Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1079255

57 (2016) 16507–16513
July

Taylor & Francis
Taylor & Francis Group

Adsorption of α-toluic acid by calcium peroxide nanoparticles

Sapana S. Madan[a], Asha Upwanshi W[b], Kailas L. Wasewar[a,*]

[a]*Advance Separation and Analytical Laboratory (ASAL), Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT), Nagpur (M.S) 440010, India, Tel. +91 712 2801561; Fax: +91 712 2801565; emails: k_wasewar@rediffmail.com, klwasewar@chem.vnit.ac.in, dhara0005@gmail.com (K.L. Wasewar)*
[b]*Department of Horticulture and Food Processing, Government of Madhya Pradesh, Bhopal, India*

Received 24 December 2014; Accepted 29 July 2015

ABSTRACT

Calcium peroxide (CaO_2) nanoparticles are cost-effective adsorbents to provide high adsorption capacity, rapid adsorption rate, and easy separation. This study investigated the adsorption of α-toluic acid in aqueous solution by CaO_2 nanoparticles. CaO_2 nanoparticles were synthesized by surface modification technique and characterized by X-ray diffraction, thermogravimetric analysis, differential thermal analysis, Brunauer–Emmett–Teller, energy dispersive X-ray analysis, and transmission electron microscopy (TEM). CaO_2 nanoparticles were 8–40 nm in diameter identified by TEM. The effects of various parameters on removal of α-toluic acid such as contact time, initial α-toluic acid concentration, CaO_2 nanoparticles dosage, agitation speed, and temperature have been investigated. Removal efficiency of 97.7% for α-toluic acid was obtained by 0.05 g/L CaO_2 nanoparticles for 13.47 g/L α-toluic acid.

Keywords: Adsorption; α-Toluic acid; Nanoparticles; Calcium peroxide

1. Introduction

The removal of organic residues from aqueous waste streams released from industries is important and necessary in view of pollution control and recovery of useful materials. Aqueous waste discharged from chemical plants typically contains low levels (a few percent or less) of small organic compounds such as carboxylic acids, amines, alcohols, and aldehydes. Carboxylic acids are recovered as a product for instance from fermentation broths and wastewaters [1]. The carboxylic acids in such aqueous solutions are usually less than 10%. Carboxylic acids are the most attractive compounds which can be made from biomass [2]. Recovery of carboxylic acid from aqueous solution attracted a great interest due to its complexity for separation because of a high water affinity [3]. α-Toluic acid is carboxylic acid with a phenyl functional group. It is a white solid with unpleasant odor. It has extensive range of biological, antibacterial, and analgesic activity [4]. α-Toluic acid is widely employed in pesticides, pharmaceutical, perfume, cosmetics industries, etc. α-Toluic acid is also used to treat type II hyperammonemia to help diminish the amount of ammonia in a patient's blood stream by forming phenylacetyl-CoA, which then reacts with nitrogen-rich glutamine to form phenylacetyl glutamine [5,6]. Also, it is one of the important reactants in the production of penicillin G [7]. Therefore, it is important to find the easy methods for recovery of α-toluic acid. A number of methods have been studied such as precipitation, distillation, membranes, ion exchange, reactive extraction, adsorption, etc. to recover carboxylic acids from aqueous

---

*Corresponding author.

solutions [8–11]. Most of these methods have their own advantages and disadvantages.

As compared to other methods, adsorption is the most promising techniques in most natural systems including physical, biological, and chemical for removal of carboxylic acids from aqueous solution [12]. Carboxylic acids are recovered from fermentation broth by weak-base polymer adsorbents [13]. Adsorption equilibria of some carboxylic acids from wastewater streams by activated carbon are investigated [14–16]. Gel adsorbents are used for the removal of some carboxylic acids from wastewater [10]. Ion exchangers are frequently used for the recovery of carboxylic acids from aqueous solution or fermentation broth [17].

The literature is available on the removal of different carboxylic acids from aqueous solution, but no work is available on adsorption of α-toluic acid from aqueous streams. Many researchers have been paying attention to develop the novel alternative adsorbents with high adsorptive capacity and low cost. In this regard, a large interest has been paid to nanotechnology. Nanotechnology provides several applications including water and wastewater treatment [18–20]. Nanoparticles have unique physical and chemical properties which received potential applications in many fields. Nanoparticles have much larger surface areas than bulk particles which make them particularly attractive as sorbents. Nanomaterials have a large fraction of atoms which are available for chemical reaction.

