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Article

Extraction of 4-HBA utilizing renewable and conventional solvents

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Abstract: 4-Hydroxybenzoic acid (4-HBA) demonstrates promising characteristics as an antioxidant, antifungal, anticancer, antidiabetic, and cardioprotective. It exhibits promising applicability in real-time applications in the pharmaceutical, cosmetic, and plastic sectors. It adds to the value of recuperating. The experiments were conducted to separate 4-hydroxybenzoic acid from a solute mixed aqueous solution using renewable solvent Karanja oil, as well as conventional solvents n-Butanol and Di-chlorobenzene. The aqueous phase of the solute was prepared using five different concentrations of 4-HBA ranging from 0.005 to 0.035 mol/L, in conjunction with double distilled water. The aqueous phase and organic solvent were mixed in a conical flask in equal volumes, with a ratio of 1-part aqueous phase to 1-part organic solvent. Afterward, the sample was placed in the orbital incubator shaker and kept to a constant temperature of 298K for a duration of four hours, with the shaker operating at 200 RPM. During the evaluation of the equilibrium of physical extraction of 4-HBA, the values for the distribution coefficient K_D, the percentage extraction efficiency %E, the partition coefficient P, and the dimerization constant D were computed and correlated with the physicochemical characteristics. The following parametric values were obtained for K_D and %E: n-Butanol (1.704, 63.02%)> Karanja oil (0.810, 44.75%) > Di-chlorobenzene (0.555, 35.69%)

1. Introduction

The energy demand steadily increases in every corner of the world. India, the world's first most populous country, is in more demand of petrochemical products than ever before. People rely on petrochemical goods for basic energy; however, fossil fuel sources are sharply depleted. Therefore, the demand for alternative sources such as renewable increases rapidly. Karanja oil has been utilized as a renewable source as a solvent for solvent extraction methods because the availability of Karanja oil is huge in India and the southern Asia region [1]. All dietary products from plants include phenolic acids (benzene ring contains carboxylic acid moiety), sometimes referred to as phenol carboxylic acids [2, 3]. It occurs naturally in a

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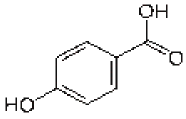
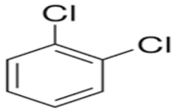
variety of foods, including banana, legumes, coconut, gooseberries, raspberries, fennel, and anise [2–5] and fermentation broth waste [6]. The two primary subgroups of hydroxybenzoic acid are hydroxycinnamic acid (C3–C6) and hydroxybenzoic acid (C1–C6) [7]. 4-HBA is present in the wastewater of the wine industry [8,9] and olive oil mills [10–13] since it is a component of the raw materials needed to make wine and olive fruits. Due to its phenolic acid composition, 4-HBA exhibits several physiological characteristics, including cardiovascular protective [14], antidiabetic, anticancer, antibacterial, antifungal, antimutagenic, antioxidative [4,5], anti-inflammatory and antisickling effects [15,16] Because of such therapeutic qualities, 4-HBA is widely used in pharmacology [17]. A variety of valuable compounds can be derived from 4-hydroxy benzoic acid, including liquid crystal polymers, a cutting-edge modern polymer with promising applications in the thermoplastic industry; the p-hydroxy benzoic acid has primary application to synthesize the blood vessel disease drug metoprolol [14, 18, 19] and the esters of p-hydroxy benzoic acid, which may be used as a preservative in pharmaceutical and cosmetic products [20,21]. p-hydroxy benzoic acid might be produced economically by carbon dioxide and sodium or potassium ions in the Kolbe-Schmitt process [22]. The biosynthesis process is also employed in creating valuable chemicals (4-HBA). The 4-HBA has occurred in effluent streams of several food-preparing units such as the industries of pulp and paper, olive oil mills, and wine [23–25]. Due to its extremely slow biodegradation, HBA affects soil quality when disposed of on land. The exceptional physicochemical characteristics and several appealing uses and the separation of these value chemicals from wastewater have several benefits, including improving the environment and stimulating the economy. The standard methods for removing or recovering 4-HBA are ozone degradation [26], solvent extraction [27], adsorption [28], and Fenton process with UV light [29]. Each of these methods has its own set of drawbacks, including low conversion, lengthy processing times, poor efficacy in diluted solutions, high energy requirements, high costs, and the production of hazardous byproducts [27,28]. Many researchers have been reported that separation of different carboxylic acids including di-carboxylic acid [30–32], 2-Hydroxypropanoic acid [33], Pyridine-2-carboxylic [34], Ethane carboxylic acid [35–37], 2-Hydroxyethanoic [38,39], 4-oxopentanoic [40,41], rosmarinic, and different carboxylic acids [42–45], using reactive extraction as it is an economical, efficient, and hygienic method that works well with diluted solutions [33,46–49]. Reactive extraction has also been used successfully to recover some phenolic acids, such as protocatechuic acid [45,50,51], gallic acid [40,42,52,53], and 4-HBA [52,54–57]. Many studies have been conducted using various environmentally friendly solvents as the organic phase, including liquid salts (ILs) [40,58,59], deep eutectic solvent [60], supercritical fluids (SCF) [31,61], and natural diluents [34,35,54,62]. The present work aims to investigate and verify the physical extraction of 4-hydroxybenzoic acid (4-HBA) with conventional solvent, n-butanol [42,47,63], and Di-chlorobenzene [39,64,65] and renewable solvent, Karanja oil [50,62]. Further, experimental analysis has been performed with several parameters such as solute concentration and type of solvent and then find the effect of these parameters on the distribution coefficient, extraction efficiency, partition coefficient, and dimerization coefficient of 4-HBA. .

