Catalytic activity of Ni complexed aminoclay towards the reduction of Cr(VI), *p*-nitrophenol and fluorescein dye

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Abstract A green-colored Ni-complexed aminoclay (AC) was synthesized and its size and crystalline nature were confirmed by HRTEM images and XRD, respectively. The AC–Ni system was used as a catalyst towards the reduction of environmental pollutants like Cr(VI), fluorescein (Fluor) and nitrophenol (NiP) individually and also their mixture. The catalytic reduction of Cr(VI) was elaborately studied under different experimental conditions. The thermodynamic parameters were determined. The AC–Ni system exhibited lower energy of activation (E_a) value. The apparent rate constant of individual components and their mixture was determined, analyzed and compared with the literature reports. The pollutants present in the mixture exhibited the lower k_{app} value due to the complex formation.

Keywords AC–Ni catalyst · Reduction reaction · Apparent rate constant · Energy of activation

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Introduction

Due to heavy population and industrialization, the quality of environment becomes worst. As a result, thousands of people are dying every year due to various diseases such as cancer and kidney failure. Among the various environmental pollutants, Cr(VI), dyes and nitrophenols (NiP) play a vital role in environmental pollution. To avoid environmental pollution, caused due to the above said key elements, various techniques particularly chemical reduction are employed. The metal or metal oxide nanoparticles are used as a catalyst for the chemical reduction purpose. The drawback of using metal or metal oxide nanoparticles during the course of the reduction reaction can be leached into the reaction medium and lead to decrease in concentration. As a result, the efficiency of the catalyst is decreased in further cycles or reusability. This motivated us to do the present investigation. The above said problems can be outwitted by a complexation reaction. With this novelty, the present investigation was made towards the green environment.

Chromium and its compounds have a wide range of applications in modern industries such as chrome tanning and plating and from them large quantities of hazardous effluents are released to the open environment. Hexavalent chromium is carcinogenic but the trivalent chromium is less toxic (Feng et al. 2012). Hence, it is necessary to reduce the Cr(VI) into Cr(III). Chemical reduction is a simple method with maximum efficiency among the various techniques available. Reduction of Cr(VI) was carried out in the presence of Fe(III)-tartrate catalyst system (Feng et al. 2012). Huang et al. (2012) reported about the catalytic reduction of Cr(VI) using Pd nanoparticle immobilized electrospun fiber. Other catalysts systems are: nanostructured polyamic acid (Omole et al. 2011), goethite

(Kim et al. 2007), silica (Gienada et al. 2016), Fe^0 (Alowitz and Scherer 2002), CCTCCAB 91095 (Song et al. 2009), molybptic phosphate (Gong et al. 2015), ATCC 33456 (Shen and Wang 1995) and Pd-supported aminoclay (AC) (Celebi et al. 2016). After thorough literature survey, we could not find any report based on the AC–Ni catalyzed reduction of Cr(VI).

p-Nitrophenol (NiP) is a refractory pollutant emerging from various chemical industries. The reduced product of NiP (i.e., aminophenol) plays a vital role in the pharmaceutical industry and the agrochemical industry as a building block. Generally, the chemical reduction of NiP is an easy process and it follows the pseudo first-order kinetics on catalytic reduction reaction. Liu et al. (2016) reported the catalytic reduction of NiP over Ni–Pd nanoparticle. Dai et al. (2016) studied the catalytic reduction of NiP with the help of amphiphilic hyperbranched polymer-encapsulated Au nanoparticles. Polyacrylonitrile-supported Ag nanoparticle was used for the catalytic reduction of NiP (Gao et al. 2016). Other catalysts like Pd/ Fe_3O_4 @ dextran (Lara et al. 2015), Ag (Naraginti and Sivakumar 2014), fly ash@polypyrrole/Au composite (Sun et al. 2016), Cu-supported graphite carbon material (Moraes et al. 2017), Pt nanoparticles (Lee et al. 2011), bimetallic dendrimer (Pozun et al. 2013) and hydroxyapatite (Sowmiya et al. 2015) were used for the catalytic reduction of NiP. After thorough literature survey, the catalytic reduction of NiP by AC–Ni catalyst system was not found. This urged the investigators to do the present investigation. The novelty of the present investigation is the catalytic reduction of NiP present in the mixture of effluents containing Cr(VI) and fluor dye molecules. It means the stereo specific reduction of NiP present in the mixture of effluents.