CaO_2 has huge application in the environment point of view such as remediation of contaminated soil and underground water, with modification of aerobic bioremediation. CaO_2 has been mostly used in agriculture, aquiculture, poultry raising, cattle breeding, and medicine. The earlier studies mentioned that the rate of oxidation between calcium peroxide and contaminant is tremendously slow [21,22]. For solving this problem, CaO_2 is used in nanosize which increases the ratio of surface to volume and hence speeds of reaction [23,24].

In the present work, calcium peroxide nanoparticles were synthesized and explored the adsorption feasibility for α-toluic acid removal. Because of relatively large surface area, it is probable that nanosize adsorbents with strong affinity toward α-toluic acid can be considered as a helpful tool in enhancing the adsorption capacity in water treatment.

2. Materials and methods

2.1. Reagents

Calcium chloride ($CaCl_2$, 99.5%), ammonia ($NH_3 \cdot H_2O$, 25%), polyethylene glycol (PEG 200), hydrogen peroxide (H_2O_2, 35%), and sodium hydroxide (NaOH) were purchased from Merck and used for the synthesis of calcium peroxide nanoparticles. Solutions were prepared with double-distilled water. The stock solutions were newly prepared for every 2 weeks and refrigerated. The pH of the solution was adjusted using 0.1 M NaOH solution. α-Toluic acids (13.47 g/L) were purchased from Acros Organics (New Jersey, USA) and same was used for preparing lower concentration solutions. A digital pH meter (Spectral Lab Instrumental Pvt. Ltd, India) was used to measure pH which was calibrated with three buffers (pH 4.0, 7.0, and 10.0) everyday. All chemicals were used in their feasible form without any further treatment.

2.2. Synthesis of CaO_2 nanoparticles

In a typical experiment, 3-g $CaCl_2$ was initially added to 30-mL distilled water, followed by addition of 15-mL ammonia solution (1 mol/L) and then 120 mL of PEG 200. To this solution, under constant stirring, 15 mL of 30% H_2O_2 was added dropwise (rate of three drops per minute). After 2 h of mixing, the solution turns yellowish. Then, NaOH solution was added until the pH of the solution becomes 11.5. The obtained nanoparticles suspension was white in color and centrifuged at 10,000 rpm for 5 min to separate nanoparticles. The nanoparticles were rinsed three times by 0.1 N NaOH solutions and two times by distilled water. The final pH of 8.4 for the residue water was obtained. The resultant nanoparticles were dried at 80°C for 2 h in a vacuum oven [24].

2.3. Characterization and stability of nanoparticles

X-ray diffraction (XRD) analysis was performed by X-ray diffractometer (PAN analytical X'pert PRO) in 2θ range from 10° to 100° with step size of 0.01° using Cu X-ray tube ($\lambda = 1.5406$ Å). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of nanoparticles were carried out with a Hitachi TG/DTA 7200. The Brunauer–Emmett–Teller (BET) surface area of nanoparticles was measured by nitrogen adsorption isotherms using surface area analyzer (Model No. Smart Sorb 92/93, Smart Instrument Co. Pvt. Ltd, India). The composition of the sample was determined by energy dispersive X-ray analysis (EDAX) spectrometer (X Flash 6130, Bruker). The particle size was confirmed using transmission electron microscopy (TEM) (JEM-2100, JEOL, NEHU, Shillong, India).

2.4. Batch adsorption study

For each experimental run, 10-mL α-toluic acid solution of known concentration was taken in 100-mL conical flask with adsorbent of known mass. A water bath shaker (REMI, RSB-12, India) and magnetic stirrer (REMI 1 MLH, India) was employed. The aqueous samples were centrifuged at 3,000 rpm for 10 min and the supernatant solutions passed through a 0.45-μm filter. The aqueous α-toluic acid concentration was determined by NaOH (0.01 N) titrations with phenolphthalein indicator. The consistency was observed within ±2% and it was checked by repeating some experiments and analysis. The effect of various parameters such as contact time (5–60 min), initial α-toluic acid concentration (4.08–13.47 g/L), CaO_2 nanoparticles dosage (0.008–0.05 g/L), agitation speed (100–400 rpm), and temperature (298–333 K) were carried out. The removal efficiency (*E*) was calculated as:

$$E\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial aqueous α-toluic acid concentration and C_e is equilibrium or final aqueous α-toluic acid concentration.

