Synthesis and catalytic evaluation of silver@nickel oxide and alginate biopolymer nanocomposite hydrogel beads

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In this study, silver-nickel oxide/ calcium alginate (Ag@NiO/Alg) hydrogel beads were synthesized. The preparation of Ag@NiO was carried out in two steps: 1) synthesizing the nickel oxide nanoparticle through precipitation method, and 2) adhering of the Ag⁺ ion from silver nitrate solution and reduction with sodium borohydride. The nanomaterial was mixed with alginate biopolymer aqueous solution and extruded through syringe in a dropwise manner into a CaCl₂ aqueous solution for inotropic crosslinking. Through this method, Ag@NiO/Alg beads were formed which were characterized by different instrumental techniques. The catalytic efficiency of Ag@NiO/Alg was evaluated for the reduction of rhodamine B (RhB) and methyl orange (MO), in the presence of sodium borohydride reducing agent. The uncatalyzed RhB and MO reduction reactions did not show a significant decrease in the absorbance value at λmax within the given experimental time. It was due to the large kinetic barrier. A small decrease in the absorbance value for uncatalyzed reaction in the presence of very high concentration of
reducing agent was observed, indicating that the reactions are thermodynamically feasible. After applying various kinetic order equations to the experimental data, the reactions were found to follow pseudo-first order kinetics using the Ag@NiO/Alg catalyst. The apparent rate constants \(k_{\text{app}}\) were determined as 0.33358 min\(^{-1}\) and 0.20882 min\(^{-1}\) for catalytic reduction of RhB and MO, respectively. Furthermore, reduction reactions were studied at varying dye concentration and catalyst dosages. The recovered catalyst was reused up to five cycles without significant drop in the activity.

**Keywords:** Alginate biopolymer; beads; nanocomposite; reduction; pollutants
Introduction

Hydrogels with 3-D interwoven structure and high-water retention capacity has found much attention among various researchers’ groups (Khan et al. 2020; Al-Ghamdi and Khan 2020). Biopolymer based hydrogels have introduced a new thought of green and sustainable catalytic system. The intermolecular attractive forces (such as covalent bonding, hydrogen bonding etc) between the polymer chains are held responsible for the uniform immobilization of metallic nanoparticles inside the polymeric matrix (Khan et al. 2016a, b). Hydrophilic nature of the hydrogels renders quasi-homogeneous properties to the nanoparticles, hence, enhancing its catalytic efficiency. Different biopolymer-based hydrogels such as carboxy methyl cellulose; chitosan, agar, bacterial cellulose, and alginate etc. have been studied so far for academically and applied in various applied fields (Chen et al. 2017a; Ali et al. 2017a, b, c; Xu et al. 2017b; Silva et al. 2019; Chanthiwong et al. 2020; Khalil et al. 2020). Amongst them alginate is one of the most extensively used polymers owing to its highly biocompatible and biodegradable nature. For instance, Gan et al utilized sodium alginate hydrogel beads as a support for graphene oxide and investigated its catalytic activity for removal of organic dyes and bisphenol A in aqueous solution (Gan et al. 2018). Lam et al utilized TiO2 nanoparticles immobilized in calcium alginate beads for photocatalytic degradation of methylene blue (Lam et al. 2017). The chemical structure of alginate consists of covalently bonded 1,4-linked α-l-guluronic acids (G) and β-D-mannuronic acids (M) as main constituents. Unlike other biopolymers which require toxic organic crosslinking agents, alginates can be ionotropically crosslinked. Owed by the presence of divalent cations (e.g., Ca$^{2+}$), ionic bridges are formed between the adjacent alginate chains which lead to its transformation into hydrogel beads in the aqueous medium (Asadi et al. 2018).

Metal nanoparticles with particle size in the range of nanometers, exhibiting excellent
mechanical and optic-electric properties, have found applications in heterogeneous catalysis. Various semiconductor metal oxides and noble metals have been studied for its applications as an efficient catalyst. Recent studies emphasize on the immobilization of noble metals (such as Ag, Au, Pt and Pd) onto the surface of semiconductor metal oxides (such as NiO, CuO etc) for considerable enhancement in its catalytic activity (Kao et al. 2017; Xu et al. 2017a; Chen et al. 2017b; Jiang et al. 2019). Noble metal nanoparticles act as an electron sink for the electron generated in the semiconductor. Due to excellent optical and catalytic properties of Ag among the various noble metals, it remains pre-dominant over others. Up-to-date different approaches have been put forward for the synthesis of AgNiO nanocomposites and studied for its application in photocatalysis, energy storage, sensors and supercapacitors etc. (Ngo et al. 2017; Nagamuthu and Ryu 2019; Karimi-Maleh et al. 2020). For instance, Karunamoorthy et al reported synthesis of AgNiO nanocomposite via hydrothermal approach and studied its applications as photocatalyst for degradation of organic pollutants (Karunamoorthy and Velluchamy 2018). Haq et al investigated green synthesis of Ag/NiO and studied its catalytic efficiency for photodegradation of organic pollutant rhodamine B (Atta-ul-Haq et al. 2019). Bagtache et al synthesized AgNiO by nitrate route and studied its photoactivity in hydrogen evolution reactions under visible light (Bagtache et al. 2019). Until now, AgNiO is not yet reported for its application in catalytic reduction of organic pollutants. Moreover, the employment of a catalyst embedding in a hydrogel host instead of using the dispersed form of the nanoparticles is beneficial as the catalyst could be easily recovered for reusing purpose. Therefore, an alginate based biopolymer was chosen as it could be ionically crosslinked without needing an environmentally toxic agent.