The wastewater obtained from the textile and dyeing industry is the root cause for the serious environmental pollution since it consists of a higher quantity of dyeing materials and larger quantity of different compounds. It is necessary to find out a way to reduce the water pollution caused by the dye materials. For this purpose, adsorption (Jayanthi et al. 2015), oxidation (Mathivathana et al. 2013), photoreduction (Mittal et al. 2009), enzymatic degradation (Apostal et al. 2012) and chemical reduction method (Borase et al. 2014) are used. Among these, chemical reduction method in the presence of a catalyst is an easy and economically cheaper one with maximum efficiency. Catalytic reduction of mixture of xanthenes type dyes were carried out in the presence of Au nanoparticles (Hassan et al. 2011). Jana et al. (2000) reported Pd nanoparticle mediated catalytic reduction of fluor. Gelatin-stabilized Au nanoparticle was used for the catalytic reduction of xanthenes type dyes (Tagar et al. 2012). Komalam et al. (2012) reported the catalytic reduction of Eosin B in the presence

of chitosan stabilized Au nanoparticles. Similarly, other nanocatalysts were used for the degradation of xanthenes type dyes (Junejo and Baykal 2014; Deka et al. 2016). On studying the literature, no report based on the AC–Ni catalyzed reduction of fluor could be found. Fluor is a xanthene type dye without any halogen substitution in the phenyl rings.

Experimental

Materials

3-Aminopropyltrimethoxysilane (APTMS) was purchased from Sigma-Aldrich, India and used as received. Magnesium nitrate was purchased from Merck, India. Potassium dichromate (PDC), nickel sulphate and sodiumborohydride (NaBH_4) were purchased from S.D fine chemicals, India. Ethanol was purchased from CDH, India. Double distilled water (DDW) was used for washing and solution preparation purposes. *p*-Nitrophenol (NiP) and fluorescein dye (Fluor) were purchased from Nice chemicals, India.

Synthesis of AC and AC–Ni complex system

To prepare AC, a standard literature procedure was followed (Celebi et al. 2016). 4.2 g of MgNO_3 was added with 100 mL of ethanol under stirring condition at room temperature. 3.8 mL of APTMS was added with MgNO_3 under stirring condition for 5 h. The resulted white slurry was isolated by centrifugation for 5 min. The supernatant liquid was discarded and the precipitate was further centrifuged with 10 mL ethanol. The centrifugation was repeated for 3–4 times to remove the unreacted reactants and other impurities. Finally, the precipitate was dried at 60 °C for 6 h, ground, weighed and stored in zipper lock cover. Thus, obtained white powder is called as AC and it is completely soluble in water.

One gram of AC was dissolved in 50 mL of DDW. 0.50 gram of nickel sulphate was added to it and stirred for 2 h at room temperature. The ratio between AC and NiSO_4 was maintained as 2:1. During the process, the Ni^{2+} ion gets complex with the amino group of AC. The changing color of reaction medium, i.e., conversion of dark green color into a pale green color confirmed the complex formation. 0.025 g of NaBH_4 was accurately weighed and mixed with the solution under mild stirring condition. The reduction of Ni^{2+} into Ni^0 was confirmed by a change in color, into a dark black. The reduction reaction was allowed to continue for another 2 h under stirring condition. The contents were treated with 50 mL ethanol and centrifuged for 5 min. The supernatant liquid had unreacted nickel sulphate and physically formed Ni

nanoparticles were removed. The centrifugation was repeated for 3–4 times to remove the impurities completely. To confirm this, the supernatant liquid was subjected to UV–Vis spectrum measurement. The washing process continued until the disappearance of peak around 200–500 nm. The black-colored precipitate was dried at 60 °C for 6 h, ground, weighed and stored in a zipper lock cover. Thus, obtained product is named as AC–Ni catalyst system.

Catalytic reduction study

The catalytic reduction study was carried out in a 5 mL capacity cuvette. The required amount of NiP (6.3×10^{-4} g) was accurately weighed and transferred to a cuvette reactor. With this 1 mg of AC–Ni catalyst, 15 mg of NaBH_4 , and, a reducing agent were added to the nanoreactor during the spectral measurement study. The cuvette is filled with 2 mL of DDW. The UV–Vis spectrum was recorded in the interval of 1 min. From the absorbance value, the apparent rate constant (k_{app}) can be calculated by plotting time against $\ln(C/C_0)$. The reduction study was carried out at 28 °C. These are the general reduction reaction conditions. During their variation, the other parameters were maintained as constant. A similar concentration of Cr(VI) or fluor dye was taken.

Determination of thermodynamic parameters

From temperature variation, the thermodynamic parameters such as ΔH and ΔS were calculated using the Eyring equation. For this purpose, the plot of $\ln(k_{\text{app}}/T)$ versus $(1000/T)$ was drawn. From the slope value, the ΔH value can be calculated. From the intercept value ΔS can be calculated using the formula: Slope = $-\Delta H/R$ and intercept = $\Delta S/R$.