3. Results and discussion

3.1. Characterization of the nanoparticles

The representative results of XRD analysis of calcium peroxide nanoparticles is shown in Fig. 1. The XRD spectra show the different diffraction peaks at 2θ values of 30.4, 35.9, 47.7, 53.5, and 60.7. These peaks matched to the (JCPDS card no. 03-0865) of CaO_2 and identified to originate from (0 0 2), (1 1 0), (1 1 2), (1 0 3), and (2 0 2) planes, respectively. The prominent peak shows the tetragonal phase of CaO_2. The observed XRD pattern can be attributed to the unit cell parameter of nanoparticles with cell constants $a = 3.53$ Å and $c = 5.83$ Å. The strong diffraction peak at (0 0 2) plane indicates the preferential growth of crystallites. According to Debye–Scherrer equation ($D = K\lambda/(\beta \cos \theta)$, where D is the mean particle size, λ is the wavelength of incident X-ray (1.5406 Å), θ is the degree of the diffraction peak, and β is the full width at half maximum (FWHM) of the XRD peak appearing at the diffraction angle θ), the crystal size of the synthesized CaO_2 nanoparticles estimated from the (0 0 2) peak width is about 16.8 nm. The pattern of CaO_2 nanoparticles show broadening of peaks and it indicates the particles are in nanosize.

Fig. 2 shows the TGA and DTA curves of CaO_2 nanoparticles. Thermal stability of CaO_2 nanoparticles studied in the temperature range of 30–500℃. Aluminum pan was used for heating and measurement was carried out in nitrogen atmosphere at the heating rate of 10℃/min. For this, a sample of 1.721 mg of CaO_2 nanoparticles was analyzed in TG/DTA machine. TGA curve shows the weight was mostly steady between 250 and 320℃ which confirms the product did not contain water of crystallization. The sample began to decompose at 345–410℃ and reached the maximum decomposition at 360℃, which was due to release of oxygen. TGA shows the weight loss at 100℃ which is due to the loss of water molecules trapped in the samples. Overall, TGA results show a loss of 19.7% in temperature of 30–500℃. Similarly, the DTA also shows sharp peak at 376.6℃ which confirms the decomposition.

The BET surface area was measured by nitrogen adsorption isotherm. Surface area of the CaO_2 nanoparticles was found to be 40.71 m^2/g. The BET surface area of CaO_2 nanoparticles comparable to other nanoparticles such as 25.94 m^2/g of amine-functionalized mesoporous

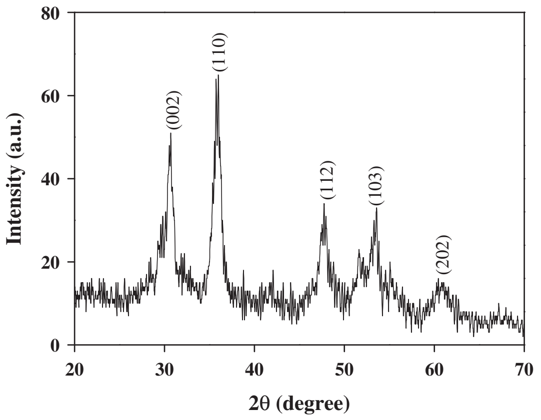

Fig. 1. XRD patterns of CaO_2 nanoparticles.

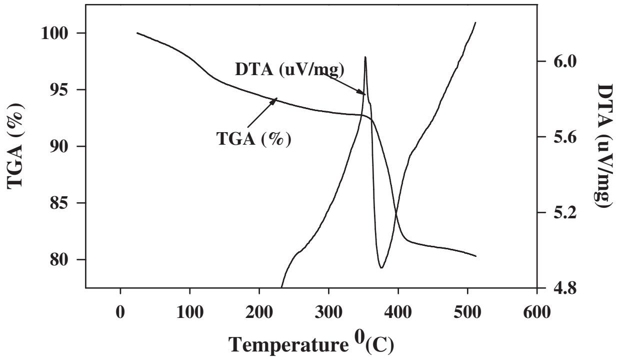

Fig. 2. TGA and DTA of CaO_2 nanoparticles.

