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Research Article

Natural Plant Extracts as Acid-Base Indicator and Determination of Their pKa Value

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Commonly used indicators for acid-base titrations are synthetic, and this work was focused to identify the eco-friendly natural indicators and to determine their pKa values. The analytical potential of the flower extracts is very promising as seen in its application in acid-base titrimetry. These selected flower extracts were found to perform well in titrating strong acid-strong base than in weak acid-strong base. We have obtained a sharp and clear colour change from red to brownish yellow for the *Bougainvillea glabra* extract, from red to yellow for the *Bauhinia purpurea* extract, and from red to brownish yellow for the *Impatiens balsamina* extract. All the three flower extracts gave clear colour change with acids and bases, and the colour change was maintained with different acids and bases. The sharp contrast between their colours in acid and base made the pigment suitable for use as acid-base indicators. As these flower extracts have very simple,cost-effective, environment friendly extraction procedure and excellent performance with sharp colour change in end points of the titrations, it would be possible to replace the standard indicators being used in conventional laboratories with natural flower indicators.

1. Introduction

Titration is the most common laboratory method of quantitative chemical analysis that is used to determine the concentration of analyte. The most of the modern laboratories are equipped with digital automatic titrators that are facilitated with sensors (pH sensor/voltage electrode), some of them do not require indicators, the accuracy is high, and human errors also reduced than conventional titration methods. However, kinetic factors concerning the chemical reaction and the response of the indicating system are of paramount importance. Cell configuration, stirring, and positioning of the end-point detector and of input of the titrant are to be considered for ensuring high accuracy. Piston burettes and peristaltic pumps are commonly being used as devices for automatic transfer of titrant in automatic titrators. The piston burettes are highly reliable, but are expensive while the peristaltic pumps are highly versatile, but require frequent calibration due to the continual changes in the physical properties of the flexible tubes employed and has a relatively short lifetime [1]. Cost of the automatic titrators together with the drawbacks concerned as the major hurdles for the usage of automatic titrators in many of the developing countries in the world and thereby conventional titrimetric methods are still extensive used by the analytical and research laboratories in these countries.

Since the world has become aware for environmental issues, various parts of the plants such as flowers and leaves are symbolic and regarded as the symbol of love wishes. Thus, flowers are wonder of the nature. The synthetic compounds are highly polluting, harmful, hazardous, and much more costly for research work as well as analytical work. Therefore, various researches are being undertaken extensively by many scientists all over the world in this field of natural products as they are less hazardous, low cost, easily available, and eco-friendly [2].

The chemical substances possess an apparent change in colour of the analyte and titrant reacting mixture very close to the point in the ongoing titration known as indicator, which helps to examine and determine the equivalence point in acid-base titrations [3, 4]. Natural dyes and pigments in plants are highly coloured substances and may show colour

changes with variation of pH [5]. Colours of the parts of the plants express their unique character. Several organic and inorganic compounds are responsible for the colour property of parts of the plant such as flavonoids, flavonols, acylated flavonoids, anthocyanins, glucosylated acylated anthocyanin, quinines, imines, polymethines, napthaquinones, anthraquinonoids, indigoids, dihydropyrans, diarylmethanes, and carotene. [6]. Some of these compounds show different colours in different pH, and thus, this property can be applied to use as a natural indicator. A pH indicator is just a weak acid-weak base with differently coloured acid and conjugate base forms. The blue and red pigments of flowers were isolated and extensively studied by Willstatter in 1913. Natural indicators such as litmus to indicate specific pH levels have been developed. The substances in the plant products such as tea, red cabbage, or grapes react with acids or bases resulting in changes at the molecular level which causes their colour to be different at different pH. Red cabbage juice has been used as a natural pH indicator [7]. This indicator contains anthocyanin, which has pigment that reacts in a different way to acids and bases [7].

Each compound which can act as indicator has specific pK_a value, and it is an important physical parameter to indicate the acidity of molecules. For most indicators, the pH range is within ±1 of its pK_a value. The objective of this work was to identify the eco-friendly natural indicators and determine their pKa values. The water extracts of three plants *Bougainvillea glabra, Impatiens balsamina,* and *Bauhinia purpurea* were used for this study.

Bougainvillea glabra is an evergreen, climbing shrub with thorny stems. Tiny white flowers usually appear in clusters surrounded by colourful papery bracts. These bracts contain eleven types of bougainvillein-v pigments (betacyanin) [8].

