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Photocatalytic properties of $Co_3O_4/LiCoO_2$ recycled from spent lithium-ion batteries using citric acid as leaching agent

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HIGHLIGHTS

- Synthesis a mixture of $Co_3O_4/LiCoO_2$ from spent Li-ion batteries.
- Citric acid for leaching of the cathodes of the spent Li-ion batteries.
- $Co_3O_4/LiCoO_2$ as catalysts in the photodegradation of the methylene blue dye.

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ABSTRACT

In this work, cobalt and lithium from the cathodes of spent lithium-ion batteries were recycled to synthesize a mixture of Co_3O_4 and $LiCoO_2$. The positive electrode was leached with citric acid in the green recycling. After being heated to 85 °C, the leaching solution formed a pink sol, and after being dried at 120 °C for 24 h, it formed a gel, which is a precursor material for Co_3O_4 and $LiCoO_2$ synthesis. A mixture of Co_3O_4 and LT-$LiCoO_2$ was obtained after the calcination of the precursor material at 450 °C for 3 h. The photocatalytic properties of the Co_3O_4 and $LiCoO_2$ were tested in the discoloration of methylene blue dye. The discoloration efficiency of methylene blue dye in the presence of Co_3O_4 and $LiCoO_2$ was 90% after 10 h and 100% after 24 h of heterogeneous catalysis. The contribution of this work is that it presents a means to produce valuable materials with photocatalytic properties from recycled batteries through a spent Li-ion battery recycling process without polluting the environment.

1. Introduction

Lithium-ion batteries possess a high energy density, a low self-discharge rate, and a long life cycle compared to Ni-MH or Ni-Cd batteries. Therefore, they have become a dominant power source for portable electronic devices and hybrid vehicles [1]. Li-ion batteries are made of a graphite anode, a non-aqueous liquid electrolyte, and a cathode of an intercalation oxide. Intercalations of mixed oxides used in cathode composition have the following compositions: $LiCoO_2$, $LiCo_{1-x}Ni_xO_2$, $LiMn_{1.5}Ni_{0.42}Zn_{0.08}O_4$ and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$. $LiCoO_2$ is the most commonly used material for Li-ion batteries because of its high energy density, high operating voltage, and good electrochemical performance. During the charging process, lithium ions de-intercalate from layered $LiCoO_2$, pass through electrolytes, and intercalate in layered graphite [2–5].

$LiCoO_2$ can exist in two structures: low-temperature (LT-$LiCoO_2$) and high-temperature (HT-$LiCoO_2$). LT-$LiCoO_2$ has a spinel-type structure, and it is obtained at temperatures below 500 °C. HT-$LiCoO_2$ has a hexagonal and lamellar structure, and it is obtained at temperatures above 500 °C [6]. Eqs. (1) and (2) describe the charging process in the anode and cathode of Li-ion batteries:

$$C + xe^- + x\,Li^+ \rightarrow Li_xC \quad (1)$$

$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xe^- + xLi^+ \quad (2)$$

The annual worldwide market for rechargeable lithium batteries is estimated at $10 billion (US), and it continues to grow. Spent Li-ion batteries generate large amounts of hazardous waste and cause the loss of valuable metals, such as lithium and cobalt [2,7]. The cobalt used in Li-ion battery manufacturing is 25% of the global demand for cobalt [4]. According to the London Metal Exchange (LME), the cobalt price in January 2016 was $22.50/kg^{-1} (US). Furthermore, cobalt is toxic to the environment, and lithium cobalt

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oxide waste needs appropriate management. Lithium is a valuable metal and important to many industrial applications, but it can create environmental problems because it is chemically reactive with H_2O, N_2, and O_2 [8]. In addition, a Li-ion battery's electrolytes contain toxic organic compounds and LiOH, which is extremely corrosive and causes damage to the environment [4]. In general, lithium and cobalt represent 5–7 wt% and 5–20 wt% of a Li-ion battery's content, respectively [9].