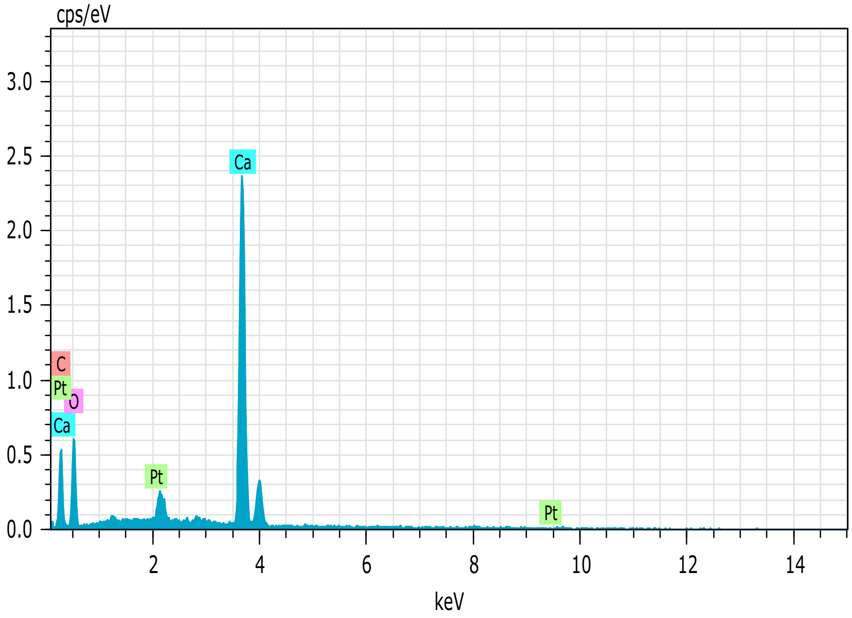

Fig. 3. EDAX of CaO_2 nanoparticles.

Fe_3O_4 nanoparticles which was used for the adsorption of heavy metal ions from water [25].

Chemical purity and stoichiometry of CaO_2 nanoparticles were studied by EDAX. Fig. 3 shows the main peaks of calcium and oxygen in CaO_2 nanoparticles sample. The atomic % of Ca and O are 35.09 and 64.91, respectively, and corresponding to stoichiometry of $Ca_{1.05}O_{1.94}$.

Fig. 4(a) and (b) shows the TEM image of CaO_2 nanoparticles. The CaO_2 nanoparticles appear very dark in TEM image, because the CaO_2 nanoparticles own a higher electron density relative to other substance. CaO_2 nanoparticles could also be tuned by varying the experimental condition. Image shows the size of the CaO_2 nanoparticles is in the range of 8–40 nm. The diffraction pattern of CaO_2 nanoparticles (Fig. 5) shows the diffractions from (0 0 2), (1 1 0), (1 1 2), (1 0 3), and (2 0 2) planes of tetragonal phase of CaO_2 nanoparticles. The diffused ring-like diffraction pattern indicates that CaO_2 nanoparticles are composed of polycrystalline of nanosize material.

3.2. Effect of contact time

Fig. 6 shows the effect of contact time on α-toluic acid adsorption by CaO_2 nanoparticles. Removal of α-toluic acid at varying contact time 5–60 min with 13.47 g/L initial aqueous α-toluic acid, 0.01 g/L nanoparticle dose at constant rpm and temperature (22 ± 2˚C) were studied. Initially, the reaction development is high and all oxidant sources are obtainable. After the change in the rate of removal, α-toluic acid oxidation rate by oxidant is decreased significantly owing to decrease in the content of oxidant in addition to α-toluic acid concentration.

It is observed that the removal efficiency increases with time in the first 10 min and then it acquires a maximum removal at the time of equilibrium, i.e. 40 min for 0.01 g/L of nanoparticles. After that there is no substantial change in removal efficiency of α-toluic acid. Thus, the contact time of 40 min was considered as the optimum time and for the further studies, contact time 60 min was considered for the safer condition. The contact time between adsorbate and adsorbent is the important design parameter for adsorption process. A small contact time in an adsorption system would have the lesser capital and operational cost.