Impatiens balsamina (garden balsam) is native to places of south Asia such as India, Sri Lanka, Bangladesh, and Myanmar. It is an annual plant growing to 20–75 cm tall, with a thick, but soft stem. The leaves are spirally arranged. The flowers are pink, red, mauve, lilac, or white. Petals contain anthocyanidin and pelargonidin as colouring pigments [9].

Bauhinia purpurea, the purple orchid tree, is an exotic tropical tree that blooms over a long period of time. The beautiful and orchid-like flowers of *Bauhinia purpurea* are native to India. The petals of *Bauhinia* contain chalcone and butein as colouring pigments [10].

2. Materials and Methods

2.1. Preparation of Extracts. Flowers of green plants *Bougainvillea glabra* and *Impatiens balsamina* were obtained from the Garden of Eastern University, Chenkalady, Batticaloa, Sri Lanka, and flower of *Bauhinia purpurea* was obtained from Thambiluvil, Ampara, Sri Lanka. The petals of each flower were collected, rinsed with distilled water, and pressed between pads of the absorbent paper to eliminate the surface water. Fresh petals (5 g) of each flower were transferred into beakers (100 mL) containing 50 mL of distilled water separately. It was heated to 50–60°C for 10 minutes. The extracts of the three flowers were separated by filtering through the clean Whatman® No. 1 (pore size 11 μm) filter paper. The extracts were kept in dry and dark place.

2.2. Acid-Base Titrations. Three types of titrations such as strong acid-strong base, strong acid-weak base, and weak acid-strong base were carried out using flower extracts as indicators, and their accuracy were compared with commercially available synthetic indicators such as methyl orange, methyl red, and phenolphthalein. Each titration was carried out in triplicate.

2.3. Preparation of Solutions Having Different pH. Volumetric flasks (50 mL) were labelled with numbers 1 to 10. The flower extract (2.0 mL) was added into each flask. 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4 solutions were also added to each flask as indicated in Table 1. Each solution was diluted to the mark with distilled water. This procedure was repeated for all the three flower extracts [11].

2.4. pH Measurement of Solutions. The pH of each solution was measured by using pH probes (PHC301) connected to calibrated Hach hq40d multiparameter.

Calibration of instrument:

(I) pH probe was connected to the meter, and locking nut was fitted properly. The meter was turned on.

(II) After pressing the "calibrate" button, the probe was rinsed with deionized water, and it was placed carefully without air bubbles into the standard pH buffer solution with slight stirring.

(III) Then, the "read" button was pressed.

(IV) The same procedure (III) was followed for each standard pH solution.

(V) Finally, the "done" button was pressed, and calibrated data were stored.

2.5. Spectrophotometric Determination of the pKa Values of Indicators. Flower extract (2.0 mL), distilled water (10.0 mL), and 8 drops of con. HCl were transferred into 50 mL of the volumetric flask and labelled as **A**, and the solution was diluted to the mark with distilled water. To the second volumetric flask labelled as **B**, flower extract (2.0 mL), distilled water (10.0 mL), and 24 drops of 4 M NaOH were transferred, and the solution was diluted to the mark with distilled water. This was repeated for all the three flower extracts.

For this investigation, Biobase BK-D580 spectrophotometer has been used. UV-visible spectra were obtained between 300 and 800 nm of the A and B of each flower extract solution and for methyl red. One wavelength (λ_1) was chosen at which the solution A absorbs strongly and solution B absorbs weakly and second wavelength (λ_2) at which solution A absorbs weakly and solution B absorbs strongly.

Table 1: Added volumes of 0.1 M Na_2HPO_4 solution and 0.1 M KH_2PO_4 solution.

Flask no.	KH_2PO_4 (mL)	Na_2HPO_4 (mL)
1	10.0	0.0
2	20.0	1.0
3	10.0	2.0
4	20.0	10.0
5	10.0	10.0
6	10.0	20.0
7	2.0	10.0
8	2.0	20.0
9	1.0	20.0
10	0.0	10.0

Finally, the absorbance of each set of 10 solutions was tabulated against blank solution at the chosen wavelengths λ_1 and λ_2 (Table 2). Here, the blank solution includes all the chemicals and distilled water except the flower extract [11–14].

