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Efficacy of natural oils and conventional chemicals in the physical extraction of 4-hydroxybenzoic acid from aqueous solution

Anuradha Nanewar Joshi [a,*], Anil Kumar Chandrakar [a], Kailas L. Wasewar [b]

[a] Department of Chemical Engineering, Guru Ghasidas Vishwavidyalaya, A Central University, Bilaspur, C.G, India
[b] Department of Chemical Engineering, Visvesvaraya National Institute of Technology, VNIT, Nagpur, India

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ABSTRACT

4-hydroxybenzoic acid (4-HBA) is a phenolcarboxylic acid and a valuable chemical with various pharmacological properties and a wide range of industrial applications. The present work is envisioned to retrieve 4-HBA from aqueous solution through physical extraction using natural oils (mustard oil, sunflower oil and soyabean oil) and chemicals (MIBK and 1-octanol) as solvent. The experimental evaluation of extraction equilibrium using aforesaid solvents is reported in the form of distribution coefficient (K_D), extraction efficiency (E_P %), partition coefficient (P) and dimerization constant (D). The results were analysed using several physicochemical aspects of the solvents utilized, such as the solvent polarity parameter, dielectric constant, and dipole moment. Further, the comparison of these extraction results was made with the results of our previous study which was with the solvents sesame oil, canola oil, benzene, toluene and p-ether. The results may be arranged in the increasing order with respect to average K_D and average E_P % for natural oils as canola oil (0.23, 18.85%) < mustard oil (0.25, 20.45%) < sunflower oil (0.27, 21.00%) < soyabean oil (0.34, 25.06%) < sesame oil (0.49, 33.24%) and for chemicals as benzene (0.08, 7.5%) < toluene (0.09, 8.25%) < p-ether (0.09, 8.32%) < MIBK (2.55, 71.41%) < 1-octanol (5.01, 83.01%).

1. Introduction

Phenolcarboxylic acids or phenolic acids belong to polyphenols and are secondary metabolites and dietary compounds. The nourishing properties of the fruits are attributed to different polyphenols especially phenolic acids. Hydroxybenzoic acids and hydroxycinnamic acids are the two categories of phenolic acids [1]. 4- hydroxybenzoic acid (4-HBA) or p-hydroxybenzoic acid belongs to the group of hydroxybenzoic acids. 4-HBA has a myriad of medicinal properties such as antioxidant, antibacterial, antisickling, cardioprotective, antidiabetic, anticancer [2–5]. 4-HBA possesses bright applications in various industries like pharmaceutical, cosmetic and food industries [6–9].

As other polyphenols, the sources of 4-HBA and its compounds are different food items. Some of them are, with respective concentration of 4-HBA, millets (16.8 mg/kg) [10], Chokeberry (551.4 mg/kg) [11] tomatoes (0.5 mg/kg) [12], eggplants (5.57 mg/kg) [13], potato peels (78 mg/kg) [14], cherry (14 mg/kg), plum (3 mg/kg), raspberry (32–56 mg/kg), gooseberry (9–14 mg/kg), anise (1030 mg/kg), white mustard (1070 mg/kg), mace (89 mg/kg), bay leaf (73 mg/kg), fennel (137 mg/kg) [15], pecans (20.9–90.1 mg/kg) [16], vanilla (438 mg/L of extract) [17] and coconut (1917 mg/kg) [18–20].

4-HBA is commercially produced by Kolbe-Schmitt reaction 4-HBA, but because of the operating conditions of high temperature and pressure this method has certain drawbacks [21]. The biosynthetic route of manufacture of 4-HBA proves to be a good alternative with some valuable by-products [22–25]. Another way of procurement of 4-HBA may be its recovery from effluent stream of different industries like olive oil mill, pulp and paper industry and winery, as it remains present in the waste of these industries [26–28]. Parabens, the esters of 4-HBA, are used as preservative in pharmaceutical as well as personal care products. The parabens get discharged with the effluent and produce 4-HBA on their decomposition in the atmosphere [29]. The 4 -HBA degrades very slowly and remains present in the atmosphere for the long time and affects the quality of the soil. Hence, retrieving 4-HBA from effluent will be both cost - effective and environmentally beneficial due to its exceptional qualities and applications.

Various methods have been used for the recovery of carboxylic acid like liquid-liquid extraction, adsorption, absorption, photo – Fenton, ultra-filtration etc. [28,30–36], each with its own set of pros and cons. Reactive extraction is a method which combines reaction and separation

* Corresponding author.
E-mail address: anu_joshi86@yahoo.com (A.N. Joshi).