3.3. Effect of initial α-toluic acid concentration

The adsorption of α-toluic acid concentration was studied by varying the initial α-toluic acid concentration at constant adsorbent dose (0.01 g/L), temperature (22 ± 2˚C), and contact time. The removal efficiency (Fig. 7) decreased from 88.3 to 33.3% with the increase in initial concentration of α-toluic acid. It is clear that the removal method can be implemented to remove α-toluic acid from aqueous solution present in any concentration. This may be clarified by the

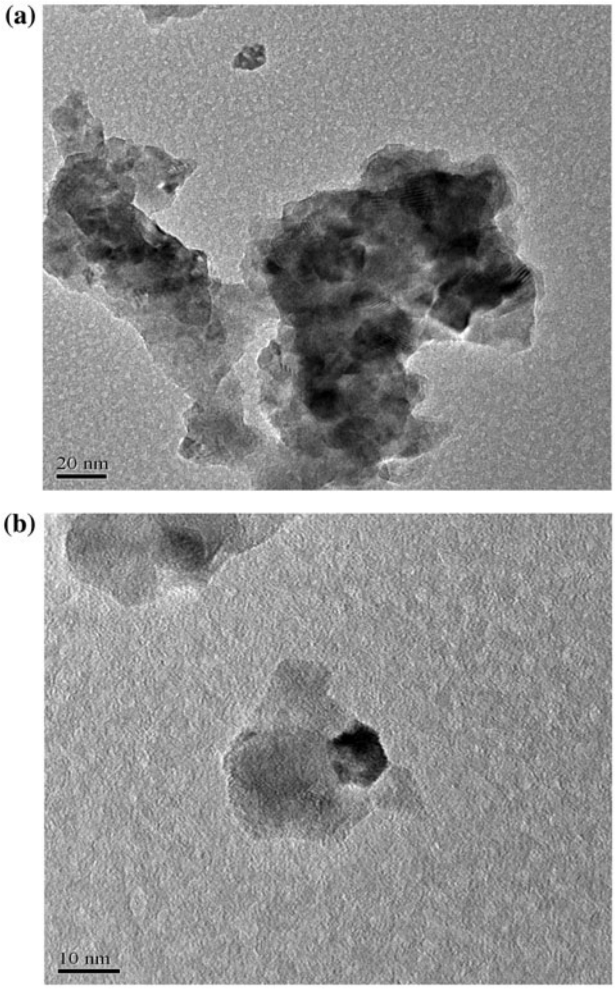

Fig. 4. TEM images of CaO_2 nanoparticles. The bars are (a) 20 nm and (b) 10 nm.

saturation of available negotiable sites of these adsorbents.

3.4. Effect of CaO_2 nanoparticles dosage

The effect of CaO_2 nanoparticles dosage (0.008–0.05 g/L), 13.47 g/L α-toluic acid at constant temperature (22 ± 2˚C), and contact time was investigated. This process is also known as optimization based on one factor at a time where one parameter is varied, and the others are kept constant [26]. It is observed from Fig. 8 that 34.34% removal efficiency was examined at the initial CaO_2 nanoparticles dosage 0.008 g/L. The removal of α-toluic acid increased with increase in CaO_2 nanoparticles dosage up to 0.05 g/L and reached to over 97.7%. The increase in CaO_2 nanoparticles dosage greatly enhanced the removal efficiency.

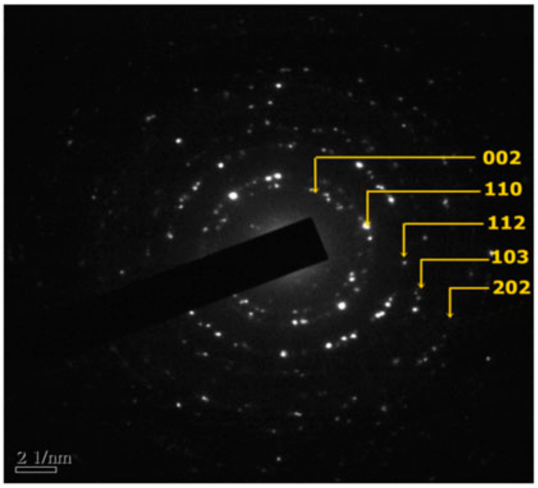

Fig. 5. Diffraction pattern of CaO_2 nanoparticles in powder form.