Modern society is concerned with the environment and the environmental damage caused by spent Li-ion batteries. Therefore, it is necessary to develop new methodologies and technologies to recycle these spent batteries in an eco-friendly way. Li-ion batteries can be recycled by pyrometallurgical, bio-hydrometallurgical, or hydrometallurgical processes. The pyrometallurgical process is characterized by high energy consumption, and it releases a large amount of toxic gases into atmosphere. The bio-hydrometallurgical process is efficient, but it requires a very long time to recycle Li-ion batteries. The hydrometallurgical process offers advantages such as low energy consumption, minimal gas emission, and recovery of pure metal [10]. This process uses strong inorganic acids to recover 99% of the cobalt and nearly 100% of the lithium from spent Li-ion batteries. During leaching, the inorganic acids release Cl_2, SO_3, and NOx, and the leaching solutions need chemical treatment. Organic acids, on the other hand, are an alternative to avoid the secondary pollution that strong inorganic acids produce. Organic acids have positive characteristics during the hydrometallurgical process: they easily and naturally degrade, and they do not release toxic gases. Citric acid has a high leaching efficiency and a low price; therefore, it is commonly used as a leaching agent for the hydrometallurgical recovery of cobalt and lithium from spent Li-ion batteries [9,11,12]. Once recovered by the hydrometallurgical process, the cobalt and lithium of spent batteries can be reused to obtain a variety of cobalt materials in the recycling process. Metallic cobalt, Co_3O_4, and $LiCoO_2$ can be obtained using techniques such as electrodeposition and chemical precipitation [1,12–14].

In the present study, citric acid was used to recover cobalt and lithium from spent Li-ion batteries. The cobalt and lithium were recycled to synthesize a mixture of Co_3O_4 and LT-$LiCoO_2$ after calcination of the precursor material. The photocatalytic properties of the Co_3O_4 and $LiCoO_2$ were tested in the discoloration of the methylene blue dye. The characterization of the recycled materials was performed by employing X-ray diffraction (XRD), scanning electronic microscopy (SEM), infrared spectroscopy (IR), and Raman spectroscopy.

2. Experimental

2.1. Cathode separation and leaching using citric acid

Spent 3.7 V Li-ion batteries from a Samsung® cell phone (model EB600BE) were used in this study. The batteries were completely discharged and manually dismantled. Plastic and steel cases were removed from the cells, and the anodes and cathodes were extracted. Cathodic active materials were detached from the supports and dried at 120 °C for 24 h to eliminate organic compounds. Finally, the active material was washed with distilled water and dried at 60 °C. Citric acid was used to dissolve Co and Li from the batteries, and H_2O_2 was employed as a reducing agent. The experimental conditions used for leaching were as follows: 2.0 mol L^{-1} of citric acid, temperature of 80 °C, time of 90 min, a liquid-solid ratio of 20 gL^{-1}, and 3 v/v% of H_2O_2 30 v/v%.

2.2. Synthesis of Co_3O_4 and $LiCoO_2$ from spent Li-ion batteries

For the synthesis of the recycled materials, 50 mL of the cathode material leaching solution was heated to 85 °C and kept in constant agitation for 5 h. The leaching solution formed a pink sol after being heated to 85 °C. The pink sol was dried at 120 °C for 24 h, and it formed a gel, which is a precursor material for lithium cobalt oxide synthesis. Fig. 1 shows a pink sol and a gel (precursor material). We obtained the lithium cobalt oxide after the calcination of the precursor material at 450 °C for 3 h. This yielded a Co_3O_4 and $LiCoO_2$ mixture.

2.3. Application of Co_3O_4 and $LiCoO_2$ in methylene blue dye discoloration

Heterogeneous catalysis was used for the discoloration of methylene blue dye. The dye solution was prepared in a concentration of 3 mgL^{-1} with the addition of 3 mL of H_2O_2. The pH of the solution was adjusted to 3 using sulfuric acid. For catalysis, 3 mg of catalyst powders was added to 50 mL of the dye solution. Photocatalysis was held in a T&M Instruments cabin light using 20-W UV light radiation (Phillips). Discoloration of the methylene blue dye was analyzed and measured with a UV–visible spectrophotometer at wavelengths of 613 nm and 664 nm. The methylene blue dye showed a maximum absorption band in the visible region at 664 nm with a small shoulder at 613 nm. The conjugation system between the two dimethylamine-substituted aromatic rings through the sulfur and nitrogen is responsible for the absorbance at 664 nm. The small shoulder at 613 nm is due to the absorbance of dye dimer, whereas the substituted benzene rings have their absorption bands in the ultraviolet region. Methylene blue is a cationic dye with a dimer responsible for coloration, as shown in Fig. 2.

