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Chemistry

Highlights

- Kinetic Study of Ni
- Spatial Variation of Water
- Water Quality Index
- Water Partition Coefficients

Discovering Thoughts, Inventing Future

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Contents of the Issue

i. Copyright Notice
ii. Editorial Board Members
iii. Chief Author and Dean
iv. Contents of the Issue

1. 1-Octanol/Water Partition Coefficients of Dialkylated Methylimidazolium Halide Salts. *1-6*
2. Seasonal and Spatial Variation of Water Quality Index of Bassi Tehsil of District Jaipur, Rajasthan, India. *7-19*
3. Adsorption and Kinetic Study of Ni(II) Ions from Aqueous Solution using Natural Syrian Zeolite. *21-29*

v. Fellows
vi. Auxiliary Memberships
vii. Process of Submission of Research Paper
viii. Preferred Author Guidelines
ix. Index

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1-Octanol/Water Partition Coefficients of Dialkylated Methylimidazolium Halide Salts

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Abstract- Dialkylated methylimidazolium halide salts are a current research topic. The 1-octanol/water partition coeffcient for these salts has come to signify the tendency of a charged organic molecule to cross a biological membrane, be sequested in soil, and indicate the lethal dose of the chemical. The purpose of this work is to add to existing data for the 1-octanol/water partition coeffcient for these salts. The novelty of this work is that dialkylated methylimidazolium salts are investigated.

Keywords: *ionic liquids, partition functions.*

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1OCTANOLWATERPARTITIONCOEFFICIENTSOFDIALKYLATEDMETHYLIMIDAZOLIUMHALIDESALTS

Strictly as per the compliance and regulations of :

1-Octanol/Water Partition Coefficients of Dialkylated Methylimidazolium Halide Salts

Marissa K. Gard [α], Elliot G. Ennis [σ] & John H. Summerfield [ρ]

Abstract- Dialkylated methylimidazolium halide salts are a current research topic. The 1-octanol/water partition coeffcient for these salts has come to signify the tendency of a charged organic molecule to cross a biological membrane, be sequested in soil, and indicate the lethal dose of the chemical. The purpose of this work is to add to existing data for the 1-octanol/water partition coeffcient for these salts. The novelty of this work is that dialkylated methylimidazolium salts are investigated.

Keywords: ionic liquids, partition functions.

I. Introduction

Green chemistry is founded on guidelines that are designed to prevent and reduce the waste associated with the production of chemicals. Any modifications to existing processes as well as the creation of new processes that lead to more efficient and recyclable solvents, safer reactions, and renewable feedstocks are successes.[1]

Ionic liquids or molten salts are molecules composed wholly of ions and occur in the liquid state. An inorganic salts such as NaCl is an ionic liquid above its melting point. Due to their high melting point many inorganic salts are of little use in daily life. Instead, chemists have turned to imidazolium-based ionic liquids. These organic salts are current candidates for green solvents. They can be highly soluble, can have high ionic conductivity, are generally inflammable, have high thermal and chemical stability, and relatively low vapor pressures compared to cyclohexane, benzene, and acetone. Typically the imidazoliumsaltsunder investigation are alkylmethylimidazolium compounds. The novelty of this work is that dialkylated methylimidazolium salts are investigated.[2]

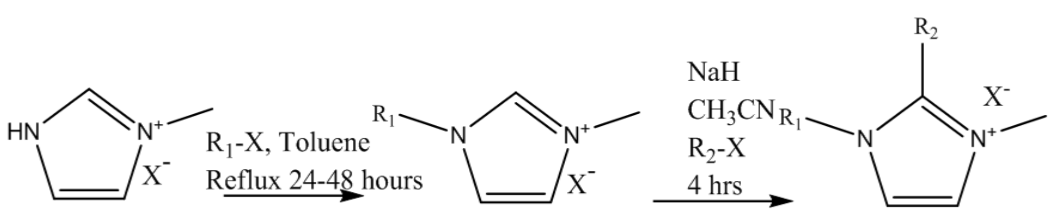
Trisubstituted imidazolium salts are a current research topic. They have been investigated as a solvent, an electrolyte solution additive, a reaction initiator, a product precursor, a molecular aggregator, and a composite material.[3]

The 1-octanol/water partition coefficient (K_{OW}) for these salts has come to signify the tendency of a charged organic molecule to cross a biological membrane,[4] and as an estimate to the salt's environmental impact before widespread use. The purpose of this work is to add to existing data for the 1-octanol/water partition coefficient for these salts.[5, 6]

II. Materials and Methods

a) Synthesis

The synthesis is shown below (Scheme 1). It is outlined in the literature.[7]



Scheme 1 : Two R groups are added to the 3-methyl-1*H*-imidazol-3-ium ion

The chemicals used in the syntheses, the CAS numbers, sources and grades are below. The proton NMR was performed on a Bruker AV-III 300 MHz spectrometer. The solvent was DSMO and the standard was $Si(CH_3)_4$. The peak assignments are below.

1-methyl-3-octyl-1H-imidazol-3-ium bromide

3-methyl-1*H*-imidazol-3-ium (1-methylimidazole 616-47-7, Aldrich, 99%, 25.00 mL), 1-bromoctane (111-83-1, Aldrich, 99%, 71.00 mL), and toluene (108-88-3, Aldrich, 99.8%, 40.00 mL) were mixed. The solution was refluxed for two days. The resulting mixture was frozen and the excess toluene was decanted. The product was thawed and washed with ethyl acetate (141-78-6, Aldrich, 99.8%). The solution was evaporated to dryness. The product was frozen and the excess reagents were decanted. δH(300 MHz; DMSO; $Si(CH_3)_4$) 8.90 (1 H, s, 2-H), 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.00 (2 H, qt, CH_2), 1.30 (10 H, s, CH_2) 0.91 (3 H, br, CH_3)) The x-ray photoelectric spectroscopy, FTIR, and ^{1}H NMR markers are also in the literature.[8, 9].

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1,2-dimethyl-3-octyl-1H-imidazol-3-ium iodide

To a stirred solution of 1-methyl-3-octyl-*1H*-imidazol-3-ium bromide (10.00 g) in acetonitrile (75-05-8, Aldrich, 99.8%, 175.00 mL) was added NaH (7646-69-7, Aldrich, 60% in mineral oil, 2.00 g). After allowing the mixture to stir four hours, iodomethane (74-88-4, Aldrich, 99%, 6.90 mL) was added and the reaction was stirred for 12 hours. The solution was filtered to remove any precipitated NaI. The resulting oil as washed with ethyl acetate (141-78-6, Aldrich, 99.8%, 3x75.00 mL) and the residual volatiles were then removed under vacuum. The residual nonvolatiles were removed by freezing and decantation. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.85 (3 H, s, 2-CH_3) 2.00 (2 H, qt, CH_2), 1.30 (10 H, s, CH_2) 0.91 (3 H, br, CH_3)) The ^{1}H NMR markers are in the literature.[10, 11]

Workers find the IUPAC nomenclature wearisome. This paper will represent the 1-methylimidazolium fragment as mim. The molecule 1-methyl-3-octyl-*1H*-imidazol-3-ium bromide is shortened to [omim]Br. Similarly, 1,2-di*m*ethyl-3-*o*ctyl-1*H*-imidazol-3-ium iodide becomes [momim]I. The two letters hx will refer to the hexyl group.