Characterization

The UV–Vis spectrum was measured using Shimadzu 3600 NIR spectrophotometer, Japan. High-resolution transmission electron microscopy (HRTEM) image was recorded using TEM 3010 instrument, a product of JEOL. X-ray diffraction study was carried out using (XRD, BrukerXS08 model instrument), an advanced scanning instrument from 2θ value of 2° – 80° at the scanning rate of 2° min^{-1} .

Results and discussion

The main aim of the present investigation is to extend the application of AC and Ni complexed AC (AC–Ni) systems to the various science and engineering field, particularly to

the catalysis field using UV–Vis spectrophotometer. During the course of the reaction, the change in absorbance was quantitatively measured from which the rate constant and order of reaction was determined. AC is water soluble and easily separable from the reaction medium by adding ethanol. The catalysis reaction is a controllable one. The catalytic activity of AC–Ni system was tested towards the reduction of Cr(VI), fluor dye and NiP like industrial pollutants under different experimental conditions. For the sake of comparison, the catalytic activity of AC was tested towards the reduction of Cr(VI) and the result is compared with the results of AC–Ni system.

HRTEM and XRD analysis

The HRTEM image of AC–Ni system is given in Fig. 1a. The image shows the agglomerated AC structure with the Ni nanoparticle (circled area) dispersion. The size of the Ni nanoparticle was determined as 13.6 nm. Figure 1b represents the SAED pattern of AC–Ni system. The pattern confirmed the amorphous nature of the AC–Ni system. The nanosized Ni plays a vital role in the catalytic reduction reaction as a nano catalyst. The XRD of pristine AC in Fig. 1c shows the presence of d_{020} , d_{110} , d_{130} , d_{200} , d_{060} and d_{330} crystal planes at 22.9° , 33.9° and 58.4° , respectively. This declares that the above synthesized AC is a semicrystalline material. In 2007, Datta et al. (2013) clearly explained the XRD peaks of AC and its metal nanoparticle composite materials. The XRD was recorded after the complexation with Ni^{2+} (Fig. 1d). The current system exhibits the above said crystalline peaks with some new peaks at 44.6 and 51.9° corresponding to the d_{111} and d_{200} crystal planes of Ni nanoparticles (Antony and Viswanathan 2011). After the complexation process with Ni^{2+} , the crystallinity of the AC is disturbed. The decrease in crystalline region concluded the amorphous nature of AC after the Ni complexation followed by reduction reaction. The XRD results supported the HRTEM report.

Catalytic reduction of Cr(VI) under different experimental conditions

The catalytic reduction of Cr(VI) was carried out with the pristine AC. The catalytic reduction of Cr(VI) into Cr(III) was quantitatively determined with the help of UV–Vis spectrophotometer (Fig. S1a–r). While increasing the reaction time, the absorbance reduced slowly at 373 nm. It means, the Cr(VI) is converted into Cr(III) in the presence of AC as a catalyst and NaBH_4 as a reducing agent. It was found that within 18 min, 99% of Cr(VI) was chemically reduced into Cr(III). To evaluate the efficiency of AC catalyst, the reduction rate constant was determined by drawing a graph between the time and $\ln(A/A_0)$ (Fig. S1s).

Fig. 1 **a** HRTEM image, **b** SAED pattern, **c** XRD of AC and **d** XRD of AC–Ni system

The plot showed a decreasing trend with a curved nature. A linear fit was made in the straight-line region of the plot. The slope and intercept values were noted. From the slope value, the apparent rate constant (k_{app}) was calculated as 0.0043 s^{-1} . The intercept value gives an idea about the induction time (T_i) of the reduction reaction. The T_i was determined as 5.71 s. When compared with the literature (Celebi et al. 2016), the present investigation yielded lower k_{app} due to the absence of nano material for catalysis reaction. The k_{app} value confirmed the requirement of nano-sized metal or metal oxide with more surface area for the catalytic reduction purpose.

The catalytic activity of AC–Ni system was tested towards the reduction of Cr(VI) at different (weight of AC–Ni) system. The UV–Vis spectrum of AC–Ni supported catalytic reduction of Cr(VI) in the presence of 15 mg of NaBH_4 and 1 mg of AC–Ni system is shown in Fig. 2a–h. While increasing the reaction time, the absorbance reduced drastically at 375 nm and within 8 min, 100% of Cr(VI)