2.4. Characterization of a cathode from spent Li-ion batteries and the recycled materials

Cathodic active materials and recycled cobalt oxide powders were submitted to XRD using Shimadzu XRD-600 equipment, model 20013, with CuKα radiation (λ = 1.5418 Å) and Bruker equipment, model D2 Phaser, with CuKα radiation (λ = 1.5406 Å) at a rate of 2° min^{-1}. Characteristic peaks were analyzed with a Crystallographica Search Match® program.

Micrographs were carried out using a JEOL 6610LV scanning electron microscope. The composition of cathodic active and recycled material powders were determined by Raman spectroscopy, module AFM Alpha 300 WITEC, with a laser of 532 nm utilized as an excitation source.

Thermal analyses of the precursor material were performed with SDT Q600 V20.9 Build 20 module DSC-TGA standard equipment, with an air flow of 100 $mLmin^{-1}$, a heating rate of 10 °$Cmin^{-1}$, and a maximum temperature of 1000 °C.

Dye discoloration was monitored by atomic absorbance and was recorded with a HACH UV–visible spectrophotometer model DR5000.

3. Results and discussion

3.1. Characterization of spent Li-ion batteries, precursor material, and recycled materials

Fig. 3A represents the typical X-ray diffraction spectrum for the cathode of a spent Samsung® Li-ion battery. According to the Crystallographica Search Match® program, the assigned peaks have similar characteristics to higher temperature $LiCoO_2$ (HT-$LiCoO_2$) (card 44–145). The $LiCoO_2$ used in Li-ion batteries is usually prepared by solid-state reaction, at higher temperatures (800 °C) and for a longer time (8 h).

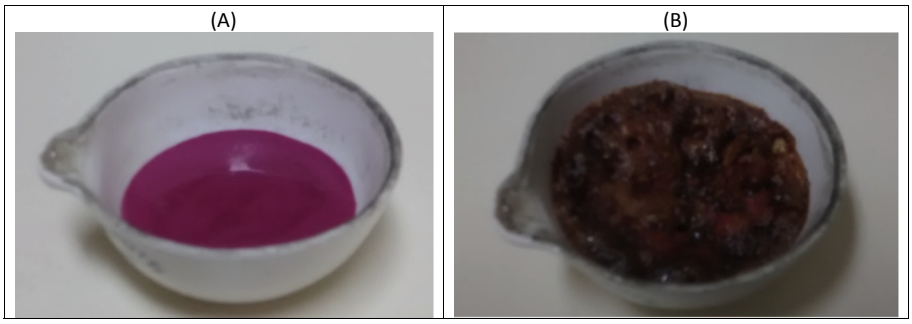


Fig. 1. (a) Pink sol, (b) Dried gel, which is a precursor material for lithium cobalt oxide synthesis.

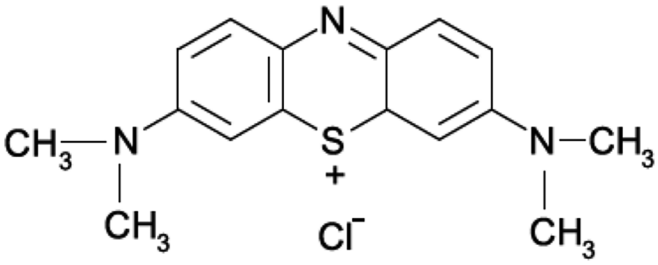


Fig. 2. Methylene blue dye molecule.