[bomim]Cl

2-butyl-1-methyl-3-octyl-*1H*-imidazol-3-ium chloride was prepare in the same manner as [momim]I with the exception that 1-chlorobutane (109-69-3, Aldrich, 99.5%, 11.6 mL) was used instead of iodomethane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (12 H, s, CH_2) 0.91 (6 H, br, CH_3))

[pomim]Cl

1-methyl-3-octyl-2-pentyl-*1H*-imidazol-3-ium chloride was prepare in the same manner as [momim]I with the exception that 1-chloropentane (543-59-5, Aldrich, 99%, 13.4 mL) was used instead of iodomethane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (14 H, s, CH_2) 0.91 (6 H, br, CH_3))

[oomim]Cl

1-methyl-2, 3-dioctyl-1*H*-imidazol-3-ium chloride was prepare in the same manner as [momim]I with the exception that chlorooctane (111-85-3, Aldrich, 99%, 18.9 mL) was used instead of iodomethane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (20 H, s, CH_2) 0.91 (6 H, br, CH_3))

[domim]Cl

2-decyl-3-methyl-2-octyl-1*H*-imidazol-3-ium chloride was prepare in the same manner as [momim]I with the exception that chlorodecane (1002-69-3, Aldrich, 98%, 22.6 mL) was used instead of iodomethane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (22 H, s, CH_2) 0.91 (6 H, br, CH_3))

[bbmim]Cl

3-methyl-1*H*-imidazol-3-ium (1-methylimidazole 616-47-7, Aldrich, 99%, 25.00 mL), 1-chlorobutane (109-69-3 Aldrich, 99.5%, 43.00 mL), and toluene (108-88-3, Aldrich, 99.8%, 40.00 mL) were mixed. The solution was refluxed for two days. The resulting mixture was frozen and the excess toluene was decanted. The product was thawed and washed with ethyl acetate (141-78-6, Aldrich, 99.8%). The solution was evaporated to dryness. The product was frozen and the excess reagents were decanted. To a stirred solution of 1-methyl-3-octyl-*1H*-imidazol-3-ium bromide (10.00 g) in acetonitrile (75-05-8, Aldrich, 99.8%, 150.00 mL) was added NaH (7646-69-7, Aldrich, 60% in mineral oil, 2.67 g) After allowing the mixture to stir four hours, 1-chlorobutane (109-69-3 Aldrich, 99.5%, 17.8 mL) was added and the reaction was stirred for 12 hours. The solution was filtered to remove any precipitated NaCl. The resulting oil as washed with ethyl acetate (141-78-6, Aldrich, 99.8%, 3x75.00 mL) and the residual volatiles were then removed under vacuum. The residual nonvolatiles were removed by freezing and decantation. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (4 H, sx, CH_2) 0.91 (6 H, t, CH_3))

[pbmim]Cl

2-butyl-1-methyl-3-pentyl-1*H*-imidazol-3-ium chloride was prepare in the same manner as [bbmim]Cl with the exception that 1-chloropentane (543-59-9, Aldrich, 99%, 20.7 mL) was used instead of 1-chlorobutane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (6 H, sx, CH_2) 0.91 (6 H, t, CH_3))

[hxbmim]Cl

2-butyl-3-hexyl-1-methyl-1*H*-imidazol-3-ium chloride was prepare in the same manner as [bbmim]Cl with the exception that 1-chlorohexane (544-10-5, Aldrich, 99%, 23.5 mL) was used instead of 1-chlorobutane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (8 H, br, CH_2) 0.91 (6 H, t, CH_3))

[dbmim]Cl

2-butyl-3-decyl-1-methyl-1*H*-imidazol-3-ium chloride was prepare in the same manner as [bbmim]Cl with the exception that 1-chlorodecane (1002-69-3, Aldrich, 98%, 34.8 mL) was used instead of 1-chlorobutane. δH(300 MHz; DMSO; $Si(CH_3)_4$) 7.91 (1 H, d, 5-H), 7.78 (1 H, d, 4-H), 5.00 (2 H, t NH), 3.75 (3 H, s, NCH_3), 2.50 (2 H, t, CH_2), 2.00 (2 H, qt, CH_2), 1.61 (2 H, qt, CH_2) 1.30 (16 H, br, CH_2) 0.91 (6 H, t, CH_3))

The UV/Vis spectra were produced on a Beckman DU-640B UV/Vis spectrophotometer. The salt, its phase, the λ_{max}, and the corresponding absorbance are shown in the Results and Discussion section. The maximum absorbance is in the neighborhood of 265.0 nm, which indicates the imidazolium ring.[12]

The compound [oomim]Cl was excluded. The spectrum was simply noise. This may indicate a very similar blank and sample. The difference between the two---the UV/Vis spectrum---is noise.[13]

The compound [momim]I shows negative absorbance. Negative absorbance has no physical meaning except that the blank absorbs more light than the [momim]I.

This work finds the 1-octanol/water partition coefficient by the slow-stirring method.[14–18] The salt was added to a solution of 1-octanol saturated with water. Each solution was stirred for 45 days at 21℃. This was done slowly to prevent emulsification.

For this work initially 5.0 µg of the organic salt was added to 5.0 mL of a saturated 1-octanol/water solution. When an emulsion formed, the solution was stirred for six hours and left to rest overnight. This removed the emulsion. Serial dilutions were done to keep the absorption values between –0.150 and 1.000. The aqueous layer was drawn off and compared to a saturated solution of 1-octanol. One extraction was done for each compound. The K_{OW} value was then calculated using

$$K_{OW} = \frac{\left(A_i \cdot df_i - A_f \cdot df_f\right) \cdot V_{\text{water}}}{A_f \cdot df_f \cdot V_{\text{octanol}}} \quad (1)$$

where A_i and A_f are the absorbances of the aqueous layer before and after extraction. V_{water} and $V_{octanol}$ are the volumes of the water and 1-octanol phases. The symbols df_i and df_f are the dilution factors used to find A_i and A_f.[19,20]

III. Results and Discussion

The UV/Vis data, the experimental log K_{OW} values, the calculated log K_{OW} values, and the absolute difference between them are shown below in Table 1.

Compound in water phase	λ_{max} in nm	Absorbance at λ_{max}	Exp. Log K_{OW}	Calc. Log K_{OW}	$\lvert\Delta$Log $K_{OW}\rvert$
[momim]I	248.0	–0.1459	–0.62	–.8850	0.27
[bomim]Cl	269.0	0.4209	1.1	0.5020	0.6
[pomim]Cl	265.0	0.21450	0.98	1.031	0.051
[domim]Cl	263.0	0.1249	5.1	3.676	1.4
[bbmim]Cl	264.0	0.6850	–1.3	–1.614	0.31
[pbmim]Cl	264.0	0.6413	–0.93	–1.085	0.16
[hxbmim]Cl	259.0	0.1866	–0.31	–0.5560	0.25
[dbmim]Cl	232.0	0.2346	1.9	1.560	0.3

Table 1: UV/Vis data, experimental log K_{OW} values, calculated log K_{OW} values, and the absolute difference between them. The calculated values were determined by the group contribution method rather than the linear free energy relation scheme.[5, 21]

Using the cLog P program[22] the calculated log K_{OW} values in Table 1 were found. The expectation is 85% of the calculated log K_{OW} values will be in error by less than 0.5, 10% by 0.5 to 1.0, and 5% by more than 1.0.[23] For this work, the values are 75%, 13%, and 13% respectively. The clog P program is best suited for molecules with typical fragments.[24] The charged five-membered ring and the long hydrocarbon chains may be misrepresented in this group additive method or the small sample size may explain the discrepancies.

