

# Synthesis, physical and electrochemical properties of $CoMn_2O_4$ : application to photocatalytic Ni<sup>2+</sup> reduction

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# Abstract

Nickel is a hazardous metal with a harmful effect on the health and environment. In this work, the photocatalytic reduction of Ni<sup>2+</sup> was examined onto the heterosystem  $CoMn_2O_4/TiO_2$  under visible light irradiation. The spinel  $CoMn_2O_4$  is prepared by co-precipitation and characterized in detail to correlate its structural, textural, morphological, compositional, optical and photoelectrochemical features. The effects of pH, catalyst dose and Ni<sup>2+</sup> concentration were optimized. The Ni<sup>2+</sup> reduction increased with decreasing both the catalyst dose and pH. The highest performance was obtained at pH 7.4, a catalyst dose of 1 g/L and Ni<sup>2+</sup> concentration of 10 mg L<sup>-1</sup> with a removal abatement of 88% after 180 min irradiation. The data were suitably fitted by the pseudo-first-order kinetic reaction with an apparent constant of 0.027 min<sup>-1</sup>. Besides, the durability and the stability of the hetero-system CoMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> were evaluated by four consecutive catalytic cycles.

**Keywords** Spinel  $CoMn_2O_4 \cdot Co$ -precipitation  $\cdot Ni^{2+}$  reduction  $\cdot$  Visible light  $\cdot$  Pseudo-first-order model

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# Introduction

One of the most concerns of the contemporizing world is the environmental pollution due to the growing progress and developed industries, which produce large amounts of various effluents (drug, pesticides, dyes, metals, etc.) [1]. The release of these contaminations in water even at low concentrations has posed a real threat to the human health [2]. Among the pollutants, the heavy metals have a tendency to react with sulfur and disrupt the activity of vital enzymes in living organisms. Nickel comes from many industries including cars' exhaust, phosphates, chemical fertilizers, food products, industrial waste [3], stainless steel, nuclear tests, batteries and baking powder [4, 5]. Its presence in water is also due to dyeing activities, mining, galvanization, smelting, manufacture of batteries, metal finishing and alloying processes. All these sources result in health problems and environmental Protection Agency has set the maximum limit at 0.1 mg/L in the drinking water. Unlike organics, it is not only unable to convert into a safe product, but has also a strong aggregation property [6].

In this respect, many chemical and physical techniques were developed to remove nickel from the aquatic medium including: ultrafiltration [7], complexation/ultrafiltration [8], complexation/membrane, filtration [9], ion-exchange [10], reverse osmosis [11], coagulation/flocculation [12], flotation [13], precipitation [14] and electrochemical reduction [15]. Nevertheless, these techniques have their own drawbacks, such as a low elimination efficiency, recyclability, high operation costs and secondary sludge production that this needs further treatments. In this regard, the heterogeneous photocatalysis appeared as an attractive strategy, which has been succeeded in the water purification [16, 17]. However, for a better performance, it needs hetero-junctions with two types of semiconductor (SCs) with appropriate electronic levels: those with a large gap band such as ZnO, TiO<sub>2</sub> or SnO<sub>2</sub> [18–21] with good chemical stability and lower photocorrosion combined to a narrow gap SC as sensitizer; the latter shifts the spectral response toward higher wavelengths [22, 23]. The use of  $TiO_2$  as an electron mediator has been widely employed for this purpose [24-26], owing to its stability and a conduction band positioned midway between  $CoMn_2O_4$ -CB and Ni<sup>2+</sup>/ level.