The above procedure was done for all the three flower extracts, and their experiment findings were compared with methyl orange indicator.

The indicators are weak base or weak acid which exhibit different colours in different pH. The equilibrium reaction of the indicator is shown in the following equation [12]:

$$\underset{\text{colour1}}{\text{HIn}} \rightleftharpoons \underset{\text{colour2}}{\text{In}^-} + \text{H}^+. \tag{1}$$

Most of the indicators are present as HIn in strong acid solution and exhibit respective colour of HIn whereas in strong basic solution, most of the indicators are present as In^- and exhibit respective colour of In^-.

The equilibrium expression of the equation (1) can be written as follows:

$$K_a = \frac{[H^+][In^-]}{[HIn]}, \tag{2}$$

where K_a is known as the dissociation constant or equilibrium constant of indicator and $[In^-]$ and [HIn] are known as concentration of basic and acidic forms of the indicator, respectively:

$$-\log K_a = -\log[H^+] - \log\left(\frac{[In^-]}{[HIn]}\right). \tag{3}$$

The equation can be written as

$$\begin{aligned} pK_a &= pH - \log\left(\frac{[In^-]}{[HIn]}\right), \\ pH &= pK_a + \log\left(\frac{[In^-]}{[HIn]}\right). \end{aligned} \tag{4}$$

The ratio values of $[In^-]/[HIn]$ were determined from the spectrophotometric measurements made at two wavelengths (λ_1 and λ_2) in order to plot pH vs. $\log[In^-]/[HIn]$.

According to Beer's law, the absorbance at λ_1 and λ_2 was

$$A_{\lambda 1} = \varepsilon_{(\lambda 1,\text{HIn})}[\text{HIn}]l, \tag{5}$$

$$A_{\lambda 2} = \varepsilon_{(\lambda 2,\text{In}^-)}[In^-]l, \tag{6}$$

where A is the absorbance, ε is the molar absorptivity, and l is the cell path length.

At any pH, the total concentration (CT) of both In^- and HIn was constant and tally of the individual concentration of both forms:

$$\text{CT} = [\text{In}]^- + [\text{HIn}]. \tag{7}$$

In low pH solution, all of the indicators are in the [HIn] form. As the result, in highly acid solution, CT = [HIn] and

$$A_{\lambda 1,\text{acid}} = \varepsilon_{(\lambda 1,\text{HIn})}[\text{CT}]l. \tag{8}$$

In high pH solution, all the indicators are in the $[In^-]$ form. As the result, in highly basic solution, CT = $[In^-]$ and

$$A_{\lambda 2,\text{basic}} = \varepsilon_{(\lambda 2,\text{In}^-)}[\text{CT}]l. \tag{9}$$

Finally, the ratio $[In^-]/[HIn]$ can be determined by dividing the ratio of equations (5)–(8) by the ratio of equations (6)–(9) [11, 12]:

$$\frac{[In^-]}{[HIn]} = \left(\frac{A_{\lambda 2} * A_{\lambda 1,\text{acid}}}{A_{\lambda 1} * A_{\lambda 2,\text{basic}}}\right). \tag{10}$$

3. Results and Discussion

All flower extracts have shown different colours in acidic and basic solutions and have different highest peaks (lambda max) in strong acidic and strong basic medium (Table 2). The end points detected for acid-base titrations using the flower extracts as indicators were found to be very similar to those of standard indicators used in laboratories (Table 3).

The pK_a values for all the flower extracts and methyl orange (for comparison) were calculated directly from the intercept of the graphs, as shown in Figure 1. The R^2 values of these three flower extracts observed to be higher (0.9551, 0.9569, and 0.9649) than those of methyl red indicator (0.9260) indicate better linear relationship for the three flower indicators compared to the synthetic indicator used for comparison. The pK_a values calculated and the pH range for the corresponding indicators are listed in Table 4.

The variation in the required volumes of titrant when flower indicators is used for strong acid-strong base titration is from 0.04 to 0.1 whereas the variation for synthetic indicators is found to have a range from 0.1 to 0.3. For strong acid-weak base titration, the variation in the required volume of titrant was from 0.03 to 0.13 while the synthetic indicators show a variation of 0.46–1.56. In the case of weak acid-strong base, variations for synthetic indicators were very high as the methyl orange indicator is not suitable for weak acid-strong base titrations. However, methyl red, *Bauhinia purpurea*, and *Impatiens balsamina* indicators show a value very close to the standard indicator, phenolphthalein. The pH range of *Bougainvillea glabra* and *Bauhinia purpurea* is very close to the pH range of phenolphthalein (8.2–10.0). Methyl orange failed to detect

Table 2: Absorption of 10 solutions at pH 7.29, 7.32, 7.36, 7.39, 7.53, 7.59, 7.95, 7.99, 8.14, and 8.52 for all the three follower extracts and methyl red indicator.