The toxicity of organic solvents in animal tissue, in soil, and in water is an ongoing concern. In this work we examine three toxicity indicators that are linked to the 1-octanol/ water partition coefficients. Positive value log K_{OW} values indicate the octanol phase is favored. These compounds are candidates for tissue storage. That is, candidates for the calculated of a bioconcentration factor (BCF). The soil sorption coefficient (K_{OC}) is the ratio of the mass of a chemical absorbed per weight of carbon in a soil to the concentration of the chemical in water. The lethal concentration of a chemical is defined as the lethal dose for half the population (LC_{50}).[25]

Two BCF models are shown in Figure 1. The lower dashed line is log(BCF) = 0.85 log(K_{OW}) – 0.70. The upper dashed line is log(BCF) = 0.79 log(K_{OW}) – 0.40.[25] The log(BCF) for benzene from these models is 1.3 and 1.1, respectively.[2]

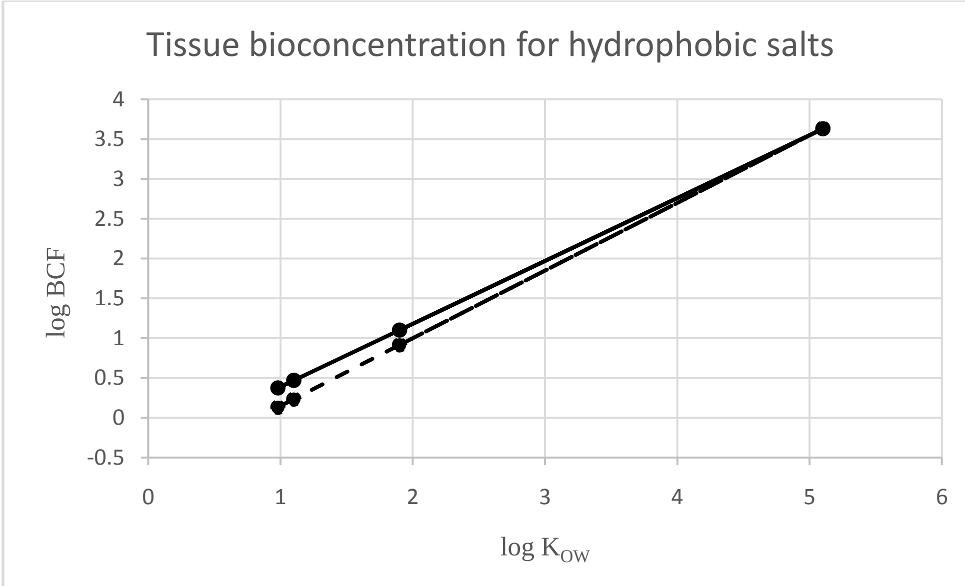

Figure 1 : Log of the tissue bio concentration for the positive $\log(K_{OW})$ salts. The lower dashed line is $\log(BCF) = 0.85 \log(K_{OW}) - 0.70$. The upper dashed line is $\log(BCF) = 0.79 \log(K_{OW}) - 0.40$.

Three K_{OC} models are shown below in Figure 2. The lower solid line is $\log(K_{OC}) = 0.989 \log(K_{OW}) - 0.364$. The middle line is $\log(K_{OC}) = 679 \log(K_{OW}) + 0.663$.The top dashed line is $\log(K_{OC}) = 0.544 \log(K_{OW}) + 1.377$.[25] The $\log(K_{OC})$ for benzene for these three models are 1.7, 2.1, and 2.5, respectively.[2]

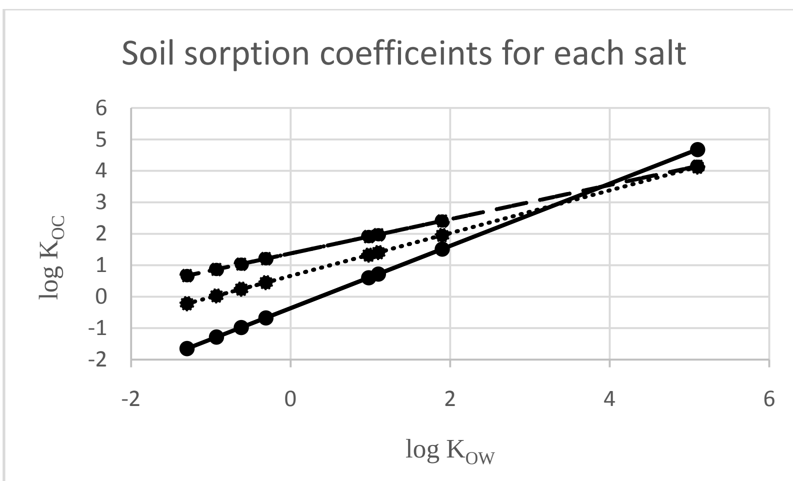

Figure 2 : Log of soil sorption coefficients for all the salts. The lower solid line is $\log(K_{OC}) = 0.989 \log(K_{OW}) - 0.364$. The middle line is $\log(K_{OC}) = 679 \log(K_{OW}) + 0.663$.The top dashed line is $\log(K_{OC}) = 0.544 \log(K_{OW}) + 1.377$

Figure 3 shows the log of the inverse lethal concentrations ($1/LC_{50}$) for each salt. The top line is $\log(1/LC_{50}) = 0.629 \log(K_{OW}) - 0.489$. The middle dotted line is $\log(1/LC_{50}) = 0.854 \log(K_{OW}) - 1.74$. The solid line is $\log(1/LC_{50}) = 0.89 \log(K_{OW}) - 1.75$.[25] The $\log(1/LC_{50})$ for benzene from these models are 0.85, 0.079, 0.15, respectively.[2]

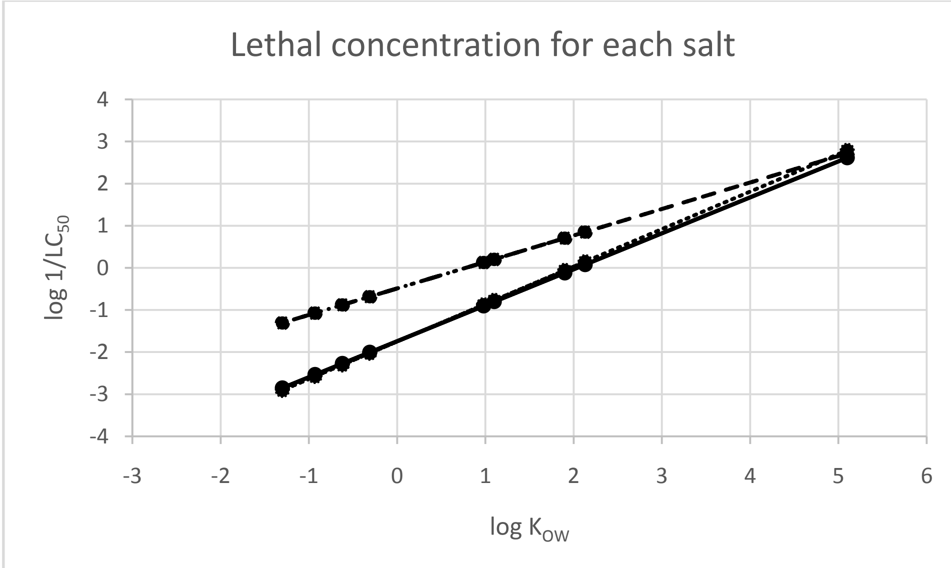

Figure 3 : The log of the inverse lethal concentrations ($1/LC_{50}$) for each salt. The top line is $\log(1/LC_{50}) = 0.629 \log(K_{OW}) - 0.489$. The middle dotted line is $\log(1/LC_{50}) = 0.854 \log(K_{OW}) - 1.74$. The solid line is $\log(1/LC_{50}) = 0.89 \log(K_{OW}) - 1.75$

IV. Conclusions

Green chemistry has taken a winding road in its search for benign solvents. Some, such as CO_2, have become firmly established.[26] Others, such as imidazolium salts, continue to be under investigation.[27–32]A physical quantity that continues to be of interest is the 1-octanol/water partition coefficients. One reason is their direct link to the environmental impact of the salts.[33, 34]