The spinel  $CoMn_2O_4$  has a strong catalytic activity for oxidation reactions of the alkyl compounds, hydrogen absorbents [27] and metals reduction; its conduction band deriving from 3d metal character has a high reducing power for the water and metals reductions [28]. Mark et al. [29] reported the photocatalytic performance of  $CoMn_2O_4$  NPS for the degradation of Methylene bleu, Malachite Green and Congo Red under solar light. On the other hand, Misra et al. have synthetized  $TiO_2@Au@CoMn_2O_4$  nanocomposites by hydrothermal route for the oxidation of rhodamine B and methyl orange [30]. Lately, 91% degradation of tetracycline hydrochloride with  $Cu_xCo_{1-x}Mn_2O_4$  within 120 min via electro-catalytic oxidation is reported [31]. However, to our knowledge no previous study of this hetero-system in the photocatalytic reduction of nickel has been reported. According to the above considerations, the main purpose of this study was to demonstrate the effectiveness of the visible light reduction of nickel onto the hetero-system  $CoMn_2O_4/TiO_2$ .

# Materials and methods

#### Synthesis of material

The co-precipitation assisted with microwave sonication was used for the preparation of  $CoMn_2O_4$ ; Co  $(NO_3)_2.6H_2O$  (Sigma-Aldrich 99%) and  $MnCl_2.H_2O$  (Sigma-Aldrich 98% purity) with a molar ratio of ½ were dissolved in distilled water. Then,  $NH_4OH$  solution was slowly added under stirring to adjust the pH at~11. The mixture was sonicated for 30 min by ultrasonic irradiation at 800 MHz (Ultrasonic homogenizer UZ Sonopuls HD 2070) and subsequently transferred in a microwave system under a power of 800 W for 15 min. Thereafter, the black precipitate was centrifuged, filtered off, thoroughly washed with distilled water and dried at 120 °C for 24 h. Finally, the recovered powder was ground in an agate mortar and annealed in air from 500 to 800 °C for 6 h (5 °C/min). The end product was subjected to different techniques for its identification. TiO<sub>2</sub> was purchased from Degussa (TiO<sub>2</sub> – P25) and used as received.

#### **Characterization techniques**

The purity of  $\text{CoMn}_2\text{O}_4$  was confirmed by X-ray diffraction (XRD) using a PANalytical Empyrean Diffractometer with a Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) in the 20 range (10–70°) at a scan rate of 0.013° min<sup>-1</sup>.

The specific surface area ( $S_{\text{BET}}$ ) was determined from N<sub>2</sub> adsorption using a BET analyzer (ASAP-2010, Micrometrics V5.01 G) under a relative pressure (P/P<sub>o</sub>) of 10<sup>-6</sup>. The sample was degassed at 140 °C (5 h), and S<sub>BET</sub> was calculated from the BET equation within the relative pressure range (0.1–1).

The morphology and microstructure of the powder have been studied by scanning electron microscopy (SEM, Quanta 650) operating with a voltage of 10 kV. The chemical composition was determined by the energy-dispersive X-ray spectroscopy (EDX) while the distribution of elements was obtained by mapping analysis. The TEM images were used for further microstructural observations on a JEOL 2100F transmission electron microscope with an acceleration voltage of 200 kV.

The XPS measurements were carried out with a Kratos axis supra spectrometer, working with a constant pass energy of 20 eV and a dual X-ray source of Al K $\alpha$  (1486.6 eV). C 1 s signal located at 284.4 eV was used as internal reference.

The chemical characterization of the functional groups of the powder was elucidated by the Fourier transform infrared spectroscopy (FTIR-8900, Shimadzu) in the range (440—4000 cm<sup>-1</sup>) using spectroscopic KBr. The diffuse reflectance was plotted between 190 and 900 nm with a UV–visible spectrophotometer (Jasco V- 650) equipped with an integrating sphere. The electrical conductivity ( $\sigma$ ) was measured in the range (340—440 K) with the two-probe technique. The powder was pressed under 2.5 bar, and the pellets were sintered at 850 °C (2 h). Silver lacquer assumed the electrical contact on the back pellet of the working electrode (WE  $\sim 1 \text{ cm}^2$ ) which was encapsulated in a glass tube, isolated by araldite and polished with SiC paper (1200).