Fig. 3B represents the Raman spectroscopy of spent battery cathodes. The most intensive bands at 590 cm^{-1} and 478 cm^{-1} in the Raman spectrum of spent batteries are characteristic of HT-$LiCoO_2$ [15]. The band at 478 cm^{-1} is attributed to the E_g mode, related to the stretching of the Co–O bonds, and the band at 588 cm^{-1} is attributed to the A_{1g} mode. The band at 679 cm^{-1} is characteristic of the Co_3O_4 formed by the decomposition reaction of $LiCoO_2$ [16]. During battery operation, when the lithium fraction in $LiCoO_2$ becomes less than 0.50, the decomposition of $LiCoO_2$ starts. The formation of Co_3O_4 represents one of the main reasons for the loss of capacity in Li-ion batteries. Co_3O_4 reacts by adsorbing the Li^+ irreversibly in their structure. Eq. (3) represents the decomposition of $Li_{0.5}CoO_2$ into O_2 and Co_3O_4 [17].

$$Li_{0.50}CoO_2 \rightleftarrows 0.50\ LiCoO_2 + \frac{1}{6}Co_3O_4 + \frac{1}{6}O_2 \quad (3)$$

Fig. 3C shows the micrographs for the cathode of a spent Li-ion battery. The spent HT-$LiCoO_2$ can be seen in the inner region of the agglomerated crystals, and, within the agglomeration, there is porosity for electrolyte penetration. Cracks can be seen on the surface of the spent HT-$LiCoO_2$.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses of the precursor material are shown in Fig. 4. The TG analysis indicates that there is a weight loss of 90 wt% when the temperature is between 200 °C and 425 °C due to the organic material calcination. When the temperature is between 450 °C and 1000 °C in the TG, there is no weight loss. In the DSC plot, an exothermic process between 365 °C and 412 °C can be observed; it is assigned to the formation of Co_3O_4 and LT-$LiCoO_2$. An endothermic process occurs between 412 °C and 842 °C due to a solid-state reaction for HT-$LiCoO_2$ formation, where lithium intercalates in the layered Co_3O_4 [18–20]. The calcination temperature of 450 °C was chosen in this study after considering TG and DSC analyses.

An IR spectra of the precursor material and material calcined at 450 °C is shown in Fig. 5. The narrow and broad bands from 3210 cm^{-1} to 3505 cm^{-1} are from the stretching vibrations of OH in the citrate precursor. The narrow band at 3287 cm^{-1} reveals the formation of a complex network of hydrogen bonding in the citric acid. Bands in the 1160–1100 cm^{-1} spectral range correspond to the bending and stretching vibrations of OH and C–O(H) for tertiary alcohols. The band at about 3400 cm^{-1} can be attributed to the crystal and/or the coordination water for lithium and cobalt citrates. The band at 1404 cm^{-1} is attributed to the vibrations of coordinated carboxyls, and the band at 1700 cm^{-1} corresponds to carbonyl [18,19,21,22]. After calcination, small amounts of organic matter remain in material calcined at 450 °C.

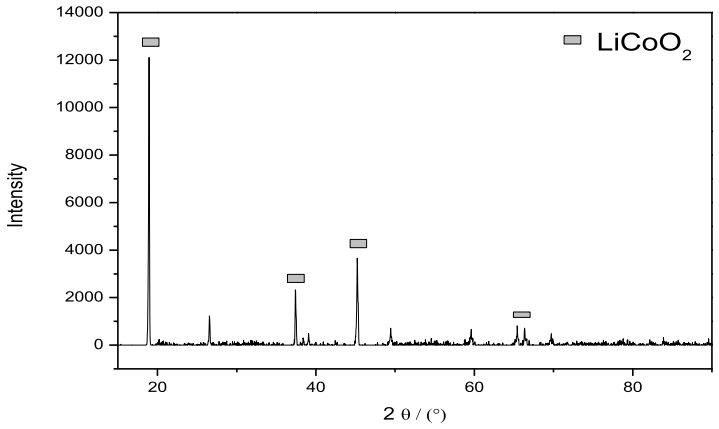
Fig. 6A represents the typical X-ray diffraction spectrum for recycled cobalt oxide material. According to the Crystallographica Search Match® program, the recycled material calcined at 450 °C is a mixture of cobalt oxide Co_3O_4 (card 43–1003) and $LiCoO_2$ (card 44–145).