Dyes are widely used for a number of applications in various industries such as textile, dyeing, plastic, pharmaceutical and many others. These organic dyes, when discharged into the running
water in untreated form causes water pollution due to their highly stable and non-biodegradable nature. They cause severe damage to the aquatic life and may also cause severe health disorders in human beings. Different physical, chemical and biological methods have been employed for the removal of these toxic organic pollutants such as adsorption, coagulation, reverse osmosis, ultrafiltration, biodegradation, oxidation, reduction etc (Kamal et al. 2015; Katheresan et al. 2018; Jamee and Siddique 2019). Amongst them catalytic reduction is considered as primary choice, owing to less time required for removal of organic pollutants. In addition, the reduction products obtained as a result of this process have found numerous applications in different fields (Kamal et al. 2016, 2019; Ali et al. 2017b, 2018).

In the current study, we have reported the synthesis of Ag@NiO by deposition of silver nanoparticles on the surface of nickel oxide prepared by precipitation method. To ensure its stability and avoid leaching out in the aqueous medium, Ag@NiO was immobilized in calcium alginate (Alg) hydrogel beads. To the best of our knowledge, immobilization of Ag@NiO onto calcium alginate hydrogel beads is not yet reported. Also, no literature has been found on utilization of Ag@NiO for catalytic reduction of organic pollutants. The catalytic performance of as-prepared Ag@NiO/Alg hydrogel beads were evaluated for catalytic reduction of organic dyes, namely, rhodamine B (RhB) and methyl orange (MO).

Experimental

Materials

Sodium alginate (NaC₆H₇O₆) was obtained from Shanghai Aibi Chemistry Preparation Co., Ltd. Calcium chloride (CaCl₂), Silver nitrate (AgNO₃) and Nickel nitrate hexahydrate (NaNO₃·6H₂O)
were purchased from Sigma Aldrich. Sodium borohydride (NaBH\textsubscript{4}) was purchased from BDH Chemical Laboratories, Poole, England. Rhodamine B (RhB) and Methyl orange (MO) were purchased from Merck. All the chemicals used were of analytical grade and were used without any further purification process. All solutions were prepared in deionized water obtained from PCSIR laboratories, Peshawar, Pakistan.

**Synthesis of Ag@NiO nanocomposite**

Firstly, nickel oxide nanoparticles were prepared by precipitation method. Briefly, 10g of NiNO\textsubscript{3}.6H\textsubscript{2}O was dissolved in 500mL of deionized water, followed by drop-wise addition of dilute ammonia water solution, until the pH reaches to 8. The precipitates formed were then filtered, washed with deionized water for several times. The filtered precipitates were then allowed to dry at 100°C and calcined at 800°C for 24h.

For the synthesis of Ag@NiO nanocomposite, 0.5g of the preformed NiO nanoparticles was well-dispersed in water under ultrasonic treatment. Then 0.1M AgNO\textsubscript{3} was added to the NiO suspension and sonicated for 1h. The deposited Ag\textsuperscript{+} ions were then reduced with 0.1M NaBH\textsubscript{4} aqueous solution. The resultant Ag@NiO was then filtered, washed, and dried at 80°C.

**Synthesis of Ag@NiO/calcium alginate hydrogel beads**

For the synthesis of Ag@NiO/Alg hydrogel beads, Ag@NiO nanomaterial was dispersed well in 20mL of distilled water and added to already prepared alginate solution (with percent composition of 2% w/v) under vigorous stirring. 0.2M CaCl\textsubscript{2} solution was prepared by dissolving 14.7g into 500mL. For the preparation of hydrogel beads, Ag@NiO/alginate suspension was taken in 5cc medical syringe and added drop by drop to CaCl\textsubscript{2} solution from 10cm height with continuous stirring at a speed of 50rpm. As soon as the drop fell into the Ca\textsuperscript{2+} ions solution, it
attained a solid spherical shape. The same procedure was employed for the formation of pure calcium alginate beads without the addition of AgNiO nanomaterial.

Characterization

The functional group analysis of Alg, Ag@NiO/Alg and Ag@NiO was conducted by Fourier transform infrared spectroscopic technique using Perkin Elmer spectrometer at a frequency range of 450 to 4000cm⁻¹ with a resolution of 4cm⁻¹ and 0.2 scanning speed. X-ray Diffraction technique was used to determine the crystalline nature of Alg, Ag@NiO/Alg and AgNiO with the help of X-ray diffractometer (model: JDX-3532, JEOL, Japan) using Nickel filtered Cu-Ka radiation of 1.5418Å in the 2θ range of 5° to 90°. The structural morphology and elemental mapping of the synthesized samples was evaluated by scanning electron microscopic (Model; JSM5910, JEOL, Japan) and energy-dispersive X-ray diffractometric techniques (using liquid nitrogen cooled Oxford 7353 EDX detector, Oxford Instruments, Abingdon, United Kingdom), respectively.