The electrochemical experiments were carried out in KOH (0.1 M) electrolyte in a three-electrode cell with Pt auxiliary electrode, SCE as reference and WE. The scan rate of the potential was set at 10 mV, and the intensity potential J(E) characteristic was plotted by a PGZ 301 potentiostat; the interfacial capacitance was measured at a frequency of 10 kHz. The electrochemical impedance spectroscopy (EIS) data were recorded over the frequency range (100 kHz–10 MHz) after stabilization of the free potential; the measurements were carried out both in the dark and under illumination with a halogen-tungsten lamp (200 W).

#### Photocatalysis

The photocatalytic tests were realized in August between 12 am and 4 pm with an average temperature of 32 °C and a solar flux of 94 mW cm<sup>-2</sup>. The stock solution was prepared by dissolving 1 g of NiSO<sub>4</sub>,  $6H_2O$  (Merck, 99%) in distilled water (1 L); five concentrations (10, 20, 30, 40 and 50 mg/L) were prepared by dilution; the pH was adjusted by addition of HCl or NaOH (0.1 M).

The tests were carried out in an open Pyrex reactor (500 cm<sup>3</sup> capacity). Before irradiation, the powder (CoMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>=100 mg /100 mg), suspended in Ni<sup>2+</sup> 200 mL solutions (10–50 mg /L), was kept in the dark under stirring for 2 h in the solution to reach the adsorption equilibrium; the reactor was then exposed to solar light for 4 h. Aliquots were regularly removed and centrifuged (4000 rpm, 10 min). The residual Ni<sup>2+</sup> concentration was analyzed by atomic absorption spectroscopy (Zeenit 700); the photoreduction rate was calculated from the relation:

$$R\% = \frac{(Ceq - C_t)}{C_{eq}} \times 100 \tag{1}$$

where  $C_{ea}$  and  $C_t$  are the concentration at equilibrium and at a time (t), respectively.

# **Results and discussion**

#### Characterization

The purity of the spinel CoMn<sub>2</sub>O<sub>4</sub> prepared by co-precipitation is confirmed by XRD analysis. The theoretical pattern depicted in Fig. 1 matches well the theoretical one indicating a single phase with high purity. All peaks are indexed in a tetragonal symmetry (space group: I4<sub>1</sub>/amd, N° 141); the distorted structure is due to the Jahn–Teller ion Mn<sup>3+</sup> with an odd number of electrons ( $3d^4$ ), leading to the configuration ( $t_{2g}^3 d_x^{2-y^{20}} d_z^{21}$ ). No starting oxides or secondary phases were detected. The refined lattice parameters: a=5.7840 Å and c=9.0910 Å, are in perfect agreement with the JCPDS Card N° 98–003-9197 [32]. The mean



Fig. 1 X-ray diffraction pattern of CoMn<sub>2</sub>O<sub>4</sub> prepared by co-precipitation

crystallite size (D=27 nm) was calculated from the full width at half maximum ( $\beta$ , rd) of the intense XRD peak (121):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

The textural properties of  $CoMn_2O_4$  composite were inferred from their adsorption desorption isotherms according to the BET analysis (Fig. 2). The isotherm is typical of IV isotherms, according to IUPAC classification with H3 hysteresis loop observed at low relative pressure (0.9–1), confirming the mesoporsity of the spinel [33]. The BET surface area of  $CoMn_2O_4$  is equal to 18.19 m<sup>2</sup> g<sup>-1</sup>.

The morphology and microstructure of the powder were analyzed by the SEM technique; the micrograph (Fig. 3) shows that the grains are fairly homogeneous with uniform shapes whose size lies between 60 and 100 nm. The grains are grouped and linked together, forming large agglomerates. Additionally, for a detailed morphological study, the synthesized  $CoMn_2O_4$  was analyzed by the TEM technique. Figure 4 depicts the TEM images of the prepared composite, where the morphology of material is characterized by an agglomeration of nanoparticles.