A Raman spectroscopy was made to complement the XRD characterization. Fig. 6B represents the Raman spectroscopy of recycled materials. Recycled material calcined at 450 °C has the most intensive Raman bands at 660 cm^{-1}. This band is characteristic of cubic spinel Co_3O_4 [23–26]. The presence of the band at 660 cm^{-1} was also verified by H. Porthault et al. [23] and Christoper et al. [24]. The authors attributed the band at 660 cm^{-1} to Co_3O_4. This assignment was based on the synthesis of LT-$LiCoO_2$ from Co_3O_4. A part of Co_3O_4 that does not react with Li^+ ions remains as an impurity in the LT-$LiCoO_2$ samples. Small bands at 190 cm^{-1} and 506 cm^{-1} are also characteristic of spinel Co_3O_4. The band at 458 cm^{-1} is attributed to spinel LT-$LiCoO_2$, and the band at 600 cm^{-1} can be attributed to both LT-$LiCoO_2$ and Co_3O_4. The band at 600 cm^{-1} is assigned to Co–O stretching modes of the CoO_6 octahedral, while the lower frequency bands (458 cm^{-1}) are assigned primarily to O–Co–O bending motions. The recycled material calcined at 450 °C is a mixture of LT-$LiCoO_2$ and Co_3O_4 compounds [23–26].

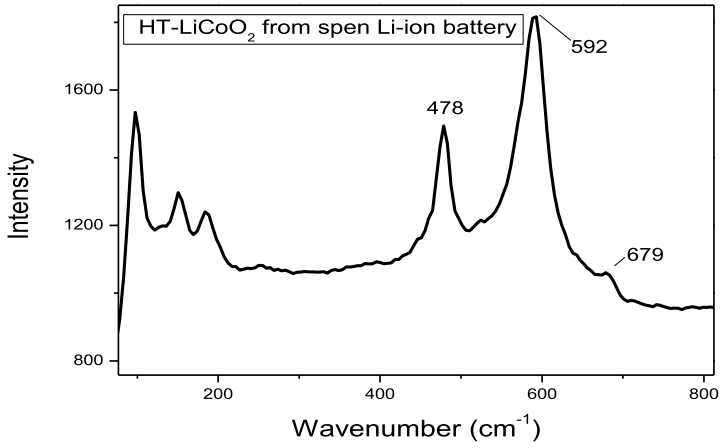
Fig. 6C shows the micrograph for the recycled cobalt oxides synthetized at 450 °C ($LiCoO_2$ and Co_3O_4). The recycled materials have porosity and agglomerated particles.

3.2. Application of Co_3O_4 and $LiCoO_2$ as catalysts of the methylene blue dye degradation

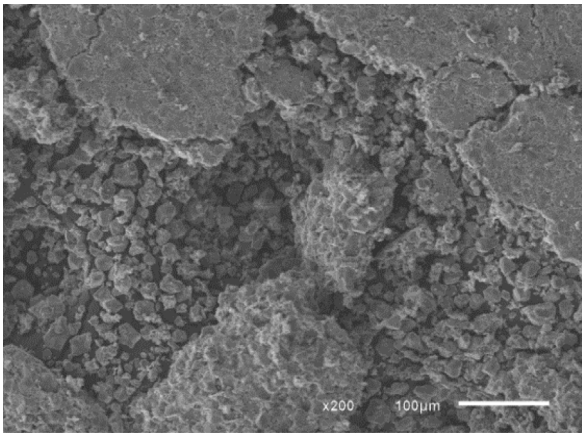
Cubic spinel cobalt oxides are semiconductor materials with good catalytic activity in photocatalysis. UV-light irradiation under semiconductors generates electrons (e^-) in the conduction bands and holes (h^+) in the valence band (Eq. (4)). The photogenerated electron-hole pair can oxidize either an organic molecule directly or an H_2O_2 forming hydroxyl radical (•OH) and OH_2•, which can attack adsorbed organic molecules, leading finally to their complete degradation (Eq. (5) and (6)) [27–30]. The total reaction among the Co_3O_4 and $LiCoO_2$, UV radiation, and H_2O_2 could be written as follows:



(A)



(B)



(C)

Fig. 3. $LiCoO_2$ cathode material from spent lithium ion batteries: (A) XRD; (B) Raman spectrum; (C) SEM images.