was reduced into Cr(III). The k_{app} and T_i values were determined by drawing the plot of time versus $\ln(A/A_0)$ (Fig. 2i) as 0.0142 s^{-1} and 3.62 s, respectively. Similarly, the catalytic reduction of Cr(VI) was carried out in the presence of 2, 3, 4 and 5 mg of AC–Ni catalyst system (the other experimental conditions were kept constant) from which the k_{app} and T_i values were calculated. The AC–Ni system exhibited a good result compared to the catalytic reduction of Cr(VI) in the presence of NaBH_4 as a reducing agent. When the k_{app} value is compared with the literature report, the present system yielded an excellent value (0.0142 s^{-1}). While using Pd–CNT (Kim and Choi 2016) and AC–Pd (Celebi et al. 2016) catalyst systems for the reduction of Cr(VI), the k_{app} values were determined as 2.33×10^{-3} and $3.30 \times 10^{-3} \text{ s}^{-1}$, respectively. When compared with the literature value, the present investigation yielded excellent results. This proved that Ni nanoparticle is a more suitable catalyst for the reduction of Cr(VI) rather than the Pd nanoparticle. To find out the

Fig. 2 UV–Vis spectrum of Cr(VI) recorded at 1 min time interval in the presence of AC–Ni system (a–h), the plot of $\ln(A/A_0)$ versus time (i) and the plot of $\ln k_{app}$ versus $\ln(\text{weight of AC–Ni})$ (j)

order of reduction reaction, the plot of $\ln(\text{weight of AC-Ni})$ versus $\ln(k_{\text{app}})$ (Fig. 2j) was drawn. The plot showed two regions. Initially, the k_{app} value increased slowly beyond 3 mg, the k_{app} value increased drastically due to the availability of more reactive sites for the reduction reaction. A linear fit was made from which the slope value was calculated as 0.60. It means 0.60 mol of AC-Ni is required to reduce 1 mol of Cr(VI). This can be written as: $R_{\text{red}} \propto [\text{weight of AC-Ni}]^{0.60}$.

The efficiency of the AC-Ni catalyst towards the reduction of Cr(VI) was tested by repeating the experiments for 6 times. Figure S2 indicates the number of cycles against k_{app} value. The results indicated that the k_{app} value did not decrease even after the 5th cycle. This can be explained as follows: (i) the stability of the AC-Ni catalyst system towards the reduction reaction. (ii) the reduction of Cr(VI) with simultaneous reduction of Ni nanoparticle. (iii) the diffusion of Ni nanoparticle into the reaction medium was arrested due to complexation reaction. The literature (Celebi et al. 2016) indicated that the k_{app} value decreased slightly after the 5th cycle. The present system did not show the decreasing trend even after the 5th cycle of repetition.

It is well-known that NaBH_4 is a good and mild reducing agent. To analyze the reduction behavior, the catalytic reduction of Cr(VI) was carried out at different concentrations of NaBH_4 at 5, 10, 15, 20 and 25 mg weight. The other experimental conditions such as $[\text{Cr(VI)}]$, (weight of AC-Ni), temperature and pH were kept constant. In the first stage, 5 mg of NaBH_4 was used for the reduction of Cr(VI). The reduction was quantitatively followed with the help of UV-Vis spectrophotometer. Figure 3a–n indicates the UV-Vis absorption spectrum

of Cr(VI) was taken at time of 1 min interval. The absorption peak found at 373 nm decreased gradually with the increase of reaction time. Within 14 min, 99.8% of Cr(VI) was reduced to Cr(III). The longer reaction time may be associated with the lesser concentration of NaBH_4 . To find out the k_{app} and T_i values, the plot of time versus $\ln(A/A_0)$ (Fig. 3o) was drawn and the plot was found to be a straight line with decreasing trend. From the slope and intercept values, the k_{app} and T_i values were calculated as 0.0060 s^{-1} and 3.01 s, respectively. The AC-Pd system yielded the k_{app} value for the catalytic reduction of Cr(VI) as $3.30 \times 10^{-3} \text{ s}^{-1}$. When compared with the AC-Pd system (Celebi et al. 2016), the present Ni complexed AC system yielded higher k_{app} value. This is due to the existence of interaction between Ni^0 and AC. Similarly, the catalytic reduction of Cr(VI) was carried out with 10, 15, 20 and 25 mg of NaBH_4 and the k_{app} values were calculated. From the k_{app} values, the order of reduction reaction can be determined by plotting $\ln[\text{NaBH}_4]$ versus $\ln k_{\text{app}}$ (Fig. 3p). From the slope, the order of reaction was determined as 1.98. This declared that 1.98 mol of NaBH_4 is required to reduce 1 mol of Cr(VI). This can be written as $R_{\text{red}} \propto [\text{NaBH}_4]^{1.98}$. This high order of reaction confirmed the simultaneous reduction of Ni nanoparticle during the catalytic reduction of Cr(VI).

