

Table 4
Dye degradation products identified using LC–MS

Dye	Products identified	m/z Value
 Reactive black 5 (MW. 903)	 1- sulphonic, 2-(4-aminobenzenesulphonyl) ethanol	280
	 1-2-7-triamino-8-hydroxy,3-6-naphthalinedisulphonate	349
 Sunset yellow FCF (MW. 452.37)	 sulphanilic acid	173
 Tartrazine (MW. 534.37)		343

~85% reduction in the colour intensity. This result suggests that the Mg/Pd system can be employed directly for the decolourization of composite (raw) industrial effluent.

4. Conclusions

In conclusion the Mg/Pd (palladium in the form of K_2PdCl_6 or Pd^0–alumina pellets) mediated reductive reactions for decolourization of textile dyes proceed in an elegant and rapid manner. It is hypothesized that this heterogeneous phase catalytic process occurs at the interface between Mg^0/Pd^0 or on Pd^0 particles. This reaction is easy to conduct and occurs under room temperature and pressure. The presence of oxygen does not affect the reaction and this is a great advantage for recalcitrant pollutants like textile dyes that normally degrade under strict anaerobic conditions. LC–MS data suggest that the loss of colour is due to the reductive cleavage of –N=N– (azo) in the dye molecules. Regarding the application, we feel that immobilized forms of palladium (i.e. Pd^0 on alumina) may be the best option for field scale since this form of catalyst can be recycled which in turn reduces the cost. The estimated cost for treatment of 1 L of solution containing 100 mg of reactive black 5 dye is ~Rs. 28.6 which involves reuse of Pd^0–alumina pellets for 10 cycles with fresh dosing of Mg^0 for each cycle. The cost of bioadsorption using *Aspergillus foetidus* [13–15] is ~Rs. 3.5 for 1 L of solution containing 100 mg of dye. The cost of biomass cultivation can be further reduced since it can be recycled atleast 10 times (unpublished results). Thus the total cost of the integrated process (bioadsorption–chemical decolourization) is ~Rs. 32 for 1 L of solution containing 100 mg of dye.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2006.05.019.

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