Determination of Phosphate in Water Samples of Nashik District (Maharashtra State, India) Rivers by UV-Visible Spectroscopy

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Abstract: The major rivers of Nashik District (Maharashtra State, India) are Godavari, Kadawa, Girna, Punad and Mosam. The major water pollutant of Nashik District Rivers is Phosphate. The amount of phosphate has been determined by the molybdenum blue phosphorous method in conjugation with UV-Visible Spectrophotometer. The data has been analyzed by least square method. The more phosphate polluted river in Nashik district is Godavari. The least phosphate polluted river in Nashik District is Punad.

Keywords: Water pollution, Phosphate, Nashik district rivers, UV-Visible spectrophotometer, Molybdenum blue phosphorus method.

Introduction

The major rivers of Nashik District (Maharashtra State, India) are Godavari, Kadawa, Girna Punad, and Mosam. The major water pollutant of these rivers is phosphate. In Nashik District, the main crops like sugarcane, onion, cotton, main fruits like grapes and pomegranates, the main vegetables like tomatoes, radish and garlic carrots are cultivated. Many farmers use organophosphates insecticides including malathion, diazinon and parathion. A large amount of fertilizers, pesticides and herbicides used on crops, and the organo phosphate insecticides used on grapes, pomegranates and vegetable in the field may get washed by rain water and reach to the river through agricultural run off. Detergents are important contributor of phosphate. Huge quantities of detergents are used annually. Most of it flushed into the sewer systems from bathrooms kitchens, laundry's, factories, and other industrial establishments.

Phosphate reflects BOD (Biological Oxygen Demand), therefore the number microbes as *Escherichia coli* (bacterium) also increase tremendously¹. The number *Escherichia coli* per unit volume of water is main parameter of water pollution. Phosphate affects degradation

lead to oxygen depletion which affects (and even kills) fish and other aquatic decomposing plants are known to produce toxins as strychnine which kills animals including cattle. Phosphate insecticides cause irreversible inhibition of the enzyme chlorine steorage. These agents are absorbed by all routes including skin, mucosa, and symptoms and include weakness, blurred vision, headache, giddiness, nausea and pain in chest². Organo phosphates may cause harmful effects on wild life. They affect calcium metabolism in birds, which affects egg lying with egg shells and consequently reproductive failure³. In the present study, the amount of phosphate present in the water samples of Nashik District rivers has been determined by the molybdenum blue phosphorous method in conjugation with UV-Visible Spectrophotometer^{4,5}.

Experimental

1. *Molybdate solution*: 12.5 g of sodium molybdate ($\text{Na}_2 \text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in 5 M H_2SO_4 and diluted to 500 mL with 5 M sulphuric acid (This is to be prepared fresh monthly 2.5 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 5 M H_2SO_4 and diluted to 100 volumetric flask.
2. *Hydrazinium sulphate Solution*: 0.15 g hydrazinium sulphate dissolved in deionised water and diluted to 100 mL volumetric flask.
3. *Potassium dihydrogen phosphate*: Qualigens AR, purity > 95.5%
4. *Sulphuric acid*: (Qualigens, AR)

Method

The molybdenum blue phosphorous method in conjunction with UV-Visible spectrophotometer is a very sensitive method^{4,5} for the determination of phosphorus at 830 nm. Phosphate in the sample can be determined at sub-ppb concentration at 830 nm. Orthophosphate and molybdate ions condense in an acidic solution to form phosphomolybdic acid, upon selective reduction (*e.g.* with hydrazinium sulphate) a blue color is produced. The intensity of the blue color is proportional to the amount of phosphate initially incorporated into the heteropoly acid. If the acidity at the time of reduction is 0.5 M in sulphuric acid and hydrazinium sulphate is the reluctant then the resulting blue complex exhibits a maximum⁶ absorbance at 820-830 nm. Intensity of the color solutions is normally measured on a visible spectrophotometer.

Field work

Water samples of Godavari, Kadva, Girna, Mosam and Punad rivers were collected from eight different places. Water samples for analysis were taken from the collection sites in the month of April, in one liter capacity plastic bottles. Table 1 summaries the water sample collection sites of Godavari, Kadva, Girna, Mosam and Punad rivers.

Calibration curve

The calibration curve is necessary to establish a relationship between the absorbance and the phosphate content for spectrophotometer analysis. Standard 10 ppm phosphate solution was prepared by dissolving 0.04393 g of Analytical reagent potassium dihydrogen phosphate in deionized water and diluted to 1000 mL. From 10 ppm solution, the 25 ppb, 50 ppb, 75 ppb, 100 ppb, 125 ppb, 150 ppb, 175 ppb, 200 ppb, solutions were prepared. These solutions were prepared as per Table 2. The absorbance of standard solutions of KH_2PO_4 were measured by using Shimadzu UV-Visible (1700) spectrophotometer at 830 nm. The calibration curve is constructed by plotting absorbance values against concentration of standard solutions. The straight line graph passing through origin has been obtained. This confirms the validity of Beer's – Lamberts law

Table 1. Water Sample collection sites of various rivers of Nashik District.