It is very essential to analyze the influence of Cr(VI) concentration on the catalytic reduction activity of AC-Ni system. Hence, the concentration of Cr(VI) varied between 1 and 5 mg. First, the reduction reaction was done with the Cr(VI) concentration of 1 mg. During the variation of Cr(VI) concentration, the other experimental parameters were kept constant. Figure 4a–g indicates the UV-Vis spectrum of Cr(VI) taken at time of 1 min interval. It is

Fig. 3 UV-Vis spectrum of Cr(VI) recorded at 1 min time interval in the presence of AC-Ni system (a–n), the plot of $\ln(A/A_0)$ versus time (o) and the plot of $\ln k_{\text{app}}$ versus $\ln(\text{weight of NaBH}_4)$ (p)

Fig. 4 UV–Vis spectrum of Cr(VI) recorded at 1 min time interval in the presence of AC–Ni system (a–g), the plot of $\ln(A/A_0)$ versus time (h) and the plot of $\ln k_{app}$ versus $\ln(\text{weight of } K_2Cr_2O_7)$ (i)

very interesting to note that within 7 min, 99.9% of Cr(VI) was reduced into Cr(III). While increasing the reaction time, the absorbance gradually decreased at 373 nm. This is due to the decrease in the concentration of Cr(VI) in the reaction medium. The decrease in the [Cr(VI)] confirmed the catalytic activity of AC–Ni system. Furthermore, the k_{app} and T_i values were determined by drawing the plot between time and $\ln(A/A_0)$ (Fig. 4h). The plot was found to be a straight line with negative trend. The k_{app} value was determined as 0.022 s^{-1} and the T_i value was determined as 3.73 s. The high k_{app} value is due to the faster reduction of Cr(VI) into Cr(III). Moreover, the concentration of Cr(VI) is also lower in this case. From the variation of Cr(VI) concentration, it was found that while increasing the Cr(VI) concentration both the k_{app} and the T_i values decreased slowly. This is due to the availability of fixed quantity of $NaBH_4$. It means the concentration of Cr(VI) increased systematically at the fixed $NaBH_4$ concentration. As a result, it showed the decreasing trend. To find out the order of reaction, the plot of $\ln[Cr(VI)]$ versus $\ln k_{app}$ (Fig. 4i) was made. The plot exhibited a decreasing trend with the slope value of 0.837 and the same confirmed the first-order dependence of [Cr(VI)]. It refers that 0.83 mol of $NaBH_4$ is required to reduce 1 mol of Cr(VI). This can be written as $R_{red} \propto [Cr(VI)]^{0.83}$. The literature report (Celebi et al. 2016) confirmed the half order dependence with respect to [Cr(VI)]. The present investigation declared the first order dependence with respect to [Cr(VI)] due to the chemical interaction of Ni nanoparticle with the amino group of AC.

It is very important to know the energy of activation (E_a) value for the catalytic reduction reaction. For this purpose, the

catalytic reduction of Cr(VI) was carried out at different temperatures such as 298, 303, 308, 313 and 318 K. During the temperature variation, the other experimental conditions were kept constant. In the first stage, the catalytic reduction reaction was carried out at 298 K. The influence of temperature on the catalytic reduction reaction was monitored by an UV–Vis spectrophotometer. The UV–Vis spectrum of Cr(VI) taken at one min time interval is given in Fig. 5a–k. While increasing the reaction time, the absorbance decreased at 373 nm. Within 11 min, 100% of Cr(VI) reduced into Cr(III). When reduction of Cr(VI) was done at other temperatures mentioned above, it was found that while increasing the temperature, the k_{app} value increased slowly. This can be explained as follows: while increasing the temperature (i) more amount of thermal energy was given to accelerate the reaction, (ii) the interactions between the reactants increased, (iii) the number of collisions also increased.

The main aim of the present investigation is to increase the rate of reduction reaction by the AC–Ni system. To optimize the heat energy for the maximum rate of reaction, the Arrhenius plot was used. The Arrhenius plot is made by $1000/T$ versus $\ln k_{app}$ (Fig. 5l). Initially, the k_{app} value decreased suddenly then it reduced slowly. The energy of activation was determined by drawing a linear fit. The slope of linear fit was multiplied by the gas constant to get the E_a value. The E_a value was determined as $25.01 \text{ kJ mol}^{-1}$. The influence of temperature on the catalytic reduction of Cr(VI) in the presence of AC–Pd catalytic system was studied thoroughly and reported in the literature (Celebi et al. 2016). When compared with the AC–Pd system, the present AC–Ni complex system consumed lower amount of E_a .