Catalytic Evaluation of Ag@NiO/Alg hydrogel beads

In order to evaluate the catalytic efficiency of Ag@NiO/Alg hydrogel beads, catalytic reduction of RhB and MO was studied. For this purpose, 2.5mL of RhB (0.05mM) and MO (0.1mM) dye solution was taken in a quartz cuvette separately, followed by addition of 0.1M NaBH₄ solution. Then depending on the required reaction conditions, a known amount of the Ag@NiO/Alg hydrogel beads was added into the reaction system. The decrease in absorbance at the λ_max of the dyes was regularly noted with the help of UV-Vis spectrophotometer after each 2 min.
Scheme 1. Preparation of hydrogel beads and its catalytic evaluation for toxic dyes reduction

Results and Discussion

Scheme 1 shows the general overview of this research work. The first part consists of preparation of the Ag@NiO nanomaterial and Ag@NiO/Alg nanocomposite beads (catalyst preparation) and the second part consists of utilization of the Ag@NiO/Alg nanocomposite beads in the reduction of RhB and MO dyes (catalytic evaluation). After preparation of the Ag@NiO nanomaterial, pure Alg, Ag@NiO/Alg nanocomposite beads, they were first subjected to various instrumental techniques as given in the following text.

FTIR Analysis

FTIR spectra of Alg hydrogel, Ag@NiO and Ag@NiO/Alg are shown in Figure 1. The spectral peaks at 475cm\(^{-1}\) and 568cm\(^{-1}\) corresponds to stretching vibrations of NiO as shown in Figure 1a (Nagamuthu and Ryu 2019). Ag nanoparticles synthesized by chemical approach do not exhibit peak in the infra-red region. No appearance of any absorption peak for Ag confirms the synthesis of metallic silver only in this approach, without the formation of oxides of silver (Beura et al. 2021). The broad absorption band at 3225cm\(^{-1}\) corresponds to the presence of hydroxyl group. The sharp peaks at 1586cm\(^{-1}\) and 1413cm\(^{-1}\) are attributed to asymmetric and symmetric stretching vibrations of the carboxylate groups, respectively. Peaks observed at 1294cm\(^{-1}\), 1076cm\(^{-1}\), and 1025 cm\(^{-1}\) are associated with stretching vibrations of C-O functional group of glycosidic linkage between β-d-mannuronic and R-L-guluronic acid and is an indication of the degree of
stability of the linear chain in the alginate (Simonescu et al. 2020). In the FTIR spectrum of Ag@NiO/Alg all peaks characteristic of Ag@NiO and Ca-Alg can be seen, as represented by Figure 1b.

![FTIR spectra](image)

Figure 1. FTIR spectra for (a) Ag@NiO (b) Ag@NiO/Alg (c) pure Alg.

**XRD Analysis**

In order to study the crystalline nature of prepared samples, pure Alg, Ag@NiO and Ag@NiO/Alg were characterized by X-ray diffractrometry technique. Figure 2a represents the XRD pattern of Alg hydrogel beads. No diffraction peak can be observed which confirms non-crystalline nature of Alg. Figure 2c indicates the XRD pattern for Ag@NiO nanomaterial. The diffraction peaks at $2\theta = 37.22^\circ$, $43.25^\circ$, $62.83^\circ$ and $75.34^\circ$ corresponds to the presence of NiO (JCPDS card No-73-1523) in the sample. Similarly, the peaks at $2\theta = 38.26^\circ$, $44.47^\circ$, $64.71^\circ$, $77.74^\circ$ and $81.91^\circ$ are in good agreement with the presence of metallic silver (JCPDS card No-87-0719) in the Ag@NiO sample. XRD peaks for nickel oxide and metallic silver coincides with
(111), (200), (220), (311) and (222) hkl planes, thus indicating their cubic crystal structures. All the characteristic peaks were observed in the XRD pattern of ALG/AgNiO hydrogel beads, which confirms the successful incorporation of AgNiO into the polymer matrix, as can be seen from Figure 2b.

Figure 2. XRD pattern of (a) Alg beads (b) Ag@NiO/Alg beads (c) Ag@NiO nanoparticles.

SEM Analysis

The surface features and morphology of pure Alg beads, Ag@NiO nanoparticles and Ag@NiO/Alg composite beads were characterized by scanning electron microscopy (SEM) as can be seen in SEM photographs (Figure 3). Figure 3a shows the SEM photographs of Ag@NiO nanoparticles. No sign of large particles was observed in the low magnification image (Figure 3a, right side). It can be seen in a left side photograph that all the particle sizes were below 100nm. Pure Alg hydrogel beads with sizes in the range of 1.5 to 2mm were prepared and subjected to morphological analysis by SEM. As shown in the left-side SEM photograph in Figure 3b, the
pure Alg beads were not completely spherical and indicated the oval shapes with some dents. The high magnification photograph of the pure Alg beads is given in the right-side of the Figure 3b. It shows porosity in the bead’s surface. Figure 3c (left-side) shows the SEM photograph of Ag@NiO/Alg nanocomposite bead. As compared to the pure Alg beads, the Ag@NiO/Alg nanocomposite bead surface has small white spots. High magnification SEM photographs in Figure 3c on left side reveals that the beads surface has small particles. Thus, the SEM analysis of the Ag@NiO/Alg nanocomposite bead suggest the successful immobilization of Ag@NiO onto Ca^{2+}-Alg hydrogel beads.
Figure 3. SEM photographs of (a) Ag@NiO nanoparticles, (b) Alg beads and (c) Ag@NiO/Alg beads.