Dialkylated methylimidazolium salts have low vapor pressure compared to typical solvents such as benzene. This work shows they can be synthesized to be water soluble or lipophilic. This work also shows that every imidazolium salt is not "green". The salts with octyl and/or decyl substituents have comparable toxicity to benzene. It has recently been shown that cholinium alkanoates may provide a set of molecules that are more ecologically friendly.[35]

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Seasonal and Spatial Variation of Water Quality Index of Bassi Tehsil of District Jaipur, Rajasthan, India

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Abstract- The present study was intended to calculate the water quality index (WQI) of Bassi Tehsil of district Jaipur, Rajasthan, India in order to assess its suitability for drinking purpose. For this ground water samples from 71 sampling sites of 50 villages of study area were collected from tube wells and hand pumps of varying depths in pre and post monsoon seasons and analyzed for ten physico-chemical parameters namely pH, Total Alkalinity, Total Hardness, Calcium, Magnesium, Chloride, Nitrate, Fluoride, Total Dissolved Solid and Electrical Conductivity. Analysis of results showed that almost all parameters were exceeding the permissible limits prescribed by BIS, ICMR and WHO. Assessment of water quality index (WQI) showed remarkable variation of water quality as WQI values ranged from 13.53 to 1052.2 in pre-monsoon and 25.72 to 1024.6 in post monsoon season. The study also revealed that drinking water of Bassi tehsil is not potable and there is an instant need to take ameliorative steps in this region to prevent the population from adverse health effects as 61.97% and 63.38% ground water samples were classified under "unsuitable for drinking" category in accordance with their WQI values in pre and post monsoon seasons, respectively.

Keywords: *groundwater quality, physico-chemical parameters, water quality index, bassi tehsil and rajasthan.*

GJSFR-B Classification : FOR Code: 090508

SEASONALANDSPATIALVARIATIONOFWATERQUALITYINDEXOFBASSITEHSILOFDISTRICTJAIPURRAJASTHANINDIA

Strictly as per the compliance and regulations of :

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Swati Saxena [α], Umesh Saxena [σ] & A. K. Sinha [ρ]

Abstract- The present study was intended to calculate the water quality index (WQI) of Bassi Tehsil of district Jaipur, Rajasthan, India in order to assess its suitability for drinking purpose. For this ground water samples from 71 sampling sites of 50 villages of study area were collected from tube wells and hand pumps of varying depths in pre and post monsoon seasons and analyzed for ten physico-chemical parameters namely pH, Total Alkalinity, Total Hardness, Calcium, Magnesium, Chloride, Nitrate, Fluoride, Total Dissolved Solid and Electrical Conductivity. Analysis of results showed that almost all parameters were exceeding the permissible limits prescribed by BIS, ICMR and WHO. Assessment of water quality index (WQI) showed remarkable variation of water quality as WQI values ranged from 13.53 to 1052.2 in pre-monsoon and 25.72 to 1024.6 in post monsoon season. The study also revealed that drinking water of Bassi tehsil is not potable and there is an instant need to take ameliorative steps in this region to prevent the population from adverse health effects as 61.97% and 63.38% ground water samples were classified under "unsuitable for drinking" category in accordance with their WQI values in pre and post monsoon seasons, respectively.

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I. Introduction

"*Jalam Jeevamrutham*" Water is one of the five elements described in "shastra" to life. It is also one of the most important commodities which Man has exploited than any other resource for sustenance of his life. Potable safe water is absolutely essential and is the basic need of all human beings on the earth. Due to modern civilization, rapid urbanization, and industrialization, subsequent contamination of surface and ground water sources, water conservation and water quality management has now a day's assumed a very complex shape. Attention on contamination and its management has become a need of the hour, because of its far reaching impact on human health.

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In India so many factors contribute to pollution of ground water such as; scarcity of water resources, uncontrolled population, urbanization, poverty, lack of education, lack of political commitment etc. Groundwater quality is highly dependent on the nature of the aquifers and on the surrounding climatic conditions (Chand, 2013; Dhok et al., 2011).

Assessment of the groundwater quality has always been important in the field of environmental quality management. One of the most effective tools for the assessment and management of the water quality is Water quality index; it offers a simple, stable, reproducible unit of measure and communicates information of water quality to the concerned citizens and policy makers (Chauhan and Singh, 2010). The water quality is difficult to evaluate from a large number of samples, each containing concentrations of many parameters. WQI is a mathematical instrument used to transform large quantities of water quality data into a single number which represents the water quality level while eliminating the subjective assessments of water quality and biases of individual water quality experts (Yogendra and Puttaaiah, 2008; Chowdhury et al., 2012; Khwakaram et al., 2012; Hussain et al., 2014).

II. Study Area

Rajasthan is known as "the land of king" and it is the largest state of the republic of India in terms of geographical spread. It is situated in the North- Western part of India having total area is around 3,42,239 Sq. Km. Which represents 10.41 % of total area of the country and population of 6.86 Crores spread over in 44,672 villages, which is 5.67 % of nations population but being just available 1% of the total water resources of the country. The state has extreme climatic and geographical condition and it suffers both the problems of quantity and quality of water (Bhalla and Bhalla, 2013; Yadav et al., 2010).

Jaipur, the capital of Rajasthan, has a total area of 11,117 sq. Km covering the 3.23% of the total area of the state, administered by 13 tehsils or sub-divisions. Our focused area of study is Bassi tehsil, out of the 13 tehsils of Jaipur district. The area of tehsil is 654.69 sq.km, located at $26^0$96' N latitude and $75^0$62'E longitude. In Bassi Tehsil there are 210 villages (famous for their leather footwear and Embroidery beading). In the study area there are no major surface water sources however; main sources of drinking water are open wells, hand pumps and bore wells (Singh et al., 2012; CGWB, 2007; JDA, 2012).

In Bassi Tehsil 84 villages are reported having fluoride concentration more than 1.5 ppm, 78 villages are exhibiting nitrate concentration more than 45 ppm and 30 villages are having Electrical conductivity more than 3000 micromhos/cm (CGWB, 2007; Mathur, 2007).

Review of literature reveals that no studies have been made to scientifically investigate the ground water contamination of the study area. The present study aims to calculate the Water Quality Index (WQI) in most rural habitations of Bassi Tehsil of Jaipur, Rajasthan, India in order to assess the suitability of ground water for human uses and it also deals with the necessity of restoring the water quality.

III. Materials and Methods

a) Sample Collection

Ground water samples from a total of 71sampling sites of 50 villages of Bassi Tehsil were collected in pre-cleaned and rinsed polyethene bottles of two litre capacity with necessary precautions (Brown et al. 1974). The total water collection in the year of 2013 is divided in to two seasons, one is pre monsoon and another one is post monsoon. The sampling is carried out, during April 2013 for pre monsoon season and in September-October 2013 for post monsoon season from manually operated tube wells and hand pumps of varying depth.

b) Physico-chemical Analysis

All the samples were analyzed for the following Physico-chemical parameters; pH, Total Alkalinity (TA), Total Hardness (TH), Calcium hardness (Ca H), Magnesium hardness (Mg H), Chloride, Nitrate, Fluoride, Total Dissolved Solid (TDS) and Electrical Conductivity (EC). The analysis of water samples were out carried in accordance to standard analytical methods (APHA, 2005). All the chemicals used were of AR grade and double distilled water used for preparation of solutions. Details of the analysis methods are summarized in Table 1.