Indicator	Parameter	Absorption of 10 solutions at pH from 7.29 to 8.52									
		7.29	7.32	7.36	7.39	7.53	7.59	7.95	7.99	8.14	8.52
Impatiens balsamina	λ_1	0.028	0.026	0.021	0.020	0.018	0.018	0.017	0.017	0.015	0.015
	λ_2	0.361	0.362	0.366	0.370	0.373	0.375	0.376	0.379	0.382	0.416
	Acid max	0.325	0.325	0.325	0.325	0.325	0.325	0.325	0.325	0.325	0.325
	Base max	0.577	0.577	0.577	0.577	0.577	0.577	0.577	0.577	0.577	0.577
Bauhinia purpurea	λ_1	0.069	0.056	0.052	0.044	0.033	0.026	0.020	0.022	0.017	0.013
	λ_2	0.581	0.604	0.614	0.646	0.642	0.641	0.659	0.663	0.674	0.712
	Acid max	0.132	0.132	0.132	0.132	0.132	0.132	0.132	0.132	0.132	0.132
	Base max	0.752	0.752	0.752	0.752	0.752	0.752	0.752	0.752	0.752	0.752
Bougainvillea glabra	λ_1	0.07	0.06	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.04
	λ_2	0.04	0.04	0.04	0.04	0.06	0.06	0.07	0.08	0.09	0.13
	Acid max	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
	Base max	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Methyl red	λ_1	0.372	0.339	0.286	0.262	0.264	0.261	0.258	0.262	0.258	0.227
	λ_2	2.326	2.363	2.392	2.314	2.357	2.368	2.379	2.398	2.452	2.760
	Acid max	2.796	2.796	2.796	2.796	2.796	2.796	2.796	2.796	2.796	2.796
	Base max	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.42

Table 3: Titration results of flower extracts and commercially available indicators.

Indicator	Titrand/titrant	Colour change	Required volume of titrant
Phenolphthalein	NaOH/HCl	Pink to colourless	8.87 ± 0.0577
	NH_4OH/HCl	Pink to colourless	14.57 ± 0.0577
	CH_3COOH/NaOH	Colourless to pink	12.07 ± 0.0577
sMethyl orange	NaOH/HCl	Yellow to red	9.17 ± 0.0577
	NH_4OH/HCl	Yellow to red	15.67 ± 0.1155
	CH_3COOH/NaOH	Red to yellow	5.27 ± 0.0577
Methyl red	NaOH/HCl	Yellow to red	8.97 ± 0.0577
	NH_4OH/HCl	Yellow to red	16.13 ± 0.0577
	CH_3COOH/NaOH	Red to yellow	12.13 ± 0.0577
Bougainvillea glabra	NaOH/HCl	Brownish yellow to red	8.97 ± 0.0577
	NH_4OH/HCl	Brownish yellow to red	15.17 ± 0.0577
	CH_3COOH/NaOH	Red to brownish yellow	12.23 ± 0.0577
Impatiens balsamina	NaOH/HCl	Brownish yellow to red	9.07 ± 0.0577
	NH_4OH/HCl	Brownish yellow to red	15.3 ± 0.1
	CH_3COOH/NaOH	Red to brownish yellow	12.13 ± 0.0577
Bauhinia purpurea	NaOH/HCl	Yellow to red	8.93 ± 0.0577
	NH_4OH/HCl	Yellow to red	15.27 ± 0.0577
	CH_3COOH/NaOH	Red to yellow	12.3 ± 0.1

sharp end points for weak acid-strong base while flower extracts of *Bougainvillea glabra* and *Bauhinia purpurea* detect the end points more precisely than synthetic indicators.