EDS Analysis

To explore the elemental constituents of the prepared samples, EDS analyses were carried out for Ag@NiO nanoparticles, Alg beads and Ag@NiO/Alg beads. The EDS elemental mapping analyses on the Ag@NiO nanocomposite reveal the presence of Ag, Ni and O elements, as can
be seen from Figure 4a. No other elements were detected which confirms that Ag@NiO was formed in pure form without any external impurities. The EDS spectrum of pure Alg can be seen from Figure 4b, which constitutes all the characteristic peaks for C, O and Ca, known to be as principal constituents of calcium alginate hydrogel beads. Fig.4c shows EDS spectrum for Ag@NiO/Alg hydrogel beads. Prominent peaks at 0.3keV = C, 0.5keV = O and 3.5keV = Ca indicates the principal constituent elements of calcium crosslinked alginate beads. The presence of strong peaks at 0.5keV = O, 0.8keV = Ni and 3.0keV = Ag confirms the successful incorporation of Ag@NiO into calcium alginate hydrogel beads.
Figure 4. EDS spectral mapping for (a) Ag@NiO nanoparticles (b) Alg and (c) Ag@NiO/Alg beads.

Catalytic Experiments

Catalytic reduction of RhB
After the successful synthesis of Ag@NiO/Alg and its confirmation by different instrumental techniques, its catalytic efficiency was evaluated by RhB dye reduction. Rhodamine B (Rh-B, [9-(2-carboxyphenyl)-6-diethylamino-3-xanthine]-diethylammonium chloride) is a cationic xanthene dye, widely used in textile and paper industries as well as in fluorescent biotechnology. Despite of its useful aspects, it has adverse effects on the environment, when discharged in untreated form into the water bodies. In order to decline its toxic effects, rendered to it by the presence of –N(C₂H₅) sites in its structure, its abatement has become crucial. For this purpose, 0.05mM aqueous solution of RhB was processed. Before going for the actual catalytic experiments, absorption spectrum of RhB was observed in the presence of Ag@NiO/Alg only, without the addition of reducing agent. Figure 5b confirms that no adsorption has been taken place with Ag@NiO/Alg. In another batch of experiment, reduction of RhB was studied in the absence of Ag@NiO/Alg using NaBH₄ as a reducing agent. Figure 5a shows UV-Vis absorption spectra for reduction of 2.5mL RhB (0.05mM) dye solution and 1mL of 0.1M NaBH₄. No notable decrease in the absorption spectrum was observed for upto 1h which indicates that RhB does not undergo self-hydrolysis with mere addition of reducing agent. Catalytic reduction is an electron transfer process between NaBH₄ and dye molecule, where NaBH₄ acts as an electron donor and dye molecule serves as an acceptor. The results from Figure 5a indicate that this electron transfer process is thermodynamically feasible but kinetically un-favourable. For actual practice, 2.5mL of RhB aqueous solution with molar concentration of 0.05mM, 1mL of 0.1M NaBH₄ solution and 0.1g of Ag@NiO/Alg hydrogel beads was placed into a quartz cuvette with a total capacity of 4mL. The decrease in absorption maxima was repeatedly recorded at 554 nm, after an interval of 2 min. Figure 5c shows the time dependent UV-Vis spectra for catalytic reduction of RhB. The disappearance of absorption maxima at 554 nm indicates the complete
conversion of RhB into leuco-rhodamine B (Abay et al. 2017). The rate of reaction $k_{app}$ was calculated from the linear slope of $\ln C_t/C_0$ vs. time as can be seen from Figure 5d. Kapp value obtained was found to be equal to 0.33358 min$^{-1}$ or this reaction. As NaBH$_4$ is used in excess, the reduction reaction is assumed to follow pseudo-first order kinetics. The linear coefficient value of $R^2=0.96$ for the correlation between $\ln C_t/C_0$ and time, validate pseudo-first order kinetics for the reduction process.

Figure 5. UV-Vis absorption spectra for 0.05mM RhB reduction (a) in the absence of catalyst with 0.1M NaBH$_4$ (b) in the absence of NaBH$_4$ with 0.1g of catalyst (c) in the presence of 0.1M
NaBH$_4$ and 0.1g of catalyst (d) kinetic plot for reduction of 0.05mM RhB with 0.1M NaBH$_4$ as a reducing agent and 0.1g of catalyst

For the purpose to investigate the effect of RhB concentration on the reduction kinetics, three different dye concentrations, say, 0.025mM, 0.05mM and 0.1mM were studied while keeping all other condition constant at 0.1M NaBH$_4$ and 0.1g of hydrogel beads. Figure 6a shows kinetic plot of lnC$_t$/C$_0$ vs. time at varying dye concentration. The calculated apparent rate constant values were 0.38469 min$^{-1}$, 0.33358 min$^{-1}$ and 0.19429 min$^{-1}$ for dye concentration of 0.025 mM, 0.05 mM and 0.1 mM, respectively. R$^2$ values were found in the range of 0.96-0.99, which refers to goodness of the fit. Decrease in reaction rate was observed with increasing dye concentration. This is because of the fact that catalyst acts as a limiting reagent, when dye concentration, hence number of dye molecules is increased. Our results are similar to the literature reports as Chook et al studied the RhB concentration effect on the reaction time and rate constant while using CNF-AgNPs as a catalyst (Chook et al. 2015). The reaction time was reported to be 5, 12 and 90 min for the reduction of 2.0 × 10$^{-4}$, 1.0 × 10$^{-4}$ and 4.0 × 10$^{-5}$ M dye concentration.