The elemental composition determined by EDX (Fig. 5) reveals the presence of Co, Mn and O elements with an average molar ratio Co/Mn of ½ which agrees with the XRF analysis and confirms the formulation of the spinel with MnO (67.15wt.%) and CoO (32.84wt.%). Moreover, the elementary mapping analysis shows a uniform distribution of these three elements (Fig. 6).

The elemental composition and the surface oxidation states of the  $CoMn_2O_4$  nanocomposite were also investigated by XPS analysis (Fig. 7). The survey



Fig. 2 N2 adsorption desorption analysis of  $CoMn_2O_4$ 



Fig. 3 Scanning electron microscopy of CoMn<sub>2</sub>O<sub>4</sub> powder synthetized by co-precipitation

spectrum shows that the oxide consists of Co, Mn and O elements, as well as C (Fig. 7a). The existence of a single C1s peak with a binding energy of 262.2 eV is assigned to the hydrocarbon contaminant [34]. Figure 7b–d reveals the high-resolution spectra of the Co 2p, Mn 2p, and O 1 s.

Co 2p spectrum (Fig. 7b) shows two major peaks with 779.88 (Co  $2p_{1/2}$ ) and 795.18 eV (Co  $2p_{3/2}$ ). Co  $2p_{3/2}$  displays two peaks at 779.48 and 781.78 eV, indicating the presence of Co<sup>2+</sup> and Co<sup>3+</sup> [35, 36]. In addition, the extra peak at



Fig. 4 TEM images of CoMn<sub>2</sub>O<sub>4</sub> nanocomposite



Fig. 5 EDX spectrum of CoMn<sub>2</sub>O<sub>4</sub>

786.88 eV is associated with the shake-up satellite, corroborating the multivalent cobalt.

Moreover, Fig. 7c discloses the binding energy of Mn ions in  $CoMn_2O_4$ . Two peaks at 641.48 and 652.98 eV are detected in the Mn 2p region, which belong energy of Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  with the fission width of 11.5 eV revealing the oxidation state of Mn [37, 38]. Both Mn  $2p_{3/2}$  peaks could be deconvoluted into three major components, the peak at 643.38 eV (Mn<sup>4+</sup>) with those at 641.78 and 640.48 eV belonging to Mn<sup>3+</sup> and Mn<sup>2+</sup>, respectively [32]. The appearance of Co<sup>3+</sup>, Mn<sup>2+</sup> and Mn<sup>4+</sup> suggests the probability of Co<sub>2</sub>O<sub>3</sub> and MnOx [39], not



Fig. 6 SEM image a. EDX elemental mapping views corresponding of O b, Co c and Mn d

detected in the XRD pattern due to the peak broadening [40]. Finally, Fig. 7d shows the XPS spectrum of O 1 s, which can be deconvoluted into five peaks (529.48 eV) attributed to metal–oxygen bonding and (531.48 eV) assigned to the metal-OH bonding [41–43]. The peaks located at 528.38, 530.58 and 532.98 eV are due to absorbed  $O_2$  on the surface, crystal lattice oxygen and chemisorbed oxygen group (OH). Such results confirm the XRD and EDX analysis.

The FTIR spectroscopy was done to identify the main functional groups in  $CoMn_2O_4$ . The spectrum (Fig. 8) shows three main bands at 398, 485 and 603 cm<sup>-1</sup> attributed to the inorganic vibrations of Co–O, Mn–O and Co–O-Mn, respectively [44], thus supporting the formation  $CoMn_2O_4$ . No peaks at ~ 1600 cm<sup>-1</sup> were observed, indicating a weak hygroscopy of our oxide.