Fig. 5 UV–Vis spectrum of Cr(VI) recorded at 1 min time interval at 298 K (a–k), the plot of $\ln k_{app}$ versus $1/T$ (l) and the plot of $\ln(k_{app}/T)$ versus $1/T$ (m)

Using Eyring equation, the thermodynamic parameters like ΔH and ΔS are calculated using the plot of $\ln(k_{app}/T)$ versus $(1000/T)$ (Fig. 5m). From the above equation, the ΔH value was determined as $16.78 \text{ kJ mol}^{-1}$ and ΔS was determined as $-40.21 \text{ J mol}^{-1} \text{ K}^{-1}$. When compared with the literature report (Celebi et al. 2016) the present system produced the lowest E_a , ΔH and ΔS value. The lower E_a value increased the k_{app} value. This is the novelty of the present investigation.

To optimize the suitable pH value for the catalytic reduction of Cr(VI), the reduction study was carried out at different pHs such as 1.5, 4.5, 7.0, 9.3, and 11.5. Under stronger acidic pH condition such as pH at 1.5 and 4.5, the NaBH_4 is highly reactive, fast and unable to follow with the help of UV–Vis spectrophotometer. In the literature, formic acid was used as a reducing agent (Celebi et al. 2016) for the catalytic reduction of Cr(VI). It is found that NaBH_4 is stable under neutral and slightly alkaline pHs (pH 7.0 and 9.3). Figure 6a–k indicates the UV–Vis spectrum of Cr(VI) recorded at one min time interval at the pH of 7.0. The spectra indicated that while increasing the reaction time at neutral pH, the absorbance reduced slowly at 373 nm. Within 12 min, 97.3% of Cr(VI) was reduced into Cr(III). Figure 6l represents the plot of time against $\ln(A/A_0)$. The plot was found to be a straight line with decreasing trend. From the slope value, the k_{app} was determined as 0.0085 s^{-1} . From the intercept value, the T_i was determined as 3.31 s. With minimum error, the k_{app} and T_i values were determined. The influence of alkaline pH (pH 9.3) was tested on the catalytic reduction of Cr(VI) system. Figure S3a–e declares that while increasing the pH value to 9.3, the absorbance at 373 nm decreased suddenly. Further, the plot of $\ln(A/A_0)$ versus time (Fig. S3f) was

made and the plot was found to be a straight line with decreasing trend. From the slope value, the k_{app} value was determined as 0.0313 s^{-1} and T_i value as 3.95 s. These results indicate that the catalytic reduction of Cr(VI) accelerated effectively at neutral pH and slightly alkaline pHs. To compare the effect of alkaline pH, the catalytic reduction of Cr(VI) at pH 11.5 was carried out. Surprisingly, it was noted that after 4 min of reaction time, there was no more reduction (Fig. S4a–g). Even after 1 h, the absorbance did not decrease. This proved that the reduction of Cr(VI) into Cr(III) did not favor because at pH 11.5, the hydroxide ions acted as a scavenger with the simultaneous precipitation of chromium hydroxide formation. As a result, there was no more decrease in absorbance value at 373 nm. The pH study indicates that the reducing agent is not stable at strongly alkaline medium. Moreover, the catalytic reduction of Cr(VI) depends on the pH of the reaction medium.

The influence of the AC–Ni catalyst in the mixture of pollutants was studied. For this purpose, NiP and fluor dye was considered. NiP follows the pseudo first-order kinetics on reduction, whereas the fluor dye is a xanthenes-type dye without any halogen substituents.

As mentioned above, the catalytic reduction of Cr(VI) and fluor dye in equimolecular mixture was carried out and followed with the help of UV–Vis spectrometer. The other experimental conditions remain constant. The spectrum produced two broad peaks at 489 nm (monomeric form of fluor dye) and 371 nm [corresponding to Cr(VI)] (Fig. 7). It is very interesting to note that during the course of the reaction both Fluor and Cr(VI) reduced simultaneously (Fig. 7a–j). The absorbance at 371 nm corresponding to Cr(VI) decreased faster. It means within 10 min, 99% of

Fig. 6 UV-Vis spectrum of Cr(VI) recorded at 1 min time interval at the pH of 7.0 (a–k) and the plot of $\ln(A/A_0)$ versus time (l)

Fig. 7 UV-Vis spectrum of equimolecular mixture of Cr(VI) and fluor dye recorded at 1 min time interval (a–j), the plot of $\ln(A/A_0)$ versus time (k) [for Cr(VI) system] and the plot of $\ln(A/A_0)$ versus time (l) (for fluor system)