These natural flower indicators are found to be very important in modern laboratories when the automatic titrators fail to titrate some reactive liquids. Hydrocarbon may react with the plastic materials used in digital titrators, and therefore, these modern digital meters cannot be used. The methods proposed by American Society for Testing and Materials, ASTM D974 and ASTM D5984, use colour-indicator titration to determine the basic constituents in petroleum products and lubricants. Colorimetric titration takes advantage of the visual changes of a chemical compound when its environment shifts from acidic to alkaline. In the other words, the colour of this indicator will change at the pH corresponding to the inflection point. Methyl red is used as the indicator, changing its colour from magenta to yellow at the pH corresponding to the inflection point. In ASTM D974, similar to D4739, hydrochloric acid is used as the titrant; a mixture of toluene and isopropyl alcohol containing a small amount of water is used as the solvent system, and *p*-naphtholbenzein is used as the colour indicator, which is orange in acid and green-brown in base [15]. These synthetic indicators could be replaced by the natural flower indicators even in modern laboratories.

4. Conclusions

The results obtained from the present study reveal that the analytical potential of the flower extracts is very promising as

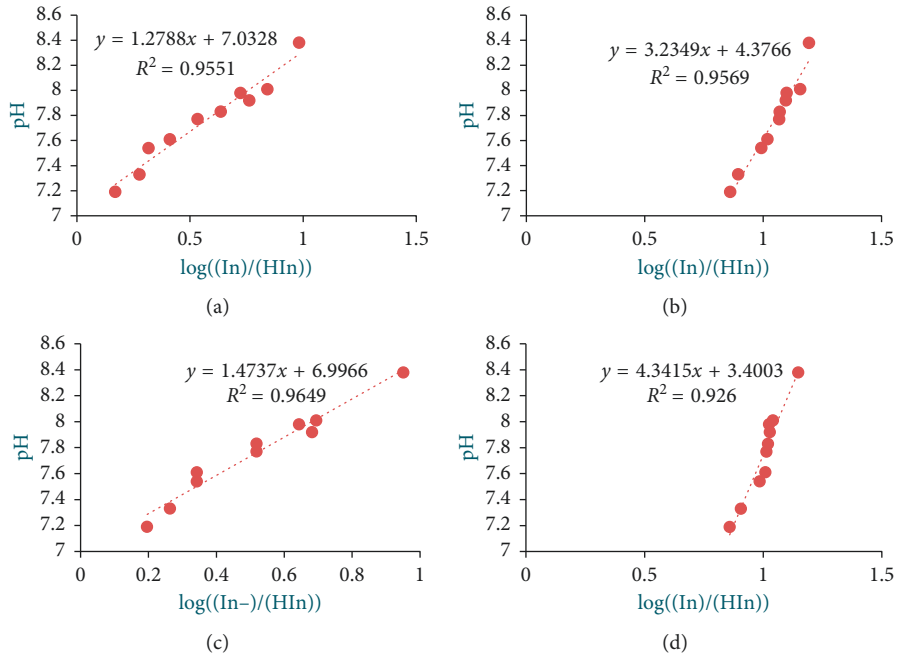

Figure 1: Graph of pH vs. log[In⁻]/[HIn] for each flower extract and methyl orange: (a) *Bauhinia purpurea*, (b) *Impatiens balsamina*, (c) *Bougainvillea glabra*, and (d) methyl orange.

Table 4: Calculated pKa and pH range of indicators.

Indicator	pKa	pH range
Bougainvillea glabra	6.9966 ≈ 7.0	6.0–8.0
Impatiens balsamina	4.3766 ≈ 4.4	3.4–5.4
Bauhinia purpurea	7.0328 ≈ 7.0	6.0–8.0
Methyl orange	3.4003 ≈ 3.4	2.4–4.4

seen in its application in acid-base titrimetry. It was found that these extracts perform best in strong acid-strong base titration compared to weak acid-strong base with a sharp and clear colour change from red to brownish yellow for the *Bougainvillea glabra* extract, from red to yellow for the *Bauhinia purpurea* extract, and from red to brownish yellow for the *Impatiens balsamina* extract. All the three flower extracts gave clear colour change with acids and bases, and the colour change was maintained with different acids and bases. The sharp contrast between their colours in acid and base made the pigment suitable for use as acid-base indicators.