The diffuse reflectance spectrum of  $\text{CoMn}_2\text{O}_4$  is presented in Fig. 9; the band gap ( $E_g$ ) is crucial in photocatalysis and is determined from the well-known relation [45]:

$$(\alpha h\nu)^{1/n} = \text{Constant} \times (h\nu - E_{g})$$
(3)

where  $\alpha$  is the optical absorption coefficient. The gap  $E_g$  is obtained from the graph  $(\alpha h\nu)^n$  versus the incident energy  $(h\nu)$ . Among them, n depends on whether the transition is direct (n=1) or indirect (n=4). The direct gap is evaluated at 1.60 eV



Fig.7 XPS spectrum of  $CoMn_2O_4$  composite **a** survey spectrum, **b** cobalt 2p, **c** manganese 2p and **d** oxygen 1 s



Fig. 8 FTIR spectra of the spinel CoMn<sub>2</sub>O<sub>4</sub>



Fig. 9 Direct optical transition of CoMn<sub>2</sub>O<sub>4</sub> prepared by co-precipitation

by extrapolation the linear part of  $(\alpha h\nu)^2$  to  $h\nu$ -axis, a value consistent with that reported elsewhere [46]; the slight difference is due to the quantum size effect.

The semiconductivity is also important in photocatalysis; for this goal we have plotted the electrical conductivity ( $\sigma$ ) vs. 1000/T in the region (340 – 440 K) (Fig. 10) obeys to an exponential law:



Fig. 10 Variation in Log  $\sigma$  as a function of 1000/T for CoMn<sub>2</sub>O<sub>4</sub>

$$\sigma = \sigma_{\rm o} \exp\left\{-E_{\rm a}/kT\right\} \tag{4}$$

The linearization of this equation gives an activation energy ( $E_a = 0.49 \text{ eV}$ ), equal to the difference between the Fermi level and the valence band ( $E_F - E_{VB}$ ). Our normal spinel has a moderate conductivity due to mixed states  $Mn^{4+/3+}$  in octahedra sharing common edges [47], where the conduction is attributed to electron hopping between these two cations located in the same crystallographic site; the oxide belongs to the class II in the Day and Robin classification with the existence of small polarons and mixed states.

#### Electrochemical and photoelectrochemical properties

This part aims to elucidate the electron transfer mechanism of  $CoMn_2O_4$  through the photoelectrochemical properties, which characterize the electrode/electrolyte interfaces and analyze the charges transfer kinetic.

The EIS analysis was performed in the dark and under irradiation after stabilization of the free potential (Fig. 11a).  $CoMn_2O_4$  exhibits a small semicircle whose diameter decreases when under irradiation, thus confirming the semiconductivity and indicating a facile charge transfer, which should lead to increased photoactivity. The simulated results are in good agreement with the experimental data.

The cyclic voltammetry (CV) was traced in the range (-1.4-0.2 V) at a scan rate of 10 mV s<sup>-1</sup>. Figure 11b shows well-separated cathodic peaks indicating at -1.2 and -0.82 V which correspond to the reduction of Co<sup>2+</sup> to Co and Mn<sup>3+</sup> to Mn<sup>2+</sup>, respectively [48, 49]; the anodic peaks at -0.53 and -0.87 V are attributed to their re-oxidations [50–52].

The capacitance potential (C<sup>-2</sup>- E) plot permits to calculate the flat band potential  $(E_{\rm fb})$  which is a key factor for determining the photocatalytic performance of the spinel (Fig. 12):

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_o e N_D} (E - E_{fb}) \tag{5}$$

The extrapolated plot to infinite capacity ( $C^{-2}=0$ ) gives a potential  $E_{fb}$  (- 0.042 V), while the negative slope indicates *p*-type behavior with holes as dominant charge carriers whose density ( $N_A = 10^{17} \text{ h}^+/\text{cm}^{-3}$ ) was calculated from the slope:  $\frac{2}{e\varepsilon\varepsilon_0} \left(\frac{dC^{-2}}{dE}\right)^{-1}$ .