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Reactive Extraction of 4 Hydroxybenzoic Acid Using Tri-*n*-Butyl Phosphate in Toluene and Petroleum Ether at 298 K

Anuradha Nanewar Joshi,* Anil Kumar Chandrakar, and Kailas L. Wasewar

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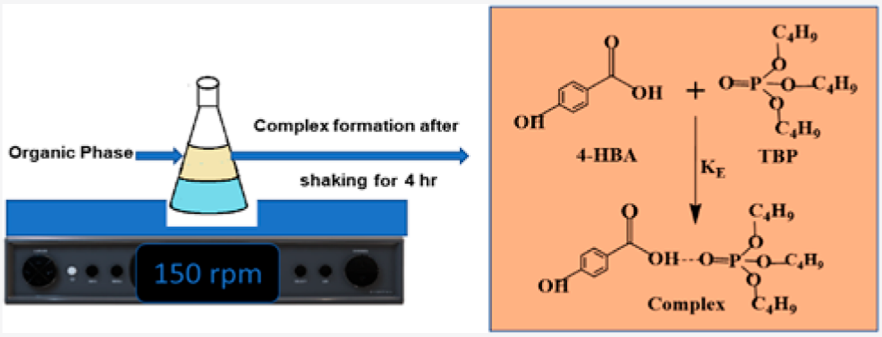

ABSTRACT: 4-Hydroxybenzoic acid has vivid applications in the polymer, pharmaceutical, cosmetic, and food industries. Therefore, it is worth separating 4-hydroxybenzoic acid from effluent streams of different industries such as the olive oil mill, pulp and paper, and wine industry. Reactive extraction is an efficient and economic technique for the separation of carboxylic acids. The experiments for the separation of 4-hydroxybenzoic acid from aqueous solution were performed using tri-*n*-butylphosphate (TBP) in toluene and petroleum ether at 298 K. The investigations were quantified in terms of the distribution coefficient (K_D), extraction efficiency (E %), loading ratio (Z), and equilibrium complexation constant (K_E). The maximum E % and K_D values were 97.14% and 24.84 in toluene and 95.14% and 15.55 in petroleum ether with TBP, respectively. The TBP−toluene system was found better than the TBP−petroleum ether for the separation of 4-hydroxybenzoic acid. The minimum solvent-to-feed ratio and the number of stages for the extraction process were also calculated, and the number of stages was seven for the TBP−toluene system and six for the TBP−petroleum ether system for a maximum TBP concentration of 0.758 mol kg^{-1}.

1. INTRODUCTION

4-Hydroxybenzoic acid (4-HBA) ($C_7H_6O_3$, *p*-hydroxybenzoic acid) is a phenolic acid (phenolcarboxylic acid) and belongs to the hydroxybenzoic acid group. 4-HBA finds its occurrence in many dietary sources such as coconut, raspberry, gooseberry, pecans, anise, vanilla, and fennel.[1−3] 4-HBA has wide application in pharmaceutical, cosmetic, and food industries. 4-HBA is used as a precursor for the liquid crystal polymers, which are modern high-tech polymers proving as a building block of the thermoplastic industry.[4,5] Parabens, derived from 4-HBA, are used as a preservative in pharmaceutical and cosmetic products.[6,7] 4-Hydroxyphenyl alcohol, a precursor for the production of an important cardiovascular drug metoprolol, is derived from 4-HBA.[8] Apart from these, 4-HBA possesses antioxidant, antibacterial, antifungal, antimutagenic, antisickling, cardioprotective, antidiabetic, anticancer, estrogenic,[9] antithrombotic, and antimicrobial[10] properties as well. The properties and applications of 4-HBA are summarized in Figure 1.

It is conventionally manufactured using petroleum-derived chemicals, but the method has drawbacks such as, a low yield, a high cost, time-consuming, and an unwarranted release of carbon dioxide.[11] The direct extraction of 4-HBA from the plant source is quite difficult, but the biosynthetic route of manufacture of 4-HBA is a very attractive pathway, for example, the shikimate pathway, which produces very useful and commercially important biproducts such as muconic acid, resveratrol, and gastrodin.[8,12−14]

Apart from the conventional industrial production and biosynthetic route of manufacturing, 4-HBA can be obtained by separation from the waste streams of the olive oil mill, winery industry, and pulp and paper industry by using different separation methods. The outstanding applications and medicinal properties of 4-HBA make it justifiable to be

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Prediction of minimum and complete fluidization velocity and transport disengaging height of the segregated coal in a cold flow fluidized bed

Gautam Prasad Dewangan & Samarendra Nath Saha

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Optimization of lead adsorption from lead-acid battery recycling unit wastewater using H_2SO_4 modified activated carbon

Saurabh Meshram [a,b,*], Raghwendra Singh Thakur [a], Ghoshna Jyoti [a], Chandrakant Thakur [b], Anupam B. Soni [b]

[a] *Department of Chemical Engineering, Guru Ghasidas Vishwavidyalaya, Bilaspur, 495009, Chhattisgarh, India*
[b] *Department of Chemical Engineering, National Institute of Technology, Raipur, 492010, Chhattisgarh, India*

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ABSTRACT

During the recycling of exhausted lead-acid battery, large amount of wastewater is discharged, which contains the toxic Pb(II) ions in high concentration. In this study, the granular activated carbon after modification with sulfuric acid has been used to remove the Pb(II) ions from this wastewater. Adsorbents were characterized using Fourier Transform Infrared, Scanning Electron Microscope, and X-Ray Diffraction analyzer. Taguchi orthogonal L16 array (4ˆ3) was used for batch adsorption study with four levels of three factors initial pH, adsorbent dose, and contact time. Optimum level of parameters was fourty + nd pH 4.5, time 240 min, and dose 0.05 g/50 mL using signal-to-noise ratio (larger-the-better response). Analysis of variance technique was used to signify the adsorption experiment model. The effect of parameters on uptake capacity of adsorbent has been evaluated. Maximum adsorbent capacity for Pb(II) uptake from wastewater of battery recycling unit was found 8.19 mg/g after modification with sulfuric acid. To further understand the mechanism of adsorption, isotherm and kinetic studies were carried out. Experimental data were well fitted with Langmuir isotherm model and pseudo-second-order kinetic model. The study suggested that H_2SO_4 modified granular activated carbon can be potentially used to remove Pb(II) from lead-acid battery recycle wastewater.