2. Methods and Materials

2.1. Materials

The chemical and solvent used in the extraction experiment were purchased as follows: 4-hydroxy benzoic acid with 98% purity was bought from Himedia, n-butanol (99% pure), Di-chlorobenzene (98%) from CDH Pvt Ltd. The Karanja oil (97.5%) was procured from Kush Proteins Pvt. Ltd. India. The chemicals and oils used in the experiment are listed in Table 1.

Table 1. Specifics of the substances utilized in the experiment.

Chemicals Name	Chemical Nomenclature (IUPAC)	Chemical Formula	Molecular geometry	Supplier	Purity
4-hydroxybenzoic acid (4-HBA)	4-hydroxybenzoic acid	$C_7H_6O_3$		HiMedia	98%
n-Butanol	Butan-1-ol	$C_4H_{10}O$		CDH Pvt Ltd.	99%
Dichlorobenzene	para-dichlorobenzene	$C_6H_4Cl_2$		CDH Pvt Ltd.	98%
Karanja Oil	-	-	-	Kush Proteins Pvt. Ltd	97.5%

2.2. Experimental Methodology

The aqueous solution of different concentrations of solute (0.005- 0.035 mol/lit) was created by dissolving the solute 4-Hydroxy Benzoic Acid(4-HBA) in double distilled water. to take into account the maximum 4-HBA content in industrial effluent stream [8–13,26,51,66] is less than 5%, accordingly the concentration range was chosen. the solute as aqueous phase and solvent as organic phase were combined in a conical flask at a 1:1 volumetric ratio and shaken for four hours at 200 RPM speed and temperature at 298 K in an orbital water bath shaker. The time analysis was conducted, and it was identified that 4 hours were needed to reach equilibrium. Two distinct phases were obtained from the mixture after it was shaken and centrifuged for five minutes at 4000 RPM. The concentration of the aqueous (solute) phase was analyzed in a UV-Photo spectrometer with a wavelength of 552nm, and the organic phase solute concentration was calculated by mass balance. The organic phase solute concentration was obtained by the difference between the initial concentration and the aqueous (solute) phase concentration. Replicating a small number of trials with the same parameters revealed consistency within ± 2%. Figure 1 presents the entire experimental flow diagram.

2.3. Statistical analysis of uncertainty

There may be significant experimental uncertainties due to instrument error and various random variations; these can be computed using Equation 1 as

$$\theta = \sqrt{\frac{\sum_{i=0}^{n}(x_j - \bar{x}_j)^2}{n-1}} \quad , \tag{1}$$

the experimental values mean is denoted by $\bar{x}_j$ and x_j is the experimental observations value, n denotes the total number of observations. The uncertainties from the experiment were acquired within the range of x± 0.003.