In the same manner, reduction of 0.05mM RhB dye was studied at three different catalyst amounts, that is 0.05g, 0.1g and 0.15g, concerning to evaluate the effect of catalyst dosage on the reaction rate. Figure 6b shows kinetic plot of lnC$_t$/C$_0$ with time for reduction of 0.05mM RhB at varying dye concentration. The $kapp$ values at 0.05 g, 0.1 g and 0.15 g were calculated to be 0.13011min$^{-1}$, 0.33358min$^{-1}$ and 0.4528 min$^{-1}$, respectively. These values clearly depict that rate of reaction increased with an increase in catalyst quantity. This increase in $kapp$ value is associated with the increase in number of active sites for the reaction to take place. Similar results were reported by Maryami et al for the catalytic reduction of Rh B (2.09 ×10$^{-5}$ M) in the presence of 5.0mg, 7.0mg and 10.0mg Pd/Perlite nanocomposite catalyst. A decrease in the
reaction time was observed in the order of 45 min (5.0 mg), 5 min (7.0 mg) and 60 s (10 mg)
(Maryami et al. 2017). Further, Zhang et al investigated the effect of Ag dosage on the catalytic
reduction of Rh B dye with an initial concentration of 20m/L (Zhang et al. 2021). An increase in
the $k_{app}$ values was reported given as 0.12 min$^{-1}$, 0.17 min$^{-1}$, and 0.21 min$^{-1}$ for Fe$_3$Pt-60mL Ag,
Fe$_3$Pt-90mL Ag and Fe$_3$Pt-120mL Ag, respectively.
Figure 6. Linear correlation of ln(C<sub>t</sub>/C<sub>0</sub>) vs. time at (a) varying RhB concentration at 0.1M NaBH<sub>4</sub> and 0.1g of catalyst and (b) varying catalyst dosage at 0.05mM RhB and 0.1M NaBH<sub>4</sub>

Catalytic reduction of MO

Similarly, catalytic efficiency of AgNiO/Alg hydrogel beads was investigated for MO dye reduction. MO is an anionic azo based dye having λ<sub>max</sub> at 464 nm in its UV-visible spectrum at neutral pH. For MO reduction reaction, 2.5mL of MO dye with molar concentration of 0.1mM and 1mL of 0.1M NaBH<sub>4</sub> was taken into a quartz cuvette, followed by addition of 0.1g of AgNiO/Alg hydrogel beads. As like in the case of RhB, before going for the actual experimentation, reduction of MO was investigated for self-hydrolysis with NaBH<sub>4</sub>. No reduction reaction was observed in the absence of catalyst, as can be seen from Figure 7a. Figure 7b shows absorption spectra for MO dye in the absence of NaBH<sub>4</sub>, which illustrates that no adsorption of dye occurred on Ag@NiO/Alg surface. Figure 7c shows time dependent UV-Vis spectra for 0.1mM MO dye in the presence of 0.1M NaBH<sub>4</sub> and 0.1g of Ag@NiO/Alg hydrogel beads. The progress of reaction was observed from decrease in the absorbance value at 464 nm. At the end, the observed peak at 464 nm is completely diminished, considered to be due to the breakage of the -N=N- (azo) bond. Apparent rate constant value was calculated from slope of the linear plot between ln(C<sub>t</sub>/C<sub>0</sub>) and time. Figure 7d shows kinetic plot of ln(C<sub>t</sub>/C<sub>0</sub>) vs. time. K<sub>app</sub> value was found to be 0.20659 min<sup>-1</sup>. The reaction follows pseudo-first order kinetics.
In order to study the effect of dye concentration on rate of reaction, MO dye reduction was studied at three varying concentrations, say, 0.05mM, 0.1mM and 0.15mM, keeping all the other parameters constant. Figure 8a shows kinetics plot of ln(Ct/C0) against time for catalytic reduction of MO at varying initial concentrations. Rate constants for these reactions were found to be equal to 0.13201 min$^{-1}$, 0.20882 min$^{-1}$ and 0.31388 min$^{-1}$, respectively. Hu et al reported a decrease in
% decolorization rate with an increase in the initial concentration of MO (10mg/L, 20mg/L, 30mg/L, 40mg/L and 50mg/L) in the presence of 0.1g of nano-MoS/TiO$_2$ composite catalyst (Hu et al. 2010).