Table 1 : Parameters and methods employed in the physicochemical examination of water samples

S.No.	Parameters	Unit	Method Employed
1.	pH	-	Digital pH-meter
2.	Total Alkalinity	Mg/L	Titrimetric method (With H_2SO_4)
3.	Total Hardness (as $CaCO_3$)	Mg/L	Titrimetric method (with EDTA)
4.	Calcium Hardness (as $CaCO_3$)	Mg/L	Titrimetric method
5.	Magnesium Hardness (as $CaCO_3$)	Mg/L	Titrimetric method
6.	Chloride (as Cl^-)	Mg/L	Titrimetric method (With $AgNO_3$)
7.	Nitrate (as NO_3^-)	Mg/L	Spectrophotometric method
8.	Fluoride (as F^-)	Mg/L	Ion Selective Electrode
9.	Total Dissolved Solids	Mg/L	Digital TDS-meter
10.	Electrical Conductivity	µmhos/cm	Digital Conductivity-meter

c) Water Quality Index (WQI) Calculation

The calculation of WQI was made using weighed arithmetic index method (Brown et al., 1972) in the following steps-

Step I- Calculation of sub index of quality rating (qn)- Let there be n water quality parameters where the quality rating or sub index (*qn*) corresponding to the nth parameter is a number reflecting the relative value of this parameter in the polluted water with respect to its standard permissible value. The value of *qn* is calculated using the following expression.

$$qn = 100[(Vn - Vio) / (Sn - Vio)]$$

where,

qn = quality rating for the nth water quality parameter.

Vn = estimated value of the nth parameter at a given sampling station.

Sn = standard permissible value of nth parameter

Vio = ideal value of *n*th parameter in pure water.

All the ideal values (*Vio*) are taken as zero for drinking water except for pH=7.0 and dissolved oxygen=14.6mg/L.

Calculation of quality rating for pH

For pH the ideal value is 7.0 (for natural water) and a permissible value is 8.5 (for polluted water). Therefore, the quality rating for pH is calculated from the following relation:

$$qpH = 100 [(VpH - 7.0)/(8.5 - 7.0)]$$

where

VpH = observed value of pH during the study period.

Calculation of quality rating for dissolved oxygen

The ideal value (*VDO*) for dissolved oxygen is 14.6 mg/L and standard permitted value for drinking water is 5 mg/L. Therefore, quality rating is calculated from following relation:

$$qDO = 100 [(VDO - 14.6)/(5 - 14.6)]$$

Where,

VDO = measured value of dissolved oxygen

Step II- Calculation of unit weight (Wn)

Calculation of unit weight (*Wn*) for various water quality parameters are inversely proportional to the recommended standards for the corresponding parameters.

$$Wn = K/Sn$$

Where,
Wn = unit weight for nth parameters
Sn = standard value for nth parameters
K = constant for proportionality
The value of 'K' can be determined by-

$$K = \frac{1}{\frac{1}{S1}+\frac{1}{S2}+\cdots\cdots\frac{1}{Sn}} = \frac{1}{\frac{1}{\sum Sn}}$$

Step III-Calculation of WQI
WQI is calculated from the following equation-

$$WQI = \Sigma\, q_n Wn \,/\, \Sigma\, Wn$$

Table 2 : Water Quality Index (WQI) range and Quality Status of Water

Water Quality Index	Description
0-25	Excellent Water Quality
26-50	Good
51-75	Poor
76-100	Very poor
>100	Unsuitable for drinking

(Brown et al., 1972; Hariharan, 2007; Yogendra and Puttaiah, 2008; Chowdhury et al., 2012; Eugene et al., 2014; Sisodia and Moundiotiya, 2006; Rao et al., 2010)

IV. Result and Discussion

a) *Physico-chemical Parameters*

The respective values of all observed water quality parameters of groundwater samples in pre and post monsoon seasons are illustrated in Table 3 and 5 respectively. Statistical Parameters of groundwater samples of study area in both seasons are summarized in Table 4 and 6.

b) *Quality Assessment using WQI*

Water quality parameters mentioned in Table 3 and 5 are considered for calculating the WQI values using the above mentioned method. The water quality weightings used in the formula are mentioned in Table 7.

i. *Seasonal Variation of WQI*

Lower WQI values indicate that water is free from impurities at the sampling site, while WQI values more than 100 represents the polluted nature of water and its unsuitability for drinking purpose. Water Quality Index values for pre and post monsoon seasons are calculated and presented in Table 8. Developed Pie-diagrams (Figure 1 and 3) states the percentage variations of different qualities of waters in pre and post monsoon seasons, while Figure 2 and 4 represents the number of sampling sites classified on the basis of WQI values. From the results, it is seen that the WQI values in pre and post monsoon seasons are in the range of 13.53 to 1052.2 and 25.72 to 1024.6 respectively. The graphical representation of WQI values of ground water samples in Pre and Post monsoon seasons depicts that there is not any significant change in WQI values with respect to water quality.

Table 3 : Physico Chemical Characteristics of Groundwater Samples– Pre Monsoon Season