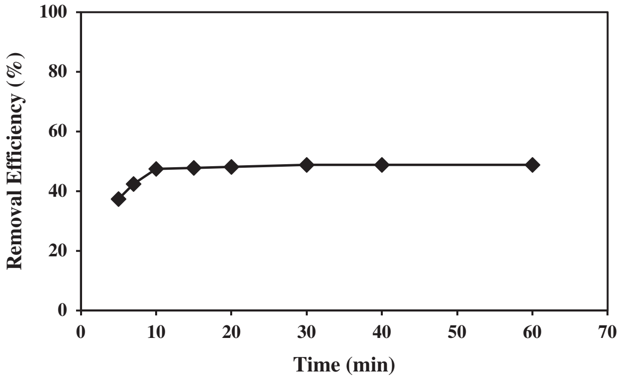

Fig. 6. Effect of contact time on the removal of α-toluic acid onto CaO_2 nanoparticles (initial α-toluic acid concentration = 13.47 g/L, adsorbent dosage = 0.01 g/L, temperature = 22 ± 2˚C).

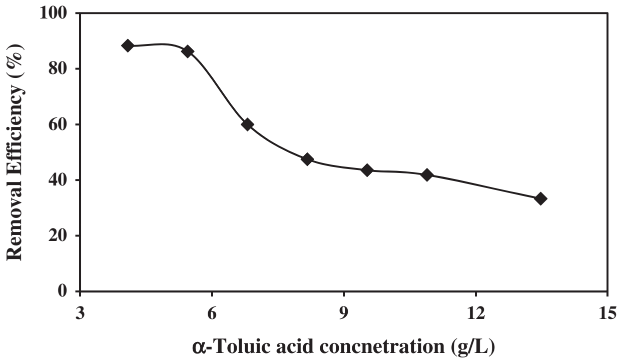

Fig. 7. Effect of initial concentration on the removal of α-toluic acid onto CaO_2 nanoparticles (adsorbent dosage = 0.01 g/L, temperature = 22 ± 2˚C, time = 60 min).

Further increase in adsorbent dosage after 0.05 g/L did not affect the removal of acid. Therefore, the optimum dosage of CaO_2 nanoparticles was found to be 0.05 g/L. It was found that α-toluic acid removal is directly proportional to the CaO_2 nanoparticles dosage. In further study, 0.01 g/L CaO_2 nanoparticles dosage was used as the quantity of synthesized CaO_2 nanoparticles was limited.

3.5. Effect of agitation speed

Agitation is an important parameter in adsorption which influences the distribution of solute in the bulk solution and formation of the external boundary film. The effect of agitation speed was investigated by varying the stirring speed from 100 to 400 rpm. As shown in Fig. 9, the percentage of adsorption was slowly increased with agitation speed. Agitation speed of 200 rpm was found as the optimum agitation speed. This effect can be accredited with the decrease in boundary layer thickness around the adsorbent particles being a result of increasing the degree of mixing.

3.6. Effect of temperature

Removal of α-toluic acid as a function of temperature (298–333 K) is shown in Fig. 10. The temperature has a significant effect on the adsorption process. The percentage removal of α-toluic acid with initial concentrations was decreased from 65.23 to 37.37% for 13.47 g/L. α-Toluic acid adsorption was normally exothermic; thus, the extent of adsorption generally increases with decrease in temperature. This trend could be allocated to the dissolution of nanoparticles at higher temperatures. It could be suggested that the adsorption and dissolution of nanoparticles occurs at the same time. The optimum adsorption temperature of α-toluic acid with CaO_2 nanoparticles was observed as 298 K.

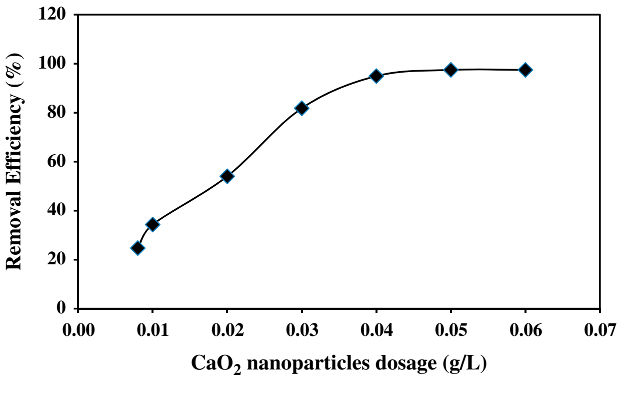

Fig. 8. Effect of adsorbent dosage on the removal of α-toluic acid onto CaO_2 nanoparticles (initial α-toluic acid concentration = 13.47 g/L, temperature = 22 ± 2˚C, time = 60 min).