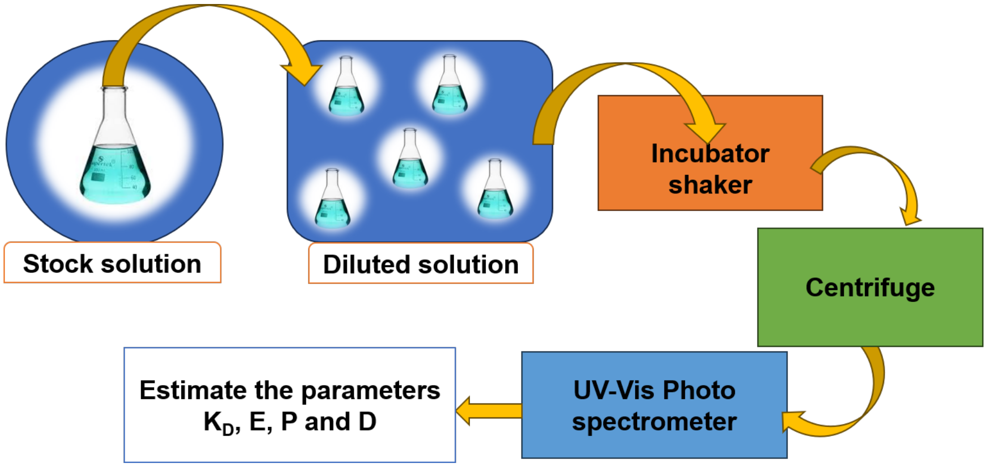


Figure 1. Extraction process flow diagram.

2.4. Physical extraction of 4-hydroxybenzoic acid

The physical separation of p-hydroxybenzoic acid was performed in the presence of two conventional solvents, n-butanol and Di-chlorobenzene, and a renewable solvent, Karanja oil. The water and acid have been shown to have a higher hydrogen bond attraction than carboxylic acid itself; this causes the carboxylic to remain in the form of a monomer. In the solvent phase, carboxylic acids exist as dimers due to the same solute molecule as a hydrogen-hydrogen coupling in non-polar or polar solvents with low polarity [37]. The physical separation of 4-hydroxy benzoic acid with chemical and renewable solvents from the aqueous phase was accomplished in three steps: acid detachment, partition of the undissociated 4-HBA molecule, and dimerization of 4-HBA.

2.4.1. Solute 4-HBA detachment in aqueous phase calculated from Equation 2 and 3

$$[HBA]_{aq} \xleftrightarrow{K_{HBA}} H^{+} + A^{-} \quad , \tag{2}$$

$$K_{HBA} = \frac{[H^{+}][A^{-}]}{[HBA]_{aq}} \quad , \tag{3}$$

where, K_{HBA} is Dissociation constant, HBA represents the 4-HBA solute concentration in mole/liter.

2.4.2. Partition Coefficient of undissociated 4-HBA molecule represent in Equation 4 and 5

$$[HBAX]_{aq} \xleftrightarrow{P} [HBAX]_{org} \quad , \tag{4}$$

where $HBAX_{aq}$ and $HBAX_{org}$ are the concentration of solute in the aqueous phase and organic phase, respectively, in mole per liter. The partition coefficient of solute (4-HBA) is represented as P and the partition coefficient may be represented numerically as follows:

$$P = \frac{[HBAX]_{org}}{[HBAX]_{aq}} \ . \tag{5}$$

2.4.3. Dimerization constant 4-HBA

In the solvent phase, the extracted molecule that has not been dissociated of 4-HBA formed a dimer molecule if inter hydrogen bond of solutes stronger than the inter hydrogen bond of solvent. The response could be described as follows in Equation 6 and 7:

$$2[HBAX]_{aq} \xleftrightarrow{D} ([HBAX]_{org})_2 \ . \tag{6}$$

From a physical extraction perspective, one crucial parameter is the overall distribution coefficient or K_D and calculated in Equation 8 to 12 as

$$D = \frac{([HBAX]_{org})_2}{([HBAX]_{org})^2} \ , \tag{7}$$

$$K_D = \frac{(HBAX^{tot}_{org})}{HBAX^{tot}_{aq}} = \frac{[HBAX]_{org} + [2HBAX]_{2.org}}{[HBAX]_{aq} + [BA^-]} \ , \tag{8}$$

$$= \frac{P[HBAX]_{aq} + 2D[HBAX]^2_{org}}{[HBAX]_{aq} + \frac{K_{HBA}[HBAX_{aq}]}{[H^+]}} \ , \tag{9}$$

$$= \frac{P[HBAX]_{aq} + 2DP^2[HBAX]^2_{aq}}{[HBAX]_{aq} + [1 + \frac{[K_{HBAX}]}{[H^+]}]} \ , \tag{10}$$