Sample Label Collection Site Godavari River	G ₁ Gangapur- gaon	G ₂ Someshwar mandir	G ₃ Asaramba-pu ashram	G ₄ Chopda launs	G ₅ Panchavati	G ₆ Tapovan	G ₇ Janardhan swami	G ₈ Saikheda gaon
Sample Label Collection Site Kadava River	K ₁ Hatoneregaon	K ₂ Nilvandigaon	K ₃ Padegaon	K ₄ Valkheda	K ₅ Kadva molungi	K ₆ Lakmapur	K ₇ Avankhed	K ₈ Pimpalg-aon ketki
Sample Label Collection Site Girna River	Gi ₁ Abhona	Gi ₂ Pale khudra	Gi ₃ Kalwan	Gi ₄ Bej	Gi ₅ Lohner	Gi ₆ Nimbola	Gi ₇ Agharkh	Gi ₈ Tehre
Sample Label Collection Site Mosam River	M ₁ Anatapur	M ₂ Taharabad	M ₃ Sompur	M ₄ Jaikheda	M ₅ Asakheda	M ₆ Nampur	M ₇ Ambasan	M ₈ Khakurdi
Sample Label Collection Site Punad River	P ₁ Umbarg-aon	P ₂ Suphala	P ₃ Siddesh-war	P ₄ Savarpada	P ₅ Bhanadp-ada	P ₆ Desrane	P ₇ Mogbh-agni	P ₈ Bhadha-van

Table 2. Preparation of standard phosphate solution.

Volume of 10 ppm P	Final volume	Conc. of Phosphate, ppb	Volume of 10 ppm P	Final volume	Conc. of Phosphate, ppb
0.000	50	0	0.625	50	125
0.125	50	25	0.750	50	150
0.250	50	50	0.875	50	175
0.375	50	75	1.000	50	200
0.500	50	100			

The slope of the line can be determined by using the equation.

$$\text{Slope} = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (x - \bar{x})^2} \quad (1)$$

To calculate intercept of the line, the equation used is,

$$\text{Intercept} = \bar{y} - m\bar{x} \quad (2)$$

$\bar{x}$ - mean value concentration.

$\bar{y}$ - mean value absorbance.

The absorbance of the solution can be expressed by straight line equation⁷.

$$\text{Absorbance} = (\text{Slope} \times \text{Concentration}) + \text{Intercept} \quad (3)$$

Rearranging the equation (3), the concentration is expressed as

$$\text{Concentration} = (\text{Absorbance} - \text{Intercept}) / \text{slope} \quad (4)$$

By using equation (4) we can calculate the amount of phosphate present in the solution. Least square method can be used to calculate value of slope and intercepts.

Results and Discussion

Table 3 shows the absorbance, amount phosphate determined by Shimadzu UV-Visible (1700) Spectrophotometer, and calculated by equation (4) of water samples of Godavari River. From Table 3, it is cleared that, the sample G₈ shows the higher value of phosphate (191 ppb by spectrophotometer and 192 ppb by calculation). Sample G₈ was collected from Saikheda Gaon. Sakhaida Gaon is 30 km away from the Nasik city. The higher concentration of phosphate at this site arises because of large industrial waste from Eklahara Thermal Power Station, and sewage, sludge water and water containing molasses from Nasik Sugar Factory. Phosphate level in the samples G₁ to G₈ increases.

Table 3. Absorbance and concentration of phosphate (by Instrument and Calculation) of water samples of Godavari River.

Water Samples	Absorbance	Amount of Phosphate (By Instrument)	Amount of Phosphate (Calculated)
G ₁	0.122	124.50	122.2
G ₂	0.130	133.58	130.2
G ₃	0.135	135.50	135.2
G ₄	0.141	142.90	141.2
G ₅	0.162	164.28	162.2
G ₆	0.166	168.20	166.2
G ₇	0.169	170.12	169.2
G ₈	0.192	191.20	192.2

The absorbance, amount phosphate determined by Shimadzu UV-Visible (1700) Spectrophotometer, and calculated by equation (4) of water samples of Kadva River are shown in the Table 4. From Table 4, it is cleared that the water sample K₆ shows the higher value of phosphate (112.11 ppb by spectrophotometer and 111.2 ppb by calculation). The collection site of sample K₆ is Lakhamapur Gaon. This collection site shows higher concentration of phosphate in water sample because of M.I.D.C. area of Lakhamapur which includes Seagram Distilleries, Everest Ceremics, and McDowell distillery. From these industries, wastage solid and liquid, sewage reach Kadwa river water. In Lakmapur village, large hectors of agriculture sector is also developed and it produces tones of grapes and vegetables. For the grapes and vegetable crops, farmers use oragnophosphate as well as phosphate fertilizers. Therefore in heavy rainy seasons precipitates come into the Kadva river basin and hence the collection site K₆ shows higher concentration of phosphate.