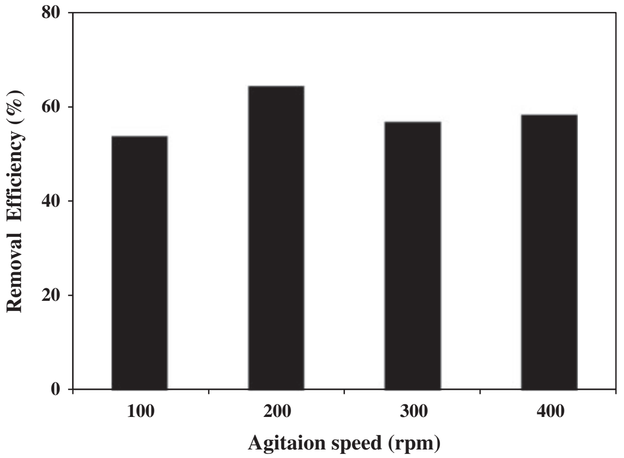

Fig. 9. Effect of agitation on the removal of α-toluic acid by CaO_2 nanoparticles (initial α-toluic acid concentration = 13.47 g/L, adsorbent dosage = 0.01 g/L, at different rpm = 100–400, temperature = 22 ± 2˚C, time = 60 min).

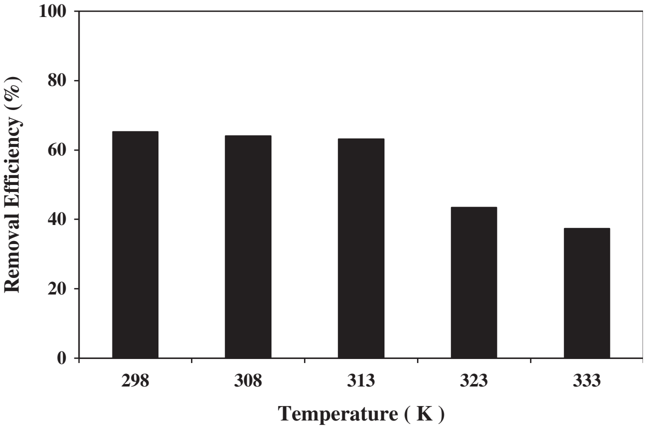

Fig. 10. Effect of temperature on the removal of α-toluic acid by CaO_2 nanoparticles (adsorbent dosage = 0.01 g/L, concentrations of α-toluic acid = 13.47, at different temperature = 298–333 K, time = 60 min).

4. Conclusion

CaO_2 nanoparticles were synthesized and explored its feasibility for removal of α-toluic acid. The particles were found to be homogeneous and in nanometer size. The results of TEM revealed the size of 8–40 nm for synthesized CaO_2 nanoparticles. The maximum removal efficiency (97.7%) of α-toluic acid could be obtained at lower initial α-toluic acid concentration. The adsorption rate of α-toluic acid is fast and equilibrium is achieved within 40 min. The removal efficiency decreases with increase in initial concentration of α-toluic acid and hence adsorption process is exothermic in nature. The result of this study forecasts that the calcium peroxide (CaO_2) nanoparticles can very well be suggested for water treatment and environmental pollution control.

References

[1] S.T. Yang, S.A. White, S.T. Hsu, Extraction of carboxylic acids with tertiary and quaternary amines: Effect of pH, Ind. Eng. Chem. Res. 30 (1991) 1335–1342.

[2] T.K. Ng, R.M. Busche, C.C. McDonald, R.W.F. Hardy, Production of feedstock chemicals, Science 219 (1983) 733–740.

[3] L.A. Tung, C.J. King, Sorption and extraction of lactic and succinic acids at $pH > pK_{a1}$. I. Factors governing equilibria, Ind. Eng. Chem. Res. 33 (1994) 3217–3223.

[4] K.K. Athankar, M.N. Varma, D.Z. Shende, C.K. Yoo, K.L. Wasewar, Reactive extraction of phenylacetic acid with Tri-n-butyl phosphate in benzene, hexanol, and rice bran oil at 298 K, J. Chem. Eng. Data 58 (2013) 3240–3248.