Similarly rate of reaction was studied at varying catalyst dosage, keeping concentration of MO and NaBH$_4$ constant. For this purpose, reduction of 0.1mM MO with 0.1M NaBH$_4$ was studied in the presence of three varying catalyst quantities, that is, 0.05g, 0.1g and 0.15g. Figure 8b shows plot of lnCt/C0 and time for MO dye reduction at varying catalyst dose. Kapp values were estimated to be 0.050487 min$^{-1}$, 0.20882 min$^{-1}$ and 0.33705 min$^{-1}$ at 0.05g, 0.1g and 0.15g catalyst dosage, respectively. In a similar manner, Islam et al reported apparent rate constant values of 1.27 × 10$^{-4}$ s$^{-1}$, 3.36 × 10$^{-3}$ s$^{-1}$ and 4.58 × 10$^{-3}$ s$^{-1}$ for MO reduction in the presence of pristine CF, CF-AuNPs-0.98 and CF-AuNPs-2.87 (Islam et al. 2017).

![Figure 8](image.png)

Figure 8. Linear correlation of lnCt/C0 vs. time at (a) varying MO concentration at 0.1M NaBH$_4$ and 0.1g of catalyst and (b) varying catalyst dosage at 0.1mM MO and 0.1M NaBH$_4$

Furthermore, the spectral data of the catalytic reduction of the RhB and MO was also analyzed for the possibility to follow other type of reaction kinetics. In addition to the pseudo-first order
reaction, the data was analyzed using the following zero (i), pseudo-first (ii),
first (iii) and second (iv) order kinetic equations,

\[ [A] - [A]_0 = -kt \]  
\[ \ln\left(\frac{[A]}{[A]_0}\right) = -kt \]  
\[ \ln[A] = -kt + C \]  
\[ \frac{1}{[A]} - \frac{1}{[A]_0} = kt \]

Where \([A]\) and \([A]_0\), and \(k\) are the dye concentration at a given time, at zero time (t) and rate constant, respectively.

Table 1 summarizes \(k_{app}\) and R-square values for the Rh B and MO reduction at varying dye initial concentration and catalyst dosage. The highest R-square values for any given reaction suggest that the experimental data was well-fitted to the pseudo-first order kinetic equation.

Table 1. Comparison of Adj. \(R^2\) and \(k_{app}\) values derived from zero order, pseudo 1st order, 1st order and 2nd order kinetics for Rh B and MO dyes in the presence of NaBH\(_4\) under varying catalyst dosage and dye concentration.

| Pollutant | Conc. | Catalyst dosage | Zero order \(R^2\) | Zero order \(k_{app}\) | Pseudo 1st order \(R^2\) | Pseudo 1st order \(k_{app}\) | 1st order \(R^2\) | 1st order \(k_{app}\) | 2nd order \(R^2\) | 2nd order \(k_{app}\) |
|-----------|-------|-----------------|-------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| RhB       | 0.05mM| 0.05g           | 0.90543           | 0.07305           | 0.98494           | 0.1323          | 0.98494         | 0.1323          | 0.73631         | -0.45           |
|           | 0.05mM| 0.1g            | 0.93152           | 0.15796           | 0.98237           | 0.33358         | 0.98237         | 0.33358         | 0.64391         | -1.231          |
|           | 0.05mM| 0.15g           | 0.98385           | 0.22035           | 0.98821           | 0.45248         | 0.98821         | 0.45248         | 0.39082         | -1.768          |
|           | 0.025mM| 0.1g           | 0.9746            | 0.2009            | 0.99347           | 0.35469         | 0.99347         | 0.35469         | 0.49893         | -1.065          |
|           | 0.075mM| 0.1g           | 0.89553           | 0.11475           | 0.99535           | 0.19429         | 0.99535         | 0.19429         | 0.75601         | -0.7111         |
A number of researchers’ groups put forward different approaches for the successful abatement of RhB and MO. Table 2 summarizes the reaction conditions and $k_{app}$ values for the reduction of the above mentioned toxic dyes in the presence of different catalytic systems, reported earlier in the literature. Ref (Zhang et al. 2021) reported a novel multifunctional Fe₃Pt–Ag nanoparticles for the SERS detection and its catalytic reduction. The highest rate constant of 0.21 min⁻¹ was observed which was lower than our study. Similarly, Wang et al prepared porous carbon protected magnetite and AgNPs (Wang et al. 2013). Besides cell imaging, the Fe₃O₄@C–Ag hybrid NPs showed a good reduction rate constant 0.14 min⁻¹ for the RhB. Mishra et al synthesized a Fe₃O₄–MnO₂ nanocomposites by a green method for the sp³ C–H functionalization of 2-methylpyridine and RhB reduction (Mishra et al. 2016). Their catalyst reduced the RhB with a rate constant of 0.08 s⁻¹. Arpit et al also used a green method of using Cladosporium oxysporum AJP03 for the synthesis of gold nanoparticles (Bhargava et al. 2016). The AuNPs were catalytically evaluated in the the reduction of RhB and its effectiveness was reported to be 1.3 × 10⁻³ s⁻¹. Similarly, many research studies used the MO as a model reducible dye to test the catalysts. In ref (Ahsan et al. 2019), the authors prepared magnetic cobalt nanoparticles on a porous carbon support using metal organic frameworks as templates. The prepared magnetic C@Co nanocatalyst catalyzed the reduction of MO with a 0.041 s⁻¹. In ref (Gupta et al. 2011), three different type of noble metal (Ag, Au and Pt) nanoparticles using a
green tannic acid reducing agent. The MO dye reduction rate constant of 0.0029 min\(^{-1}\) was experimentally measured for the PtNPs. Similarly, 5,7-dihydroxy-6-methoxy-3',4'-methylenedioxyisoflavone (Dalspinin) stabilized AuNPs (Umamaheswari et al. 2018) and poly(methacrylic acid) (p(MAc)) microgels stabilized nickel nanoparticles (Ajmal et al. 2014) were used for the MO reduction. The reduction rate constants of 1.7 \times 10^{-3} \text{s}^{-1} and 0.002 \text{s}^{-1} were reported for the DLP-AuNPs and p(MAc)--Ni catalysts. Ag@NiO/Alg hydrogel beads in this research show best catalytic activity of all the catalytic systems enlisted in Table 1, evident from their rate constant values.