Cr(VI) was reduced into Cr(III), whereas 83% of fluor dye reduced slowly. This confirmed that both Cr(VI) and fluor reduced at different rates and it is necessary to determine the k_{app} individually. The k_{app} for the Cr(VI) and the fluor were determined from the plots of time versus $\ln(A/A_0)$ (Fig. 7k, l) as 0.476×10^{-2} and $0.568 \times 10^{-2} \text{ s}^{-1}$, respectively. The T_i values for the Cr(VI) and fluor were determined as 0.188 and 0.523 s, respectively. The induction time for dye reduction is 2.8 times greater than that of Cr(VI) reduction. Nevertheless, the fluor underwent fast reduction reaction with higher k_{app} value. It means the reduction of Cr(VI) was disturbed when it is present in the

mixture of effluents. When it is present alone, it undergoes vigorous reduction reaction with higher k_{app} value. Anyhow, the reduction of fluor in the mixture of effluent decreased 10 times due to the reasons mentioned above. During the course of the reaction, there was a competition between Cr(VI) reduction and fluor reduction. Based on the structure, resonance stabilization energy, and pH of the medium, the reduction reaction occurred. When the k_{app} value is compared with the literature report, $3.30 \times 10^{-3} \text{ s}^{-1}$ (Celebi et al. 2016), the present system exhibited higher value. This indicates that for better efficiency, the nano catalyst should be chemically bound with

the AC. The AC is acting as a supporting agent as well as avoids leaching of the Ni nanoparticle to the reaction medium during the course of the reaction.

Equimolecular mixture of NiP and Cr(VI) were considered to find out the k_{app} value of Cr(VI). The other experimental conditions were maintained at constant. The UV–Vis spectrum was recorded at 1 min time interval and shown in Fig. 8a–n. The appearance of one peak at 389 nm confirmed the complex formation between Cr(VI) and NiP. NiP gives an absorption peak at 400 nm and Cr(VI) produces an absorption peak at 375 nm. During the course of reduction reaction, the absorbance at 389 nm decreased slowly. Within 15 min, 95% of effluent mixture was reduced. The k_{app} value was calculated from the slope of the plot of time versus $\ln(A/A_0)$ (Fig. 8o). The k_{app} value was calculated as $0.753 \times 10^{-2} \text{ s}^{-1}$, whereas the T_i was calculated as 0.47 s. This indicates that the induction time is very low and due to the formation of complex, the k_{app} value was also found to be very low. Again, the present catalyst system yielded higher k_{app} value than the previous report (Celebi et al. 2016) and proved to be the better reduction reaction ability. This proved that the present catalyst system is effective towards the catalytic reduction of single or bicomponent systems. In 2015, Das et al. (2015) reported the k_{app} value of $7 \times 10^{-3} \text{ s}^{-1}$ for the catalytic reduction of NiP using plant extract decorated Au nanoparticles. When compared with the literature, the present system yielded somewhat higher k_{app} value.

It is necessary to compare the catalytic reduction constant of each pollutants such as Cr(VI), fluor and NiP present in the mixture. To determine the k_{app} value, the equimolecular mixture of Cr(VI), fluor and NiP were

considered (three component system). The UV–Vis spectrum taken at 1 min time interval is given in Fig. 9a–o. The three component system produced two absorbance peaks at 489 nm (corresponding to the monomeric structure of fluor dye) and 389 nm [corresponding to the complex form of NiP and Cr(VI)]. As usual, the NiP and Cr(VI) formed a stable complex in the three component system too and produced one broad absorbance peak at 389 nm. While increasing the reduction time, the absorbance at 389 and 489 nm decreased slowly. This confirmed the simultaneous reduction of NiP, Cr(VI) and fluor dye. Within 15 min, 84% of complex and 91% of fluor dye were reduced. To find out the k_{app} value, the plots of time versus $\ln(A/A_0)$ (Fig. 9 p, q) were drawn corresponding to NiP–Cr(VI) complex system and fluor dye system, respectively. For the complex system, the k_{app} value was determined as $0.085 \times 10^{-2} \text{ s}^{-1}$ with the T_i value of 0.18 s. The k_{app} value for the fluor dye system was determined as $0.455 \times 10^{-2} \text{ s}^{-1}$ and the T_i value as 0.274 s. When compared with the single component and bicomponent systems, the three components system yielded lower k_{app} value for the complex system. When compared with the AC–Pd system (Celebi et al. 2016), the present system produced lower k_{app} value for the mixture of Cr(VI) and NiP system.