[5] Y. Hammad, R. Nalin, J. Marechal, K. Fiasson, R. Pepin, A.M. Berry, P. Normand, A.M. Domenach, A possible role for phenyl acetic acid (PAA) on alnus glutinosa nodulation by Frankia, Plant Soil 254 (2003) 193–205.

[6] Y.K. Xie, L.Z. Pei, Y.Q. Pei, Z.Y. Cai, Determination of phenyl acetic acid by cyclic voltammetry with electrochemical detection, Measurement 47 (2014) 341–344.

[7] H.K. Gaidhani, K.L. Wasewar, V.G. Pangarkar, Intensification of enzymatic hydrolysis of penicillin G: Part 1. Equilibria and kinetics of extraction of phenyl acetic acid by Alamine 336, Chem. Eng. Sci. 57 (2002) 1979–1984.

[8] H. Uslu, Linear solvation energy relationship (LSER) modeling and kinetic studies on propionic acid reactive extraction using alamine 336 in a toluene solution, Ind. Eng. Chem. Res. 45 (2006) 5788–5795.

[9] A.F. Tuyun, H. Uslu, Extraction equilibria of picolinic acid from aqueous solution by tridodecylamine (TDA), Desalination 268 (2010) 134–140.

[10] Y.S. Aşçı, I.M. Hasdemir, Removal of some carboxylic acids from aqueous solutions by hydrogels, J. Chem. Eng. Data 53 (2008) 2351–2355.

[11] A. Keshav, K.L. Wasewar, S. Chand, Extraction of propionic acid with tri-n-octyl amine in different diluents, Sep. Purif. Technol. 63 (2008) 179–183.

[12] S. Kumar, K.L. Wasewar, B.V. Babu, Intensification of nicotinic acid separation using organophosphorous solvating extractants by reactive extraction, Chem. Eng. Technol. 31 (2008) 1584–1590.

[13] R.L. Evangelista, Z.L. Nikolov, Recovery and purification of lactic acid from fermentation broth by adsorption, Appl. Biochem. Biotechnol. 57–58 (1996) 471–480.

[14] I. Inci, Adsorption of malic acid on charcoal activated, Asian J. Chem. 17 (2005) 475–480.

[15] I. Inci, Removal of citric acid by activated carbon adsorption, Asian J. Chem. 16 (2004) 649–653.

[16] I. Inci, Adsorption equilibria of glycolic acid by activated carbon, Rev. de Chim. 54 (2003) 199–201.

[17] B.J. Liu, Q.L. Ren, Sorption of levulinic acid onto weakly basic anion exchangers: Equilibrium and kinetic studies, J. Colloid Interface Sci. 294 (2006) 281–287.

[18] H. Banejad, E. Olyaie, J. Khodaveisi, Use of nano-scale materials in water treatment application: opportunities and challenges, I.RE.C.E. 1 (2010) 341–346.

[19] A. Afkhami, M. Saber-Tehrani, H. Bagheri, Simultaneous removal of heavy metal ions in wastewater samples using nano-alumina modified with 2,4-dinitrophenylhydrazine, J. Hazard. Mater. 181 (2010) 836–844.

[20] A. Afkhami, R. Moosavi, Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles, J. Hazard. Mater. 174 (2010) 398–403.

[21] A. Northup, D. Cassidy, Calcium peroxide (CaO_2) for use in modified Fenton chemistry, J. Hazard. Mater. 152 (2008) 1164–1170.

[22] D. Cassidy, R.L. Irvine, Use of calcium peroxide to provide oxygen for contaminant biodegradation in a saturated soil, J. Hazard. Mater. 69 (1999) 25–39.

[23] http://www.continentalremediation.com.

[24] E. Olyaie, H. Banejad, A. Afkhami, A. Rahmani, J. Khodaveisi, Development of a cost-effective technique to remove the arsenic contamination from aqueous solutions by calcium peroxide nanoparticles, Sep. Purif. Technol. 95 (2012) 10–15.

[25] X. Xi, Q. Weib, J. Yang, L. Yan, R. Feng, G. Chen, B. Dua, H. Li, Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe_3O_4 nanoparticles, Chem. Eng. J. 184 (2012) 132–140.

[26] P. Panneerselvam, N. Morad, K.A. Tan, Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution, J. Hazard. Mater. 186 (2011) 160–168.