$$= \frac{P + 2DP^2[HBAX]_{aq}}{[1 + \frac{[K_{HBAX}]}{[H^+]}]} \ . \tag{11}$$

Because of its low pKa of 4.54 [67], 4-HBA is considered a weak acid. To ensure that the pH value remained below the pKa value, an adequate diluted solution was created. The denominator for the diluted solutions of equation 11 may be neglected because the $K_{HBAX}/[H^+]$ have a low quantity for a solution with a significantly lower pH than pKa., and therefore the equation 12 can be redrafted as

$$K_D = P + 2DP^2[HBAX]_{aq} \ , \tag{12}$$

K_D is found as a ratio of HBA^{tot}_{org} and HBA^{tot}_{aq} .The extraction equilibrium relationship obtained from solute concentration in aqua-phase and distribution coefficient K_D. The relationship predicts the Partition coefficient, P as the intercept and dimerization coefficient, D as the slope. These two important parameters of physical extraction reveal the extraction capacity of solute. Additionally, the distribution coefficient (K_D) values employed to calculate the percentage of extraction efficiency, as follows Equation 13:

$$\%E = \frac{K_D}{1 + K_D} \times 100 \ . \tag{13}$$

2.4.4. Solvent regeneration

Recovery of the solute from the organic phase and solvent regeneration constitute the second stage of the procedure. The back extraction and solvent regeneration have been reported by numerous researchers. A variety of techniques are described, including the use of HCl, TMA (tri methyl amine), temperature swing, diluent swing, and NaOH. Based on available research, the most effective way for solvent regeneration is to use TMA instead of any other method [46,47].

3. Results and Discussion

As per the proposed work, the physical separation (or extraction) of 4-HBA from its aqueous solution was accomplished using two conventional solvents, n-butanol and Di-chlorobenzene, and a natural solvent Karanja oil. The impact of n-butanol, Di chlorobenzene and Karanja oil on the percentage extraction efficiency (E%) and distribution coefficient (K_D) [46,49,52] is depicted in Table 2, 3 and 4 respectively. A comparative analysis of various physical extraction characteristics, including partition coefficient (P), dimerization constant (D), extraction efficiency (E%), and distribution coefficient (K_D) obtained through experimental is shown in Table 5. The distribution coefficient can also be thought of as a measure of the solute's affinity between two phases. It is the ratio of acid concentration in the aqueous and organic phases, and as such, it indicates the selectivity of the solvent or organic phase relative to water or the aqueous phase. (K_D) is found in the range for conventional solvents 0.314-1.704 and 0.030-0.555 for n-butanol and Di-chlorobenzene, respectively, in Table 2 and Table 3. The (K_D) varies for natural renewable solvents from 0.096-0.810 for Karanja oil. Figure 2 shows the equilibrium curve of 4-HBA extraction, which reveals the various physicochemical characteristics linkage between solute and solvents used in the experiments. Many authors have made an effort to connect the properties such as the solvent polarity parameter, dielectric constant, and dipole moment with the physical extraction parameters [46,52].

Table 2. Physical extraction of 4-HBA with conventional diluent n-butanol at 298±1.

C_0 (mol/L)	C_{aq} (mol/L)	C_{org} (mol/L)	K_D	Avg K_D	%E	Avg %E	pH_0	pH_{aq}	P	D
0.005	0.0038	0.0012	0.314	1.055	23.92	47.63	3.8	3.9	0.258	1143.30
0.010	0.0058	0.0035	0.604		37.67		3.7	3.8		
0.020	0.0087	0.0100	1.149		53.47		3.6	3.7		
0.030	0.0117	0.0176	1.504		60.07		3.4	3.6		
0.035	0.0130	0.0221	1.704		63.02		3.3	3.4		

Table 3. Physical extraction of 4-HBA with conventional diluent Di-chlorobenzene at 298±1.

C_0 (mol/L)	C_{aq} (mol/L)	C_{org} (mol/L)	K_D	Avg K_D	%E	Avg %E	pH_0	pH_{aq}	P	D
0.005	0.0049	0.0001	0.030	0.321	2.93	22.55	3.7	3.8	0.075	2573.88
0.010	0.0079	0.0014	0.184		15.53		3.6	3.7		
0.020	0.0140	0.0048	0.344		25.58		3.6	3.7		
0.030	0.0197	0.0097	0.493		33.04		3.5	3.6		
0.035	0.0225	0.0125	0.555		35.69		3.4	3.5		

Renewable solvents such as Karanja oil accomplish relatively less extraction efficiency, %E, and distribution coefficient, K_D, as compared to conventional solvents n-Butanol but better than Di chlorobenzene for the physical extraction of p-hydroxy benzoic acid or phenolic acids. The reason might be the natural solvents are generally nonpolar and have low dipole-moment and dielectric-constant.