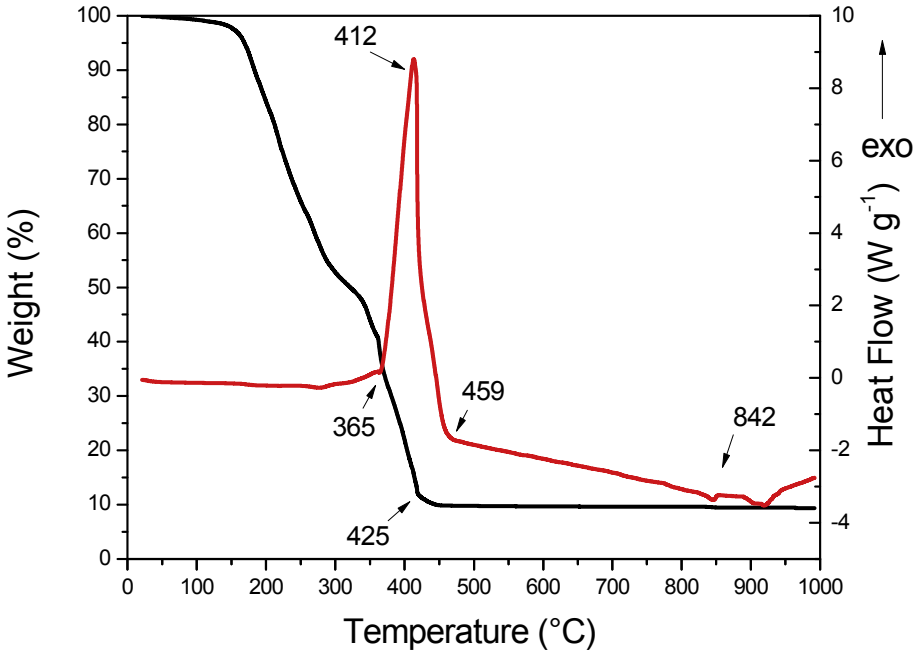


Fig. 4. TG (black plot) and DSC (red plot) analyses of the precursor material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