S.No.	Village	Source	Sample No.	Colour	Odour	pH	Alkalinity	TH	CaH	Ca^{+2} ions	MgH	Mg^{+2} ions	Cl^-	NO_3^-	F^-	TDS	EC
1	Akhepura	HP	S1	UO	UO	7.9	411	529	237	94.8	292	70.95	400	56	0.71	2216	3165
		TW	S2	UO	UO	8.4	305	115	43	17.2	72	17.49	31	15	1.44	778	1111
2	Anantpura	HP	S3	UO	UO	7.9	748	360	151	60.4	209	50.78	278	22	0.37	2100	3000
		TW	S4	UO	UO	8.3	462	161	67	26.8	94	22.84	176	18	1.8	1470	2100
3	Banskho	HP	S5	UO	UO	7.5	651	516	172	68.8	344	83.59	137	28	2.12	1696	2422
		TW	S6	UO	UO	8.4	396	105	40	16	65	15.79	123	12	1.99	1298	1855
4	Barala	HP	S7	UO	UO	7.5	586	192	78	31.2	114	27.7	333	78	2.05	2146	3065
5	Bassi	HP	S8	UO	UO	8.4	258	158	64	25.6	94	22.84	202	86	1.14	1590	2271
		TW	S9	UO	UO	7.8	333	156	67	26.8	89	21.62	163	44	0.79	1191	1701
6	Benada	HP	S10	UO	UO	7.6	435	732	336	134.4	396	96.22	315	131	0.93	1740	2486
7	Bharampur	HP	S11	UO	UO	7.7	368	188	78	31.2	110	26.73	176	20	0.42	920	1314
8	Chainpuriya	HP	S12	UO	UO	7.7	562	115	46	18.4	69	16.76	80	12	1.3	1034	1477
9	Chapariya	HP	S13	UO	UO	7.7	426	163	70	28	93	22.59	60	70	1.13	760	1085
10	Charangarh	HP	S14	UO	UO	7.4	243	264	121	48.4	143	34.74	33	29	0.71	792	1131
11	Chatarpura	HP	S15	UO	UO	7.6	707	112	45	18	67	16.28	65	19	4.67	1200	1714
12	Danau Kalan	HP	S16	UO	UO	8.2	582	46	22	8.8	24	5.83	20	22	1.4	1055	1507
13	Danau Khurd	HP	S17	UO	UO	7.7	409	568	206	82.4	362	87.96	484	8	0.9	2644	3777
		TW	S18	UO	UO	8.2	458	284	121	48.4	163	39.6	140	22	2.9	1680	2400
14	Garh	HP	S19	UO	UO	8.1	651	108	44	17.6	64	15.55	361	118	1	1962	2803
15	Ghasipura	HP	S20	UO	UO	8.4	344	88	32	12.8	56	13.6	20	38	0.03	847	1210
		TW	S21	UO	UO	8.3	766	74	33	13.2	41	9.96	51	26	11.4	1613	2304
16	Ghata	HP	S22	UO	UO	7.1	402	437	198	79.2	239	58.07	601	11	0.86	2593	3704
		TW	S23	UO	UO	7.3	467	632	297	118.8	335	81.4	468	14	0.7	2171	3101
17	Gudha Meena	HP	S24	UO	UO	7.8	423	160	66	26.4	94	22.84	23	18	0.27	980	1400
18	Gumanpura	HP	S25	UO	UO	7.8	460	317	128	51.2	189	45.92	380	16	0.88	2310	3300
		TW	S26	UO	UO	7.9	595	528	238	95.2	290	70.47	259	72	1.4	1764	2520
19	Gwalini	HP	S27	UO	UO	7.9	520	374	171	68.4	203	49.32	22	8	1.8	1333	1904
20	Hans Mahal	HP	S28	UO	UO	7.6	157	424	187	74.8	237	57.59	220	7	0.32	1182	1688
21	Hanumanpura	HP	S29	UO	UO	7.7	552	123	51	20.4	72	17.49	83	27	0.8	967	1381
		TW	S30	UO	UO	8.2	784	67	23	9.2	44	10.69	95	24	12.5	1473	2104
22	Jhajhwar	HP	S31	UO	UO	7.4	523	668	283	113.2	385	93.55	1430	58	0.41	4235	6050
		TW	S32	UO	UO	8.4	254	109	45	18	64	15.55	107	45	0.8	980	1400
23	Jhar	HP	S33	UO	UO	7.9	412	233	102	40.8	131	31.83	44	37	0.65	960	1371
24	Kalyanpura	HP	S34	UO	UO	8.5	527	89	36	14.4	53	12.87	28	34	1.3	1122	1603
		TW	S35	UO	UO	8.2	530	65	22	8.8	43	10.44	41	16	1.8	1190	1700
25	Kaneta	HP	S36	UO	UO	7.8	286	364	144	57.6	220	53.46	1424	6	0.11	4762	6802
		TW	S37	UO	UO	8.4	564	77	34	13.6	43	10.44	40	14	0.7	1050	1500
26	Kaneti	HP	S38	UO	UO	7.5	586	867	322	128.8	545	132.43	1075	236	1.06	4890	6985
27	Kanota	HP	S39	UO	UO	8.3	409	203	90	36	113	27.45	296	33	0.62	1835	2621
		TW	S40	UO	UO	8.4	741	91	36	14.4	55	13.36	225	8	1.7	1983	2833
28	Kashipura	HP	S41	UO	UO	7.5	695	105	40	16	65	15.79	90	21	3.2	1305	1864
29	Keshopura	HP	S42	UO	UO	7.6	555	350	140	56	210	51.03	644	5	0.75	2520	3600
30	Kuthada Kalan	HP	S43	UO	UO	7.1	233	66	25	10	41	9.96	20	22	0.77	709	1013
31	Lalgarh	HP	S44	UO	UO	7.6	510	284	122	48.8	162	39.36	230	15	1.42	1240	1771
32	Mundali	HP	S45	UO	UO	7.7	482	117	46	18.4	71	17.25	55	12	4.2	1321	1887
		TW	S46	UO	UO	8.2	734	90	34	13.6	56	13.6	152	26	3.38	1682	2404
33	Nagal Karna	HP	S47	UO	UO	7.4	371	154	57	22.8	97	23.57	60	11	4.35	1295	1850
		TW	S48	UO	UO	8.1	795	73	32	12.8	41	9.96	80	26	5.9	1610	2300
34	Parasoli	HP	S49	UO	UO	7.7	412	774	397	158.8	377	91.61	320	2	1.17	2146	3065
		TW	S50	UO	UO	8.4	464	78	35	14	43	10.44	60	23	2.2	1050	1500
35	Parempura	HP	S51	UO	UO	7.8	431	641	283	113.2	358	86.99	444	18	1.15	3474	4963
36	Patan	HP	S52	UO	UO	7.1	655	622	264	105.6	358	86.99	885	10	0.52	3535	5050
37	Peepalabai	HP	S53	UO	UO	7.2	160	374	209	83.6	165	40.09	266	82	1.84	1680	2400
		TW	S54	UO	UO	8.2	435	400	185	74	215	52.24	65	26	8.95	1505	2150
38	Peipura	HP	S55	UO	UO	7.8	532	267	118	47.2	149	36.2	250	11	1.35	1750	2500
		TW	S56	UO	UO	8.4	435	110	40	16	70	17.01	35	28	1.5	875	1250
39	Rajwas	HP	S57	UO	UO	7.6	648	463	205	82	258	62.69	551	52	1.33	2306	3295
40	Ramser	HP	S58	UO	UO	7.3	520	254	103	41.2	151	36.69	60	18	3.8	1050	1500
		TW	S59	UO	UO	8.4	464	118	44	17.6	74	17.98	50	25	2	1053	1504
41	Ratanpura	HP	S60	UO	UO	7.9	532	299	135	54	164	39.85	80	32	1.02	1435	2050

S.No.	Village	Source	Sample No.	Colour	Odour	pH	Alkalinity	TH	CaH	Ca^{+2} ions	MgH	Mg^{+2} ions	Cl^-	NO_3^-	F^-	TDS	EC
		TW	S61	UO	UO	8.4	552	88	35	14	53	12.87	60	19	1.07	1129	1613
42	Roopura	HP	S62	UO	UO	7.5	263	107	42	16.8	65	15.79	130	24	1.44	1113	1590
		TW	S63	UO	UO	8.1	415	430	200	80	230	55.89	81	25	8.75	1610	2300
43	Sambhariya	HP	S64	UO	UO	7.4	314	232	96	38.4	136	33.04	58	14	0.07	356	508
44	Shankarpura	HP	S65	UO	UO	7.6	588	134	53	21.2	81	19.68	58	6	4.2	1028	1469
45	Siya Ka Bas	HP	S66	UO	UO	7.7	235	234	98	39.2	136	33.04	62	91	0.85	1225	1750
46	Tehda	HP	S67	UO	UO	8.2	276	145	62	24.8	83	20.16	221	20	1.4	1478	2111
47	Tekchandpura	HP	S68	UO	UO	7.8	328	306	133	53.2	173	42.03	40	14	0.2	563	804
48	Tilpatti	HP	S69	UO	UO	7.8	642	194	81	32.4	113	27.45	80	14	0.9	1280	1828
49	Todabhata	HP	S70	UO	UO	8.5	328	65	22	8.8	43	10.44	52	24	2	984	1405
50	Tunga	HP	S71	UO	UO	7.6	36	38	16	6.4	22	5.34	15	10	0.1	63	86

Where- TA = Total Alkalinity, TH = Total Hardness, CaH = Calcium Hardness, MgH = Magnesium Hardness, Cl = Chloride, NO_3^- = Nitrate, F^- = Fluoride, TDS = Total Dissolved Solids, EC = Electrical Conductivity.

All parameters are expressed in mg/L except pH and EC. EC is expressed in μmhos/cm.

Ca^{+2} = Ca mg/L (as $CaCO_3$), Mg^{+2} = Mg mg/L (as $CaCO_3$).

UO = Unobjectionable, HP = Hand Pump, TW = Tube Well.