The conventional solvent alcohol has a strong polarity nature and shows better extraction efficiency and distribution coefficient, followed by the nonpolar and functional solvent Di-chlorobenzene. Some other factors like ion pair and hydrogen bonding play a pivotal role in solvent and solute interaction [35,65]. The low interaction amid the solute and solvent has shown the lower extraction efficiency and distribution coefficient. The highest extraction efficiency, 63.02%, was achieved for n-butanol alcohol for conventional solvent and lowest for dichlorobenzene, 35.69The efficiency shown by n-butanol due its high polarity, and proton donor tendency and lower viscosity compared to other solvent. However, the n-Butanol and Dichlorobenzene obtained from fossil fuel resources which represent one of the drawbacks against the renewable solvent Karnaja oil.

Table 4. Physical extraction of 4-HBA with Natural Solvent Karanja at 298±1.

C_0 (mol/L)	C_{aq} (mol/L)	C_{org} (mol/L)	K_D	Avg K_D	%E	Avg %E	pH_0	pH_{aq}	P	D
0.005	0.0046	0.0004	0.096	0.486	8.78	30.18	3.7	3.9	0.114	1916.98
0.010	0.0074	0.0019	0.261		20.70		3.6	3.8		
0.020	0.0124	0.0063	0.512		33.84		3.5	3.7		
0.030	0.0168	0.0126	0.749		42.82		3.4	3.6		
0.035	0.0194	0.0157	0.810		44.75		3.4	3.5		

This renewable solvent is available naturally and abundantly in southern asia and India [1]. The extraction efficiency 44.75% of 4-HBA is shown in Table 4. The high extraction efficiency with Karnja oil is due to presence of large amount of mono unsaturated (16%) and poly unsaturated acid (51.5%). These oleic acid and linoleic acid have oxygenated double bond and active hydroxyl group. The presence of these kind of groups, favours the strong interaction with phenol carboxylic acids. The high percentage of extraction efficiency of 4-HBA with renewable solvent shows the better substitute of conventional solvents [20,21]. Non-Polar Dichlorobenzene showed less extraction capacity among all other solvents due to its structural properties and high interfacial force with 4-HBA [18,37,65]. The cohesive force of solute (4-HBA) is more than the adhesive force with solvent due to the chlorine functional group. which indicates less affinity with 4-HBA than water molecules. The functional group represents the softer electrophilic sites of the molecule and hence shows the weaker acid bond between solute and solvent.

Table 5. comparison of Physical extraction of 4-HBA with different solvent at 298±1.

Solvent	Range of K_D	Avg K_D	Range of %E	Avg %E	P	D
n-butanol	0.314-1.704	1.055	23.92-63.02	47.63	0.258	1143.30
Dichloro benzene	0.030-0.555	0.321	2.93-35.69	22.55	0.075	2573.88
Karanja oil	0.096-0.810	0.486	8.78-44.75	30.18	0.114	1916.98

The maximum extraction efficiency (E%) of 4-HBA was obtained using several solvents followed as Dichlorobenzene (35.69%) < Karnaja oil (44.75%) < n-Butanol (63.02%) which shown in Table 5. It was also observed that from Figure 2, the extraction efficiency and distribution coefficient increase as increasing concentration of solute due the hydration properties and solubility of solute in water may be one of the reasons. The solute-solvent interaction force was strengthened as the solute concentration increased because more solute molecules were available to interact with the solvent.

The intercept and slope of the Equation 13) were obtained as Partition coefficient (P) and dimerization (D), respectively. Partition coefficients P and D of each solvent are shown in Table 2 to Table 4. Figure 3 shows that as the distribution coefficient increases, the partition coefficient increases; however, the dimerization decreases, which means the solute-solvent interaction is more than the solute-solute interaction.

From Figure 3, it was revealed that the partition coefficient and dimerization are vice versa in nature. The dimerization coefficient value was shown in Table 2 to Table 4 for Dichlorobenzene (2573.88), Karanja oil (1916.98), n-Butanol (1143.30), and partition coefficient varies in the range of low efficient to highly efficient solvent 0.075, 0.114 and0.258 for Dichlorobenzene, Karanja oil and n-Butanol respectively.