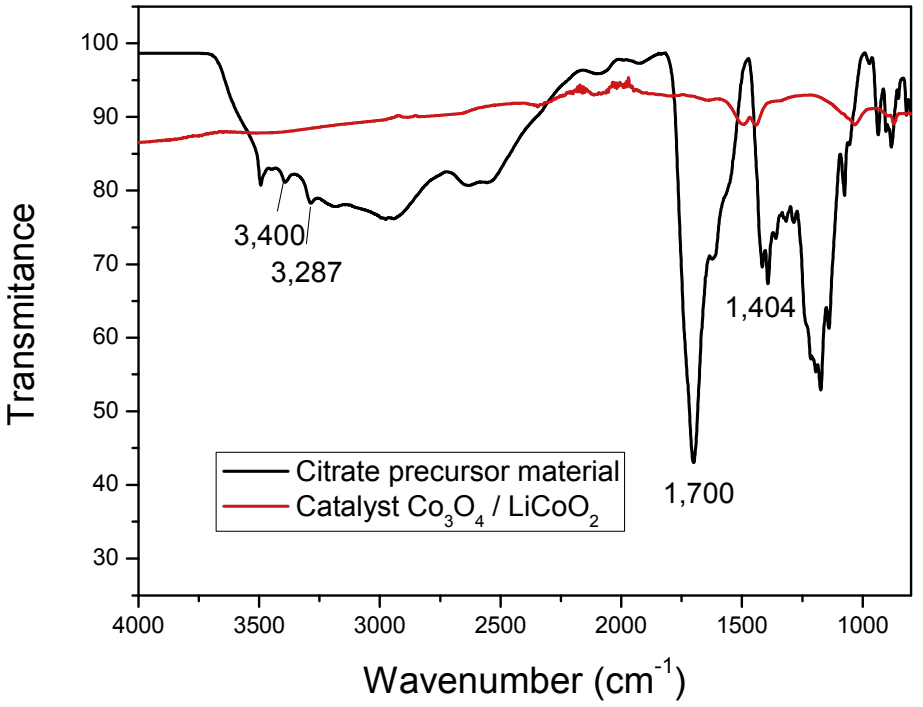


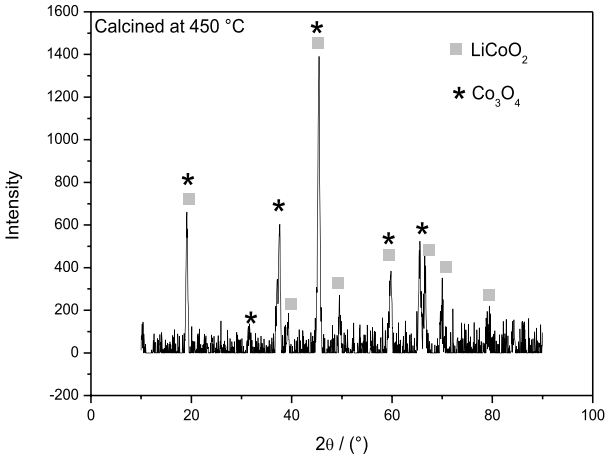
Fig. 5. IR spectra the precursor material and cobalt oxides obtained after precursor material calcination at 450 °C.

$$Co_3O_4 + LiCoO_2 + h\upsilon \rightarrow Co_3O_4 + LiCoO_2 + \left(e^-_{CB} + h^+_{VB}\right) \quad (4)$$

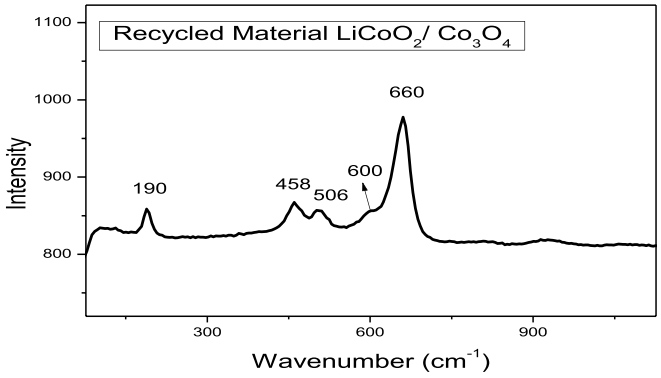
$$H_2O_2 + e^- \rightarrow 2OH\cdot \quad (5)$$

$$H_2O_2 + OH\cdot \rightarrow OH_2\cdot + H_2O \quad (6)$$

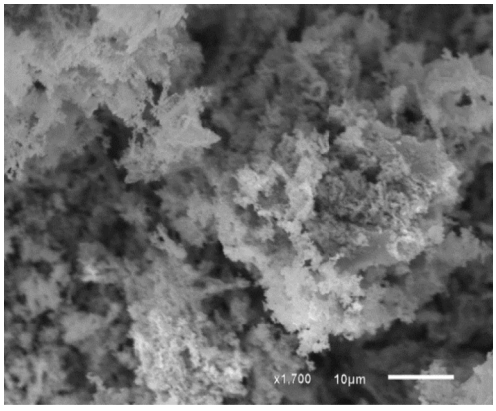
The discoloration of methylene blue dye was monitored by a UV–visible spectrophotometer at wavelengths of 613 nm and 664 nm, as shown in Fig. 7A. The discoloration rate for absorption peaks at 664 nm and 613 nm is shown in Fig. 7B. The absorption peak at 664 nm diminished faster than the peak at 613 nm. This indicates that the demethylation of the dimer occurs faster than the cleavage of aromatic rings [27]. The average discoloration rate (μg/h) was calculated as follows:



(A)

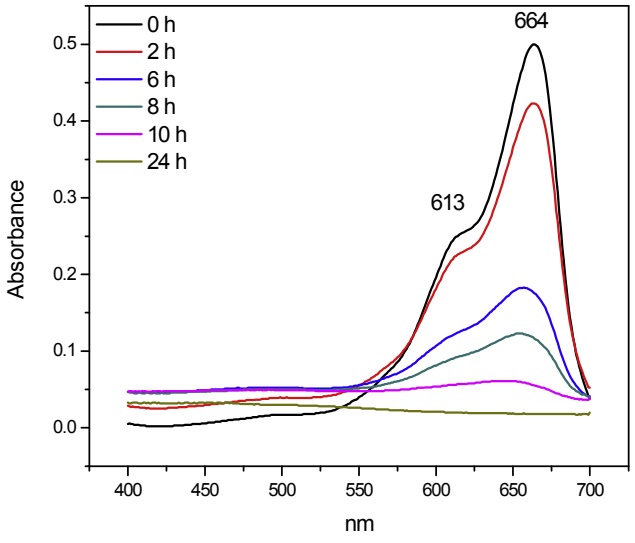


(B)