The availability and the simple extraction procedure with excellent performance and accurate results would make these natural flower indicators suitable substitutes for synthetic indicators used in many laboratories and research institutes. In a nutshell, industries, research laboratories, schools, and chemical companies that make use of indicators for the determination of acidity, alkalinity, humidity, extent of reactions, and so forth would find the preliminary results from this study valuable in producing efficient indicators from flowers as substitutes or possible replacement for standard indicators. The American Society for Testing and Materials (ASTM) is using colorimetric titration with synthetic indicators as the standard method for providing a means to quantify the immunity of a lubricant against the damaging effects of acidic constituents. These synthetic indicators could be replaced by the natural flower indicators in the modern laboratories. However, the disadvantage of the flower extract is that they need to be prepared freshly since they are susceptible to fungal growth after three days.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

This work was done in the laboratory at the Department of Chemistry, Faculty of Science, Eastern University, Sri Lanka.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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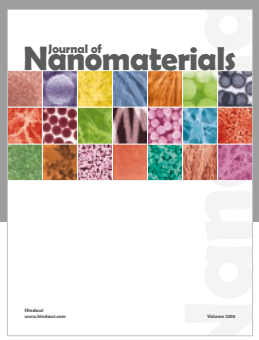

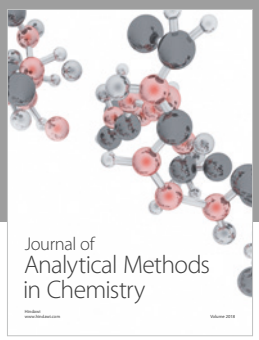

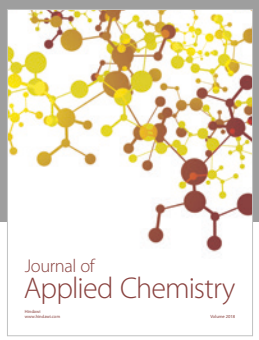

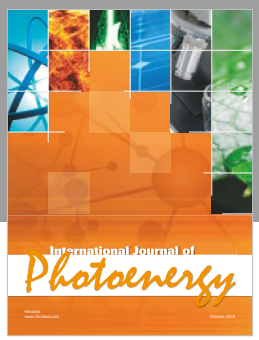

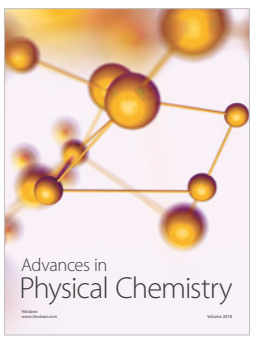

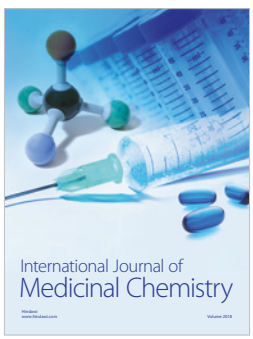

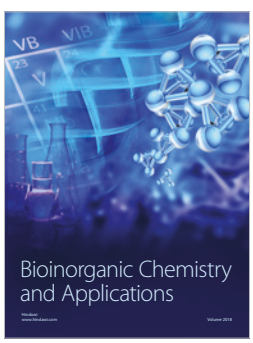

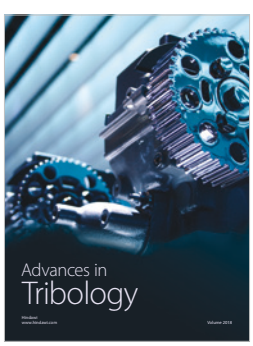

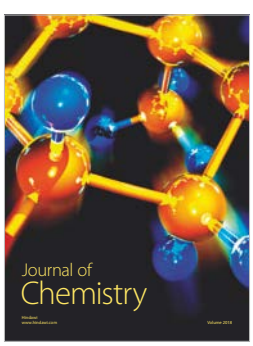

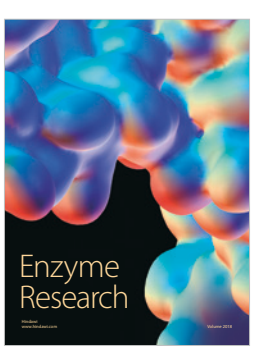

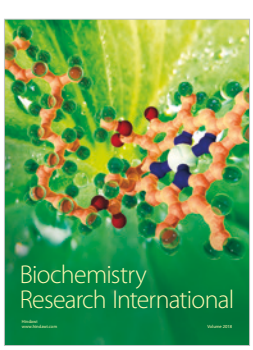

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