Table 4 : Minimum, Maximum and Average Characteristics of Groundwater Sampling Stations – Pre Monsoon Season

S.No.	Parameter	Minimum	Maximum	Average	Standard Deviation
1.	pH	7.1	8.5	7.86	0.39
2.	Total Alkalinity (mg/L)	36	795	469.47	162.55
3.	Total Harness (mg/L)	38	867	260.19	201.90
4.	Calcium Hardness (mg/L)	16	397	111.23	90.30
5.	Ca^{+2} Ions (mg/L)	6.4	158.8	44.49	36.12
6.	Magnesium Hardness (mg/L)	22	545	148.95	113.86
7.	Mg^{+2} Ions (mg/L)	5.34	132.43	36.19	27.66
8.	Chloride (mg/L)	15	1430	222.01	290.48
9.	Nitrate (mg/L)	2	236	32.16	35.64
10.	Fluoride (mg/L)	0.03	12.5	1.96	2.41
11.	TDS (mg/L)	63	4890	1589.88	899.48
12.	EC (μmhos/cm)	86	6985	2271.05	1285.04

Table 5 : Physico-Chemical Characteristics of Groundwater Samples – Post Monsoon Season

S. No.	Village	Source	Sample No.	Colour	Odour	pH	Alkalinity	TH	CaH	Ca^{+2} ions	MgH	Mg^{+2} ions	Cl^-	NO_3^-	F^-	TDS	EC
1	Akhepura	HP	S1	UO	UO	8.1	410	406	180	72	226	54.91	306	102	1.36	1581	2259
		TW	S2	UO	UO	8.6	294	82	32	12.8	50	12.15	22	21	1.94	616	880
2	Anantpura	HP	S3	UO	UO	7.7	607	284	122	48.8	162	39.36	194	15	0.85	1493	2132
		TW	S4	UO	UO	7.7	517	540	245	98	295	71.68	417	29	0.73	2074	2962
3	Banskho	HP	S5	UO	UO	7.8	580	478	173	69.2	305	74.11	193	31	0.92	1630	2328
		TW	S6	UO	UO	8.5	363	98	41	16.4	57	13.85	98	14	1.54	1207	1724
4	Barala	HP	S7	UO	UO	7.7	484	110	45	18	65	15.79	118	7	1.8	668	954
5	Bassi	HP	S8	UO	UO	7.6	459	161	68	27.2	93	22.59	171	94	0.81	1274	1820
		TW	S9	UO	UO	7.4	255	187	80	32	107	26	113	56	0.51	1356	1937
6	Benada	HP	S10	UO	UO	8.5	838	254	111	44.4	143	34.74	107	59	0.98	1612	2303
7	Bharampur	HP	S11	UO	UO	7.8	482	364	163	65.2	201	48.84	146	21	0.6	1044	1491
8	Chainpuriya	HP	S12	UO	UO	7.7	703	261	113	45.2	148	35.96	118	11	1	1206	1723
9	Chapariya	HP	S13	UO	UO	7.7	282	211	88	35.2	123	29.88	28	27	0.9	424	605
10	Charangarh	HP	S14	UO	UO	7.7	168	220	92	36.8	128	31.1	40	27	0.32	432	617
11	Chatarpura	HP	S15	UO	UO	7.6	698	147	63	25.2	84	20.41	60	18	2.6	956	1365
12	Danau Kalan	HP	S16	UO	UO	7.6	454	159	66	26.4	93	22.59	34	24	1.17	712	1018

S. No.	Village	Source	Sample No.	Colour	Odour	pH	Alkalinity	TH	CaH	Ca^{+2} ions	MgH	Mg^{+2} ions	Cl^-	NO_3^-	F^-	TDS	EC
13	Danau Khurd	HP	S17	UO	UO	7.2	312	660	237	94.8	423	102.8	103	106	0.45	910	1300
		TW	S18	UO	UO	7.8	382	337	151	60.4	186	45.19	84	29	2.6	1478	2111
14	Garh	HP	S19	UO	UO	7.8	422	777	392	156.8	385	93.55	355	94	1.02	1685	2407
15	Ghasipura	HP	S20	UO	UO	7.7	365	127	51	20.4	76	18.46	21	13	0.55	640	914
		TW	S21	UO	UO	7.9	817	92	37	14.8	55	13.36	54	19	11.9	1271	1816
16	Ghata	HP	S22	UO	UO	7.9	443	313	140	56	173	42.03	246	14	1.43	1414	2020
		TW	S23	UO	UO	7.7	514	501	217	86.8	284	69.01	367	17	0.96	1669	2384
17	Gudha Meena	HP	S24	UO	UO	7.6	403	199	88	35.2	111	26.97	20	19	0.4	642	917
18	Gumanpura	HP	S25	UO	UO	7.7	384	208	89	35.6	119	28.91	103	8	2	808	1154
		TW	S26	UO	UO	7.8	509	404	181	72.4	223	54.18	183	53	2.5	1205	1721
19	Gwalini	HP	S27	UO	UO	7.7	510	270	125	50	145	35.23	80	6	1.4	891	1273
20	Hans Mahal	HP	S28	UO	UO	7.6	476	1100	423	169.2	677	164.5	1455	20	2.08	5434	7763
21	Hanumanpura	HP	S29	UO	UO	7.1	560	316	144	57.6	172	41.79	507	95	1.6	2196	3137
		TW	S30	UO	UO	7.5	812	92	33	13.2	59	14.33	148	37	12.2	1837	2624
22	Jhajhwar	HP	S31	UO	UO	7.9	575	440	190	76	250	60.75	436	41	1.1	2204	3149
		TW	S32	UO	UO	8.6	278	76	31	12.4	45	10.93	154	38	1.08	647	924
23	Jhar	HP	S33	UO	UO	7.8	488	271	118	47.2	153	37.17	63	32	0.41	926	1322
24	Kalyanpura	HP	S34	UO	UO	7.8	256	307	134	53.6	173	42.03	30	18	0.8	487	696
		TW	S35	UO	UO	7.8	318	83	29	11.6	54	13.12	52	13	1.2	607	867
25	Kaneta	HP	S36	UO	UO	7.7	223	268	105	42	163	39.6	57	14	0.5	804	1148
		TW	S37	UO	UO	8.2	459	56	26	10.4	30	7.29	34	21	0.39	651	930
26	Kaneti	HP	S38	UO	UO	7.4	674	347	129	51.6	218	52.97	80	2	0.14	918	1312
27	Kanota	HP	S39	UO	UO	7.5	415	361	148	59.2	213	51.75	342	40	1.3	1436	2051
		TW	S40	UO	UO	7.8	689	134	61	24.4	73	17.73	266	11	2.3	1606	2294
28	Kashipura	HP	S41	UO	UO	7.6	411	161	64	25.6	97	23.57	86	19	1.35	910	1301
29	Keshopura	HP	S42	UO	UO	7.6	330	227	92	36.8	135	32.8	80	26	0.49	1333	1904
30	Kuthada Kalan	HP	S43	UO	UO	7.6	785	262	110	44	152	36.93	42	21	0.5	800	1142
31	Lalgarh	HP	S44	UO	UO	7.7	505	185	80	32	105	25.51	105	49	0.9	1042	1488
32	Mundali	HP	S45	UO	UO	7.8	600	106	42	16.8	64	15.55	92	21	5.6	1131	1616
		TW	S46	UO	UO	8.3	822	77	31	12.4	46	11.17	206	32	4.02	1951	2787
33	Nagal Karna	HP	S47	UO	UO	7.7	389	119	43	17.2	76	18.46	148	2	1.9	608	869
		TW	S48	UO	UO	8.5	859	53	21	8.4	32	7.77	112	19	3.25	822	1174
34	Parasoli	HP	S49	UO	UO	7.8	440	553	280	112	273	66.33	326	15	1.43	1322	1889
		TW	S50	UO	UO	8.5	516	48	22	8.8	26	6.31	56	34	1.8	693	990
35	Parempura	HP	S51	UO	UO	7.8	403	520	200	80	320	77.76	475	13	0.8	2880	4114
36	Patan	HP	S52	UO	UO	7.7	535	479	199	79.6	280	68.04	652	18	1.22	2468	3526
37	Peepalabai	HP	S53	UO	UO	7.8	206	228	123	49.2	105	25.51	58	25	0.5	408	583
		TW	S54	UO	UO	7.7	513	248	99	39.6	149	36.2	38	16	5.3	723	1033
38	Peipura	HP	S55	UO	UO	7.7	700	242	106	42.4	136	33.04	446	24	1.23	1946	2780
		TW	S56	UO	UO	8.2	504	97	34	13.6	63	15.3	47	41	1.3	1016	1451
39	Rajwas	HP	S57	UO	UO	7.6	704	428	183	73.2	245	59.53	320	27	1.3	2883	4118
40	Ramser	HP	S58	UO	UO	7.3	540	210	85	34	125	30.37	100	13	1.3	1040	1485
		TW	S59	UO	UO	8.3	483	89	27	10.8	62	15.06	66	21	1.06	924	1320
41	Ratanpura	HP	S60	UO	UO	7.8	860	260	113	45.2	147	35.72	193	8	1.13	1600	2286
		TW	S61	UO	UO	7.9	871	190	75	30	115	27.94	130	19	2.65	1440	2057
42	Roopura	HP	S62	UO	UO	7.8	353	243	110	44	133	32.31	60	30	1.4	722	1031
		TW	S63	UO	UO	8.4	511	627	283	113.2	344	83.59	58	28	8.49	1159	1656
43	Sambhariya	HP	S64	UO	UO	7.6	425	145	60	24	85	20.65	30	30	2.25	920	1314
44	Shankarpura	HP	S65	UO	UO	7.8	540	197	85	34	112	27.21	80	2	3.6	1125	1607
45	Siya Ka Bas	HP	S66	UO	UO	7.6	313	179	73	29.2	106	25.75	56	71	1.13	773	1104
46	Tehda	HP	S67	UO	UO	7.7	425	174	72	28.8	102	24.78	172	24	1.55	1140	1629
47	Tekchandpura	HP	S68	UO	UO	7.8	254	292	130	52	162	39.36	40	12	0.25	529	756
48	Tilpatti	HP	S69	UO	UO	7.8	633	366	153	61.2	213	51.75	114	22	0.76	1306	1867