The energies of the valence band (VB) and conduction band (CB) of  $CoMn_2O_4$  are calculated from the relations:

$$E_{VB} = 4.75 + eE_{fb} + 0.059(pH - pH_{pzc}) + E_a$$
(6)

$$E_{CB} = E_{VB} - E_g \tag{7}$$



Fig. 11 a EIS plot of  $CoMn_2O_4$  in the dark and under visible light irradiation measured in 0.1 M KOH aqueous solution. **b** Cyclic (I-E) characteristic





(pHpcz=6.4) is the pH at the point of zero charge (pzc); it is determined from the equilibrium pH of a solution containing an excess of  $CoMn_2O_4$  powder and corresponds to the pH for which the surface charge is zero. The values of VB and CB are (0.5 V/5.23 eV) and (- 1.1 V/4.63 eV) in the dark and light, respectively.

#### Photocatalytic activity and kinetic study

#### Effect of initial pH and catalyst dose

The optimization of the operating parameters contributes to enhance the photoreduction of Ni<sup>2+</sup> over the hetero-system  $CoMn_2O_4/TiO_2$ . The effect of pH, catalyst dose and Ni<sup>2+</sup> initial concentrations (C<sub>o</sub>) on the photoreduction efficiency is investigated. However, before proceeding with the photocatalysis, the adsorption–desorption was performed in the dark. In addition, it should be noted that the hetero-system  $CoMn_2O_4/TiO_2$  displays an adsorption efficiency of 24% after 2 h.

The pH of wastewater containing nickel averages 3, depending on the nature of co-existing compounds [53]. In this study, the pH effect on the Ni<sup>2+</sup> reduction was studied over the range (2—7.4), while the concentration  $C_o$ , hetero-system percentage and irradiation time were taken equal to 10 mg/L, 50 wt.% CoMn<sub>2</sub>O<sub>4</sub> / 50 wt.%TiO<sub>2</sub> and 4 h, respectively. It has been observed that the Ni<sup>2+</sup> reduction increases with augmenting pH and reaches an efficiency of 88% at neutral pH (Fig. 13a). The Ni<sup>2+</sup> reduction falls to 80, 69, 53 and 29% for pHs 7, 6, 4 and 2, respectively. A possible explanation of this trend can be attributed to pH<sub>PZC</sub> of TiO<sub>2</sub> (=6.8) [54]; the catalyst surface is negatively charged: the species [CoMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>] is predominant and absorb Ni<sup>2+</sup> ions by electrostatic attractions [55]. Conversely, the weak performance at low pH is due to the competitive reduction of H<sup>+</sup> as shown in our previous work [56]. Therefore, pH 7.4 was selected for the further experiments.

The hetero-system improves the charge separation responsible for redox reactions on the catalyst surface and shifts the light absorption of  $\text{TiO}_2$  toward the visible region [57, 58]. For this purpose, we determine the optimal percentage of  $\text{CoMn}_2\text{O}_4$  and  $\text{TiO}_2$  required for the Ni<sup>2+</sup> photoreduction rate. The effect of the percentage weight (x%  $\text{CoMn}_2\text{O}_4$  / y%  $\text{TiO}_2$ ) was examined under solar irradiation by varying x from 0 to 100% wt %, while keeping  $\text{C}_0$  at 10 mg/L and pH at 7.4. It has been observed that the photoactivity is higher than that of individual semiconductor showing clearly the synergy effect.

Figure 13b indicates that the best performance occurs for a mass ratio (50/50). This enhancement is due to the fact that  $TiO_2$  excess covers the active sites on the  $CoMn_2O_4$  surface and hinders the charge separation efficiency. This reduction is attributed to the dispersion of the sensitizer onto  $TiO_2$  which acts as recombination centers of (e<sup>-</sup>/h<sup>+</sup>) pairs.