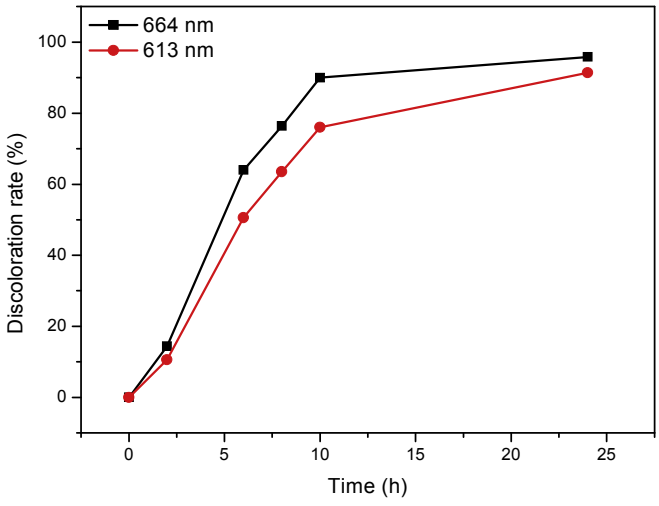


(C)

Fig. 6. Recycled material: (A) XRD; (B) Raman spectrum; (C) SEM images.



(A)



(B)

Fig. 7. A) Dye degradation monitored by UV-spectrophotometry, B) Discoloration rate of methylene blue dye for absorption peak at 664 nm and 613 nm.

$$\text{Average discoloration rate} = \frac{C\,D\,1000}{100 \times t} \tag{7}$$

where C is the initial concentration of dye (mgL^{-1}) and D is the dye discoloration (%) after time t (h). In this experiment, the average discoloration rate after 10 h was 270 $\mu g h^{-1}$.

The catalysis was also subjected to a kinetic analysis of a second-order reaction. Data were analyzed according to the kinetic equation of the second order, given by Eq. (8):

$$\frac{1}{C} = \frac{1}{C_0} - kt \tag{8}$$

where C_0 is the initial concentration of methylene blue, C is the concentration of methylene blue at time t, and k is the rate constant equation.

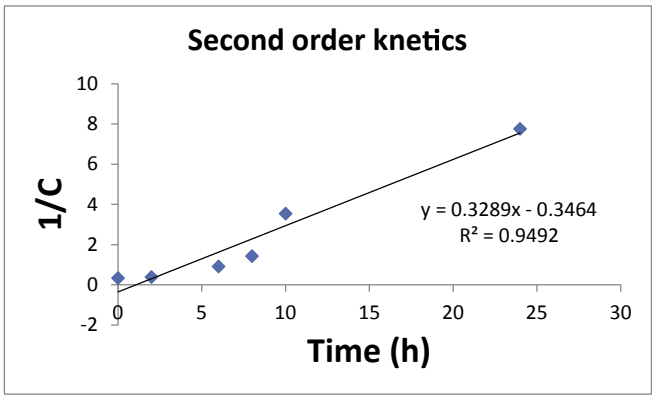


Fig. 8. Kinetics of the methylene blue dye molecule discoloration.

The graph of 1/C versus time (t) shown in Fig. 8 has good linearity with $R^2 = 0.9492$, and the rate constant $k = 0.3289\ mol^{-1}Ls^{-1}$. The methylene blue dye discoloration is a second-order reaction.

4. Conclusions

In this study, citric acid was used as an organic acid leaching agent in order to develop an eco-friendly recycling route for spent Li-ion batteries. Cobalt and lithium recovered from the leaching solution were used to form a sol-gel material. The precursor material, which was calcined at 450 °C, formed a mixture of Co_3O_4 and $LiCoO_2$, which was tested as a catalyst of discoloration in methylene blue dye. The total discoloration that occurred indicates that Co_3O_4/$LiCoO_2$ is a promising catalyst. The discoloration of dye molecules in the presence of the catalyst had an efficiency of 90% after 10 h and 100% after 24 h of heterogeneous catalysis. The contribution of this work is that it presents a means to produce valuable materials having catalytic properties from spent Li-ion batteries through an effective recycling process without polluting the environment.

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