1. Introduction

A major part of the lead required to produce storage battery comes from the Lead-acid battery (LAB) recycling process. About 90% of the total discarded LAB are recycled, which supplies the secondary lead and reduces pollution. During the recycling, wastewater is generated containing lead concentration of 2–300 mg/L and pH of about 1–1.5 [1]. This wastewater upon discharge may leach into the soil and contaminate groundwater and affect the quality of drinking water supply. Long-term exposure to lead can harm kidney, brain, liver, reproductive system, and central nervous system [2]. Gottesfeld and Cherry (2011) [3] reported that nearly 4000 children had been affected due to lead poisoning since 2009 in China. Matlock et al. (2002) [1] reported that according to an estimation, every 1 out of 11 preschoolers has lead in blood at a dangerous level in America. Keep in mind the effect of Pb(II), the Environmental Protection Agency of United States regulates the maximum permissible amount of Pb(II) in drinking water at 15 μg/L, while the World Health Organization permits the allowable level to be as low as 10 μg/L [4].

The conventional neutralization method to treat battery recycling unit wastewater forms the lead hydroxide, which is separated by precipitation [5]. Matlock et al. (2002) [1] used the precipitation method to remove lead from the wastewater of the battery recycling plant by producing a stable Pb-BDET precipitate with the help of potassium salt of 1,3-benzene diamido ethane thiol dianion ($BDET^{2-}$) ligand. An electrokinetic cell made up of titanium electrodes was used to collect the sulfate and lead ions of wastewater in different compartments upon DC supply by Maruthamuthu et al. (2011) [6]. A multi-stage process comprising complexation-ultrafiltration-electrolysis has been studied by Zhang et al. (2012) [7] to remove and recover lead from wastewater of a lead-acid secondary battery plant. Volpe et al. (2009) [8] used the cementation method to recover metallic lead by using urea acetate solution and reducing agents of metallic iron. Wang et al., 2020 [9] used the adsorption method using Magnetic supramolecular polymer composite and found a reduction of lead from 18.07 mg/L to 0.091 mg/L. Meshram et al. (2020) [10] also used the adsorption method using the

* Corresponding author. Department of Chemical Engineering, Guru Ghasidas Vishwavidyalaya, Bilaspur, 495009, Chhattisgarh, India.
E-mail address: s.meshram@ggu.ac.in (S. Meshram).

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Micro filtration of *Moringa Oleifera* juice using hallow fibre membrane technology for clarification

Soumitra Tiwari
Department of Food Processing and Technology, Atal Bihari Vajpayee Viswavidyalaya, Bilaspur, C.G. PIN 495001

S. N. Saha
Department of Chemical Engineering School of IT, Guru Ghasidas (Central University) Viswavidyalaya, Bilaspur C.G. PIN 495001

***Abstract*---**Moringa Oleifera plant is growing many countries including tropical and sub tropical region. It contain numerous nutrition due to vitamins and proteins. The plant leaf extract having phenolics and flavanoids such as gallic acids, chlorogenic acid, ferulic acid, kaempferol, ellagic acid, vanillin and quercetin. The juice is convenient to herbal health drinks combination of different medicinal juices, read to use and serve beverages etc. Moringa Oleifera leave juice has been extracted by grinder then juice were treated with enzyme and centrifuged. The treated juice were clarified by using hallow fibre micro membrane for cold pasteurization. The turbidity, total soluble solid, pH, refractive index, viscosity colour and clarity were analysed on different treatment. It was concluded that best results were obtained in terms of Clarity (47.62%T), Turbidity (5.333 NTU), TSS (5.933°B), pH (5.2725%), Viscosity (1.136667 mPa) for micro filtered juice. The optimum values for the operating condition of micro filtration were 98.0665 kpa pressures with 0.45 µm pore size.

***Keywords*---**Micro filtration, *Moringa Oleifera,* hallow fibre.

Introduction

Moringa Oleifera is a native tree plant from Asia and Africa. It is mostly grown in India, Africa, South America, Mexico and Philippines (Paul & Didia 2012). Now days the Moringa is used as a rich source of food and food products due to its considerable inherent nutritional, antioxidant and phytochemical benefits; as well as its ability to survive in diverse climatic conditions. It has multi-functional utilities in agriculture, medicine, live stock, human and other biological systems (Falowo et al 2018, Ndubuaku et al 2015). The trees many parts such as leaf,

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