**Table 2. Comparison of catalytic activity of Ag@NiO/Alg with previously reported work.**

| Pollutant | Catalyst | Dye conc. | Dye vol. | NaBH\(_4\) conc. | NaBH\(_4\) vol. | Rate constant | Ref. |
|-----------|----------|-----------|----------|------------------|-----------------|---------------|-----|
| RhB       | Fe\(_3\)Pt-120 mL Ag | 20 mg L\(^{-1}\) | 2 mL | 0.1 M | 0.5 mL | 0.21 min\(^{-1}\) | (Zhang et al. 2021) |
|           | Fe\(_3\)O\(_4\)@C--Ag hybrid NPs | \(2 \times 10^{-5}\) mol/L | 5 mL | 0.01 mol/L | 10 mL | 0.14 min\(^{-1}\) | (Wang et al. 2013) |
|           | Fe\(_3\)O\(_4\)--MnO\(_2\) NCs | 0.025 mM | 2 mL | 0.2 M | 0.4 mL | 0.08 s\(^{-1}\) | (Mishra et al. 2016) |
|           | AuNPs | \(2.5 \times 10^{-5}\) M | 5 \times 10^{-3} M | 1.3 \times 10^{-3} \text{s}^{-1} | (Bhargava et al. 2016) |
| MO        | AgNiO/Alg | 0.05 mM | 2.5 mL | 0.1 M | 1 mL | 0.33358 min\(^{-1}\) | Present work |
|           | C@Co | 20 ppm | 4 mL | 0.1 M | 0.5 mL | 0.041 s\(^{-1}\) | (Ahsan et al. 2019) |
|           | Pt NPs | \(5 \times 10^{-3}\) M | 50 \muL | 0.5% | 100 \muL | 0.0029 min\(^{-1}\) | (Gupta et al. 2011) |
|           | DLP-AuNPs | 1 \times 10^{-4} M | 3 mL | 1 \times 10^{-3} M | - | 1.7 \times 10^{-3} \text{s}^{-1} | (Umamaheswari et al. 2018) |
|           | p(MAc)--Ni | 4 \times 10^{-4} M | 50 mL | 0.756 g | - | 0.002 s\(^{-1}\) | (Ajmal et al. 2014) |
|           | AgNiO/Alg | 0.05 mM | 2.5 mL | 0.1 M | 1 mL | 0.20882 min\(^{-1}\) | Present work |

**Statistical analysis**

In order to validate the experimental conditions, simple linear regression model, variance of coefficients and ANOVA has been applied to catalytic reduction of Rh B and MO dyes. the data obtained from simple linear regression has been summarized in Table 4. Adjacent R\(^2\) value
above 0.9 for all of the given data showed that the experimental data is highly significant and also indicated goodness of the fit. Furthermore, significance of the experimental data was validated by the ANOVA calculations, as can be concluded from p-values (=0.000) in Table 3.

Table 5 shows variance of coefficient for the reduction of Rh B and MO under varying conditions of Alg@AgNiO and dye concentration. It can be concluded that the given table is highly significant (with lower p-values than the chosen alpha values).

Table 3. ANOVA table for RhB and MO reduction in the presence of 0.1g of Alg@AgNiO and 0.1M NaBH4.

| Model | DF  | Sum of Squares | Mean Square | F Value  | Sig.  |
|-------|-----|----------------|-------------|----------|-------|
| RhB   | Regression | 1  | 9.9294 | 9.9294 | 141.38345 | 0.000 |
|       | Residual   | 5  | 0.35115 | 0.07023 |   |   |
|       | Total      | 6  | 10.28055 |   |   |   |
| MO    | Regression | 1  | 3.05241 | 3.05241 | 425.44726 | 0.000 |
|       | Residual   | 4  | 0.0287 | 0.00717 |   |   |
|       | Total      | 5  | 3.0811 |   |   |   |

Table 4. Regression Model for Rh B and MO dye reduction under varying conditions of dye concentration and catalyst dosage.

| Pollutant | Conc. | Catalyst dosage | R   | R square | Adjusted R square | Error  |
|-----------|-------|-----------------|-----|----------|-------------------|--------|
| RhB       | 0.05mM | 0.05g           | 0.99226 | 0.98458 | 0.98303 | 0.10424 |
|           | 0.05mM | 0.1g            | 0.99292 | 0.98589 | 0.98237 | 0.16693 |
|           | 0.05mM | 0.15g           | 0.99557 | 0.99116 | 0.98821 | 0.15605 |
|           | 0.025mM| 0.1g            | 0.99755 | 0.9951  | 0.99347 | 0.09087 |
|           | 0.075mM| 0.1g            | 0.99864 | 0.99728 | 0.99689 | 0.06106 |
| MO        | 0.1mM  | 0.05g           | 0.99229 | 0.98465 | 0.98245 | 0.10492 |
|           | 0.1mM  | 0.1g            | 0.99533 | 0.99069 | 0.98836 | 0.0847  |
|           | 0.1mM  | 0.15g           | 0.99791 | 0.99582 | 0.99442 | 0.07428 |
|           | 0.05mM | 0.1g            | 0.99513 | 0.99028 | 0.98542 | 0.10561 |
|           | 0.15mM | 0.1g            | 0.99035 | 0.98079 | 0.97804 | 0.12383 |