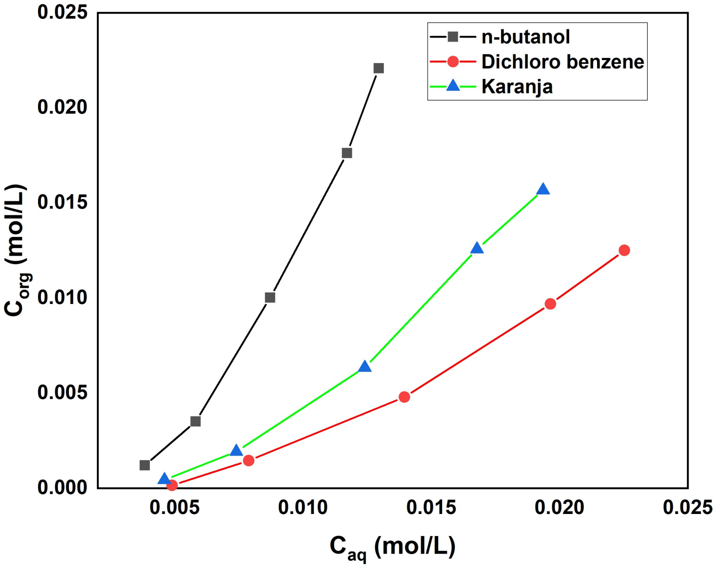


Figure 2. Extraction equilibrium of 4-HBA with different solvents.

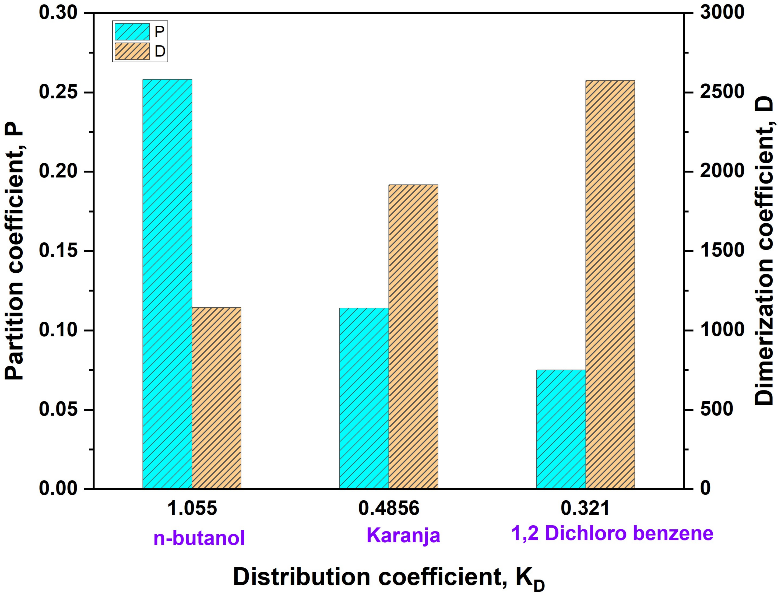


Figure 3. Comparison of partition coefficient and dimerization w. r. t. distribution coefficient for different solvent.

4. Conclusions

The physical extraction of 4-HBA was performed in the presence of several solvents, including conventional and renewable. The n-butyl alcohol has shown better extractive efficiency 63.03% and distribution coefficient 0.256 among all used solvent in this work. However, the typical solvent is very hazardous, is obtained from fossil fuel resources, and cannot be used in many pharmaceutical and food industries. Natural oil was utilized as a non-toxic and renewable solvent, and an improved extraction efficiency of around 44% was demonstrated for Karnaja oils. The data gathered from results Figures 2 and 3, and Tables 2 to 5 encourage using renewable a solvent. Renewable solvent (Karanja oil) has a lower environmental impact than petroleum-based solvents. Their biodegradability and less toxic nature reduce ecosystem damage during manufacture, use, and disposal. The use of renewable solvents for chemical extraction can lead to environmental sustainability, economic viability, and technological innovation in the chemical industry (food, plastics, and pharmaceutical sectors). Renewable solvents can help organizations become more sustainable, minimize their environmental impact, and boost competitiveness. Reactive extraction of 4-HBA studies with Karanja oil, conventional solvents and extractant will be conducted in the future. These studies will improve the solute 4-HBA separation, which is crucial for separating the fermentation broth waste.

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