#### Effect of initial concentration

The charge transfer between  $Ni^{2+}$  and photoelectrons facilitates the reduction, and the  $Ni^{2+}$  adsorption on the catalyst surface affects significantly the photoactivity.



Fig. 13 a Influence of pH. b Influence of the mass ratio of  $CoMn_2O_4$  and  $TiO_2$  on the  $Ni^{2+}$  photoreduction

Therefore, the influence of the Ni<sup>2+</sup> concentration  $C_o$  on the reduction onto  $(CoMn_2O_4/TiO_2)$  by varying  $C_o$  from 10 to 50 mg/L, at free pH 7.4, catalyst dose of 1 g/L and solar irradiation time of 4 h was studied (Fig. 14a). As expected, the photoreduction is enhanced for low Ni<sup>2+</sup> concentrations  $C_o$ . The abatement reaches 88% for 10 mg/L after 180 min, whereas for  $C_o$  value of 50 mg/L, the



Fig. 14 a Evolution of  $Ni^{2+}$  concentrations as a function of irradiation time. (b) Kinetic of the  $Ni^{2+}$  versus time of irradiation

photoreduction declines down to 48% because the number of the photoactive site becomes not sufficient to reduce all  $Ni^{2+}$  ions and this is due to the decrease in  $(e^{-}/h^{+})$  pairs. On the other hand, the photons flux was weakened before reaching the semiconductor surface, leading to a low photoreduction.

$\begin{array}{l} \textbf{Table 1}  First-order \ kinetic \\ constant \ (K_{app}), R^2 \ and \ t_{1/2} \ under \\ different \ initial \ concentration \\ Ni^{2+} \end{array}$		C <sub>o</sub> (mg/L)					
		10	20	30	40	50	
141	$K_{app}$ (min <sup>-1</sup> )	0.0276	0.0176	0.0147	0.006	0.0051	
	R <sup>2</sup>	0.966	0.968	0.992	0.977	0.90	
	$t_{1/2}$ (min)	25.114	39.383	47.152	115.524	135.911	

Table 2 Comparison of photocatalytic efficiency of other previously reported works for reduction of Ni<sup>2+</sup> in recent years

Catalyst	Co (mg $L^{-1}$ )	Catalyst dose ( $g L^{-1}$ )	Irradiation time ( min)	Removal effi- ciency (%)	Reference
CuCo <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	30	1.0	180	60	[55]
CuFe <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	30	1.0	210	72	[54]
ZnMn <sub>2</sub> O <sub>4</sub>	18	0.5	140	77.5	[59]
CoMn <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	10	1	180	88	This work

# Kinetic study of Ni<sup>2+</sup> photoreduction

The photoreduction kinetic over the hetero-system  $CoMn_2O_4/TiO_2$  was also considered. The linear plots indicate an apparent pseudo-first order which fits well the experimental data at low concentrations. The linear relationship between ln  $(C_0/C)$  and the irradiation rate follows a pseudo-first-order kinetic:

$$-\frac{dC}{dt} = \mathbf{K}_{\mathrm{app}} \times \mathbf{C} \tag{8}$$

 $K_{app}$  (mn<sup>-1</sup>) is the apparent rate constant; the integration of Eq. (6) can be expressed as follows:

$$Ln\left(\frac{C_0}{C_t}\right) = \mathbf{K}_{\mathrm{app}} \times \mathbf{t} \tag{9}$$

where C (mg/L) is the Ni<sup>2+</sup> concentration at specific time (*t*). The plot  $\ln(C_o/C)$  versus reaction time (*t*) for different  $C_o$  concentrations is shown in (Fig. 14b), and as expected,  $K_{\text{app}}$  decreases with increasing  $C_o$  (Table 1). The half-life time (*t*<sub>1/2</sub>) is calculated by the following relationship:

$$t_{1/2} = \frac{\mathrm{Ln}(2)}{K_{app}} \tag{10}$$

To evaluate the reduction of  $Ni^{2+}$  by  $CoMn_2O_4/TiO_2$ , a comparison is made with other works (Table 2). Our hetero-system has relatively high performance and seems satisfactory for treating wastewater contaminated with nickel.