Table 5. Variance of coefficients for Rh B and MO dye reduction with varying catalyst and dye concentration in the presence of NaBH4.
| Model               | Pollutant  | B       | Std. Error | Beta | T     | Sig. |
|---------------------|------------|---------|------------|------|-------|------|
| (Constant)          |            | 0.738   | 0.095      |      | 7.735 | 0.000|
| 0.05g Alg@AgNiO     | Rh B       | -0.146  | 0.006      | -0.992 | -25.266 | 0.000|
| (Constant)          |            | 0.358   | 0.181      |      | 1.984 | 0.104|
| 0.1g Alg@AgNiO      | Rh B       | -0.298  | 0.025      | -0.983 | -11.891 | 0.000|
| (Constant)          |            | 0.084   | 0.121      |      | 0.695 | 0.537|
| 0.15g Alg@AgNiO     | Rh B       | -0.452  | 0.025      | -0.996 | -18.339 | 0.000|
| (Constant)          |            | 0.014   | 0.070      |      | 0.194 | 0.859|
| 0.1g Alg@AgNiO      | Rh B       | -0.355  | 0.014      | -0.998 | -24.688 | 0.000|
| (Constant)          |            | 0.129   | 0.047      |      | 2.739 | 0.025|
| 0.1g Alg@AgNiO      | Rh B       | -0.194  | 0.004      | -0.998 | -43.919 | 0.000|
| (Constant)          |            | 0.099   | 0.064      |      | 1.533 | 0.169|
| 0.05g Alg@AgNiO     | MO 0.1mM   | -0.143  | 0.007      | -0.992 | -21.187 | 0.000|
| (Constant)          |            | 0.068   | 0.061      |      | 1.117 | 0.327|
| 0.1g Alg@AgNiO      | MO 0.1mM   | -0.209  | 0.010      | -0.995 | -20.627 | 0.000|
| (Constant)          |            | -0.011  | 0.058      |      | -0.183 | 0.867|
| 0.15g Alg@AgNiO     | MO 0.1mM   | -0.314  | 0.012      | -0.998 | -26.726 | 0.000|
| (Constant)          |            | 0.076   | 0.088      |      | 0.860 | 0.480|
| 0.1g Alg@AgNiO      | MO 0.05mM  | -0.337  | 0.024      | -0.995 | -14.272 | 0.005|
| (Constant)          |            | 0.068   | 0.061      |      | 1.117 | 0.327|
| 0.1g Alg@AgNiO      | MO 0.1mM   | -0.209  | 0.010      | -0.995 | -20.627 | 0.000|
| (Constant)          |            | 0.074   | 0.071      |      | 1.053 | 0.323|
| 0.1g Alg@AgNiO      | MO 0.15mM  | -0.148  | 0.007      | -0.992 | -22.346 | 0.000|

### Reusability tests

Recyclability is a key factor for evaluating catalytic efficiency in heterogeneous catalysis. Although Ag@NiO/Alg exhibited high catalytic activity, it is crucial to study the stability of the nanocatalyst. Therefore, 0.1g of Ag@NiO/Alg was utilized for reduction of 0.05 mM RhB and 0.1mM MO (2.5 mL each in a separate batch of reactions) with 1 mL of 0.1M NaBH₄ solution. After the completion of reaction, Ag@NiO/Alg hydrogel beads were recovered from the reaction media, washed with deionized water and reutilized in another series of reaction. The same process was repeated for up to five cycles. % reduction for each successive cycle was calculated by using the formula;
Percentage % of decolorization = \frac{\text{Initial dye concentration} - \text{Final dye concentration}}{\text{Initial dye concentration}} \times 100

Figure 9 shows that % reduction of the catalyst remained unaffected (96-97% for RhB and 87-88% for MO) for up to five consecutive cycles which confirms the high stability of Ag@NiO inside Ca\(^{2+}\)-Alg hydrogel beads.

Conclusion

In summary, Ag nanoparticles were immobilized on NiO, followed by incorporation into calcium alginate hydrogel beads, by ionotropic crosslinking procedure. The as prepared Ag@NiO/Alg
hydrogel beads were characterized by XRD, SEM, FTIR and EDS techniques. The catalytic activity of Ag@NiO/Alg was evaluated against catalytic reduction of two toxic organic pollutants, RhB and MO, in the presence of sodium borohydride as a reducing agent. The calculated kapp values revealed it as an excellent catalyst. Furthermore, ease of its separation from reaction medium and its recyclability up to five cycles, without any noticeable change in its catalytic activity, provided evidence for Ag@NiO/Alg as an efficient catalytic system.

Declaration of competing interest

The authors report no conflicting interest in any capacity, competing, or financial.
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