Table 4. Absorbance and concentration of phosphate (by Instrument and Calculation) of water samples of Kadva River.

Water Samples	Absorbance	Amount of Phosphate (By Instrument)	Amount of Phosphate (Calculated)
K ₁	0.081	83.212	81.2
K ₂	0.084	83.751	84.2
K ₃	0.089	90.120	89.2
K ₄	0.091	91.543	91.2
K ₅	0.104	105.400	104.2
K ₆	0.111	112.110	111.2
K ₇	0.092	93.540	92.2
K ₈	0.093	94.650	93.2

The absorbance, amount phosphate determined by Shimadzu UV-Visible (1700) Spectrophotometer, and calculated by equation 4 of water samples of Girna River are given in the Table 5. From Table 5, it is clear that the sample Gi₅ shows the higher value of phosphate (102.11 ppb by spectrophotometer and 101.2 ppb by calculation). The sample Gi₅ was collected from the middle part of Girna river (Lohner Gaon). At this site phosphate level in water sample is high because of Vasaka sugar factory at banking of Girna River. The polluted water with molasses of sugar factory dissolves in Girna river sides which contains higher concentration amount of phosphate. Girna River is less polluted as compared to Godavari and Kadwa.

Table 5. Absorbance and concentration of phosphate (by Instrument and Calculation) of water samples of Girna River.

Water Samples	Absorbance	Amount of Phosphate (By Instrument)	Amount of Phosphate (Calculated)
Gi ₁	0.068	69.840	68.2
Gi ₂	0.070	71.0130	70.2
Gi ₃	0.076	77.130	76.2
Gi ₄	0.078	78.180	78.2
Gi ₅	0.101	102.110	101.2
Gi ₆	0.099	100.200	99.2
Gi ₇	0.096	98.170	96.2
Gi ₈	0.097	98.190	97.2

Table 6 shows the absorbance, amount phosphate determined by Shimadzu UV-Visible (1700) Spectrophotometer, and calculated by equation 4 of water samples of Mosam River. From Table 6, it is understood that sample M₇ shows the higher value of phosphate (79.170 ppb by spectrophotometer and 79.200 ppb by calculation). The sample M₇ was collected from Ambasan Gaon. Ambasan Gaon is nearer to Nampur, sewage and sludge of Nampur village dissolves in Mosam River. Hence, the sample M₇ shows the higher amount of phosphate. Mosam River is less polluted than Girna River.

Table 6. Absorbance and concentration of phosphate (by Instrument and Calculation) of water samples of Mosam River.

Water Samples	Absorbance	Amount of Phosphate (By Instrument)	Amount of Phosphate (Calculated)
M ₁	0.055	54.124	55.2
M ₂	0.062	63.125	62.2
M ₃	0.063	63.870	63.2
M ₄	0.068	68.140	68.2
M ₅	0.077	78.164	77.2
M ₆	0.078	79.168	78.2
M ₇	0.079	79.170	79.2
M ₈	0.078	78.191	78.2

Table 7 presents the absorbance, amount phosphate determined by Shimadzu UV-Visible (1700) Spectrophotometer, and calculated by equation 4 of water samples of Punad River. From Table 7, it is inferred that sample P₇ shows the higher value of phosphate (72.91 ppb by spectrophotometer and 70.2 ppb by calculation) The water sample P₇ was collected from Mogbhagni Gaon which is nearer to Kalwan. Because of agriculture sector of Kalvan Gaon, the sample P₇ shows higher concentration of phosphate. Punad River is less polluted than other rivers of the Nasik district. Comparative graph of higher amount of phosphate and the collection sites of higher polluted areas of various rivers of Nasik district is shown in Figure 1

Table 7. Absorbance and concentration of phosphate (by Instrument and Calculated) of water samples of Punad.

Water Samples	Absorbance	Amount of Phosphate (By Instrument)	Amount of Phosphate (Calculated)
P ₁	0.051	52.12	52.2
P ₂	0.053	54.63	53.2
P ₃	0.062	63.87	62.2
P ₄	0.068	68.14	68.2
P ₅	0.069	68.16	69.2
P ₆	0.069	69.74	69.2
P ₇	0.070	72.91	70.2
P ₈	0.071	71.19	71.2

Figure 1. Comparative graph of higher amount of phosphate and the collection sites of higher polluted areas of various rivers of Nasik District.

Conclusions

1. Godavari river is largely polluted by phosphate than other rivers of the Nasik district while Punad River is less polluted.
2. Decrease in order of phosphate pollution of Nashik district river is Godavari > Kadva > Girna > Mosam > Punad

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