## **Cycles stability**

The reusability of the photocatalyst is a deciding factor for practical applications [60]. For this aim, a series of recycling experiments for Ni<sup>2+</sup> photoreduction have been carried out under the same experimental conditions and the results are shown in Fig. 15a. As can be seen, after the fourth run, the removal abatement has decreased from 88 to 77%. This reduction (11%) is ascribed to clogging of active sites in the course of process. Also, the SEM images (Fig. 15b and c) of the recovered catalyst after the fourth run show that the structure of CoMn<sub>2</sub>O<sub>4</sub> remains almost unchanged, indicating the photostability of CoMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>.





Fig. 15 a Cycling runs in the photocatalytic reduction of Ni<sup>2+</sup> using  $CoMn_2O_4/TiO_2$ . b and c SEM images after the fourth recycling of the recovered  $CoMn_2O_4/TiO_2$ 

Based on the above findings, the electrons generated by irradiation in  $CoMn_2O_4$ -CB (- 1.10 V) are transferred into the TiO<sub>2</sub>-CB (- 0.97 V) acting as an electron bridge (Fig. 16), which subsequently reduces Ni<sup>2+</sup>. This shows the injection phenomenon where the relevant reactions on  $CoMn_2O_4/TiO_2$  are:

$$p - \text{CoMn}_2\text{O}_4 + h\nu \rightarrow \text{CB} - \text{CoMn}_2\text{O}_4(\text{e}^-) + \text{VB} - \text{CoMn}_2\text{O}_4(\text{h}^+)$$
 (11)

$$n - \text{TiO}_2 + h\nu \rightarrow \text{CB} - \text{TiO}_2(e^-) + \text{VB} - \text{TiO}_2(h^+)$$
 (12)

$$CB - CoMn_2O_4(e^-) + n - TiO_2 \rightarrow CoMn_2O_4 + TiO_2(2e^-)$$
(13)

$$\operatorname{TiO}_2(2 \,\mathrm{e}^-) + \,\operatorname{Ni}^{2+} \to \operatorname{Ni} + \,\operatorname{TiO}_2 \tag{14}$$

The activation of TiO<sub>2</sub> by the photons  $UV_A$  improves considerably the Ni<sup>2+</sup> reduction. The deposited Ni is short-circuited to TiO<sub>2</sub> where hydrogen is easily liberated because of the low H<sub>2</sub> over-voltage, and this is also responsible of the deceleration of Ni deposition.

## Conclusion

This work was devoted to the preparation of the spinel  $CoMn_2O_4$  by co precipitation method and the physical and electrochemical properties, which have been combined to establish the potential/energy diagram. The reduction of Ni<sup>2+</sup>, an environmentally





Fig. 16 Mechanistic scheme for the reduction of  $Ni^{2+}$  under solar light

harmful metal released unregulated in the natural environment by industrial effluents, was studied under solar irradiation. The experimental results revealed that the Ni<sup>2+</sup> photoreduction reached 88% within 3 h of irradiation for (50% CoMn<sub>2</sub>O<sub>4</sub>/50% TiO<sub>2</sub>) of total catalyst dose of 1 g/L, pH 7.4 and 10 mg/L of initial concentration. Under the working conditions, the photocatalytic reduction followed the pseudofirst order with a rate constant of 0.0276 min<sup>-1</sup>. Besides, the stability of the hetero-system has been studied by conducting recyclability tests up to 4 consecutive cycles using CoMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> nanocomposite, indicating that the nanoparticles may be reused without substantial weigh loss. The photoactivity slows it down over illumination time because of the progressive occupation of photoelectrochemical sites and by competition in water reduction.

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