For the sake of comparison, the catalytic reduction of NiP was carried out in the presence of AC–Ni catalyst system. The UV–Vis spectrum was taken at 1 min time interval (Fig. S5a–e). It was found that within 5 min, 99.9% of NiP reduced into aminophenol. To find out the k_{app} , the plot of time versus $\ln(A/A_0)$ (Fig. S5f) was drawn. The plot was found to be a straight line with decreasing

Fig. 8 UV–Vis spectrum of equimolecular mixture of Cr(VI) and NiP recorded at 1 min time interval (a–n) and the plot of $\ln(A/A_0)$ versus time (o)

Fig. 9 UV–Vis spectrum of equimolecular mixture of Cr(VI), NiP and fluor dye recorded at 1 min time interval (a–o), the plot of $\ln(A/A_0)$ versus time (p) [for Cr(VI) + NiP complex system] and the plot of $\ln(A/A_0)$ versus time (q) (for fluor system)

trend. From the slope value, the k_{app} value was determined as $6.16 \times 10^{-2} \text{ s}^{-1}$. The T_i value was determined from the intercept as 1.60 s. The present system produced somewhat higher k_{app} value than the literature report (Celebi et al. 2016). Sowmiya et al. (2015) reported about the catalytic reduction of NiP in the presence of structurally modified PECH/hydroxyapatite nanocomposite system with the k_{app} value of $2.303 \times 10^{-3} \text{ s}^{-1}$. When compared with their report, the present system also exhibited good results.

The catalytic reduction of fluor dye was carried out in the presence of AC–Ni catalyst with the help of UV–Vis spectrometer. The UV–Vis spectrum of fluor taken at 1 min time interval in the presence of AC–Ni catalyst is given in Fig. S6a–e. In this system also within 5 min all the fluor dye molecules were reduced. The spectrum shows a peak at 489 nm corresponding to the monomeric form of fluor dye and one small hump at 459 nm corresponding to the dimeric structure of fluor. To calculate the k_{app} , the absorbance at 489 nm was considered and the plot of time versus $\ln(A/A_0)$ (Fig. S6f) was made. Once again, the plot was found to be a straight line with decreasing trend. From the slope value, the k_{app} value was calculated as $5.12 \times 10^{-2} \text{ s}^{-1}$. The T_i value was calculated as 1.28 s. The present system produced somewhat higher k_{app} value than the literature report (Celebi et al. 2016).

The catalytic reduction of Cr(VI) was followed with the three electron transfer reaction (Abinayasri et al. 2017). In the literature (Song et al. 2009), it was reported that the phenol itself can reduce the Cr(VI) with simultaneous self-oxidation process. Hence, in the present investigation, the NiP and Cr(VI) followed a complex and was reduced by NaBH_4 . The reducing agent has 4 H atoms, whereas the Cr(VI) requires three electrons to attain an octet

configuration. This was proved by the weight of $\text{K}_2\text{Cr}_2\text{O}_7$ variation and it followed the 0.83 order of reaction. The remaining one electron was transferred to the reaction medium and the same can be consumed by the Ni nanoparticle for its own further reduction. So that till 5th cycle, there will be no decrease in k_{app} value. In the case of NiP, the active $-\text{NO}_2$ group is reduced to $-\text{NH}_2$ group via phenolate anion formation. Here, the functional group is reduced meanwhile in fluor dye the $\text{C}=\text{C}$ bond present in the middle ether ring is reduced. This requires two electrons for its reduction. Fluor is also having one phenolic $-\text{OH}$ group, but there was no complex formation between fluor dye and Cr(VI). This explained the structure and acidity required for the complex formation. The UV–Vis kinetic results proved that the individual reduction activity of the pollutants are extremely good, but when it is mixed with other pollutants their reduction activity is somewhat disturbed due to the various hydrogen bonding and van der Waals forces. The presence of secondary forces of attraction between the pollutants delayed the catalytic reduction reaction by producing lower k_{app} value.

Conclusion

From the above spectral study, the important points are gathered and presented here as conclusion. The HRTEM image confirmed the size of Ni nanoparticle as 13.6 nm. The XRD profile indicated the presence of d_{200} and d_{111} crystal planes corresponding to the Ni nanoparticle. The variation in (weight of AC–Ni), NaBH_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ exhibited the 0.60, 1.98 and 0.83 order of reaction towards the reduction of Cr(VI), respectively. The E_a value was

determined as $25.01 \text{ kJ mol}^{-1}$ towards the reduction of Cr(VI). The ΔH and ΔS values were calculated as $16.78 \text{ kJ mol}^{-1}$ and $-40.29 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Under strongly acidic pH, the reduction reaction was very fast. The Cr(VI)–fluor dye mixture exhibited 2.8 times higher induction time for the reduction of fluor dye. The UV–Vis spectrum of Cr(VI) and NiP mixture confirmed the complex formation between them. The catalytic reduction of Cr(VI), NiP and fluor mixture showed the lowest k_{app} value than their individual k_{app} . The present AC–Ni system exhibited the highest k_{app} value towards the reduction of Cr(VI) when compared with the literature.

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