S. No.	Village	Source	Sample No.	Colour	Odour	pH	Alkalinity	TH	CaH	Ca^{+2} ions	MgH	Mg^{+2} ions	Cl^-	NO_3^-	F^-	TDS	EC
49	Todabhata	HP	S70	UO	UO	7.8	550	129	54	21.6	75	18.22	63	20	1.8	1043	1490
50	Tunga	HP	S71	UO	UO	7.8	290	780	395	158	385	93.55	288	309	0.65	1604	2291

Table 6 : Minimum, Maximum and Average Characteristics of Groundwater Sampling Stations – Post Monsoon Season

S.No.	Parameter	Minimum	Maximum	Average	Standard Deviation
1.	pH	7.1	8.6	7.80	0.31
2.	Total Alkalinity (mg/L)	168	871	495.04	174.15
3.	Total Harness (mg/L)	48	1100	276.26	195.79
4.	Calcium Hardness (mg/L)	21	423	118.38	87.05
5.	Ca^{+2} Ions (mg/L)	8.4	169.2	47.35	34.82
6.	MagnesiumHardness (mg/L)	26	677	157.88	111.31
7.	Mg^{+2} Ions (mg/L)	6.31	164.51	38.36	27.05
8.	Chloride (mg/L)	20	1455	171.04	206.72
9.	Nitrate (mg/L)	2	309	32.77	40.60
10.	Fluoride (mg/L)	0.14	12.2	1.82	2.20
11.	TDS (mg/L)	408	5434	1252.28	746.36
12.	EC (μmhos/cm)	583	7763	1788.87	1066.23

Table 7 : Unit Weightage of parameters for Drinking Water based on standard values

S.No.	Parameter	Standard Value (Sn)	Recommending Agency	Ideal Value (V_{id})	Unit Weight (Wn= K/Sn)
1.	pH	8.5	BIS/ICMR/WHO	7.0	0.097427
2.	Total Alkalinity	120	ICMR/WHO	0	0.006901
3.	Total Hardness	300	BIS/ICMR	0	0.002760
4.	Calcium	75	BIS/ICMR/WHO	0	0.011042
5.	Magnesium	30	BIS/ICMR/WHO	0	0.027604
6.	Chloride	250	BIS/ICMR	0	0.003313
7.	Nitrate	45	BIS/ICMR/WHO	0	0.018403
8.	Fluoride	1.0	BIS/ICMR/WHO	0	0.828133
9.	Total Dissolved Solids	500	BIS/ICMR/WHO	0	0.001656
10.	Electrical Conductivity	300	ICMR/WHO	0	0.002760

(All values are in mg/l except pH and EC)

Table 8 : Calculated WQI values and quality rating of water in the study area in Pre and Post Monsoon Seasons

S. No.	Village	Source	Sample No.	Pre- Monsoon		Post- Monsoon	
				WQI Value	Quality Rating	WQI Value	Quality Rating
1	Akhepura	HP	S1	81.883	VP	135.79	Unsuitable
		TW	S2	134.0011	Unsuitable	176.02	Unsuitable
2	Anantpura	HP	S3	51.405	Poor	86.357	VP
		TW	S4	166.1971	Unsuitable	81.65	VP
3	Banskho	HP	S5	195.8513	Unsuitable	97.203	VP
		TW	S6	180.74	Unsuitable	143.66	Unsuitable
4	Barala	HP	S7	186.73	Unsuitable	159.75	Unsuitable
5	Bassi	HP	S8	114.01	Unsuitable	82.41	VP
		TW	S9	79.036	VP	54.006	Poor
6	Benada	HP	S10	103.56	Unsuitable	105.01	Unsuitable
7	Bharampur	HP	S11	47.101	Good	66.214	Poor

S. No.	Village	Source	Sample No.	Pre- Monsoon		Post- Monsoon	
				WQI Value	Quality Rating	WQI Value	Quality Rating
8	Chainpuriya	HP	S12	119.65	Unsuitable	98.208	VP
9	Chapariya	HP	S13	107.41	Unsuitable	86	Poor
10	Charangarh	HP	S14	69.478	Poor	37.48	Good
11	Chatarpura	HP	S15	399.4	Unsuitable	228	Unsuitable
12	Danau Kalan	HP	S16	130.45	Unsuitable	108.21	Unsuitable
13	Danau Khurd	HP	S17	96.57	VP	57.788	Poor
		TW	S18	259.05	Unsuitable	231.79	Unsuitable
14	Garh	HP	S19	104.02	Unsuitable	110.81	Unsuitable
15	Ghasipura	HP	S20	18.051	Ex	55.921	Poor
		TW	S21	961.89	Unsuitable	1000.5	Unsuitable
16	Ghata	HP	S22	86.605	VP	135.02	Unsuitable
		TW	S23	77.189	VP	99.02	VP
17	Gudha Meena	HP	S24	35.005	Good	44.383	Good
18	Gumanpura	HP	S25	90.947	VP	177.55	Unsuitable
		TW	S26	139.77	Unsuitable	225.97	Unsuitable
19	Gwalini	HP	S27	166.34	Unsuitable	129.46	Unsuitable
20	Hans Mahal	HP	S28	40.613	Good	209.21	Unsuitable
21	Hanumanpura	HP	S29	78.8	VP	149.53	Unsuitable
		TW	S30	1052.2	Unsuitable	1024.6	Unsuitable
22	Jhajhwar	HP	S31	61.684	Poor	113.24	Unsuitable
		TW	S32	82.195	VP	105.51	Unsuitable
23	Jhar	HP	S33	68.938	Poor	49.235	Good
24	Kalyanpura	HP	S34	125.18	Unsuitable	79.435	VP
		TW	S35	163.72	Unsuitable	109.45	Unsuitable
25	Kaneta	HP	S36	32.02	Good	53.715	Poor
		TW	S37	73.891	Poor	45.58	Good
26	Kaneti	HP	S38	128.4	Unsuitable	25.72	Good
27	Kanota	HP	S39	70.143	Poor	123.71	Unsuitable
		TW	S40	159.55	Unsuitable	205.19	Unsuitable
28	Kashipura	HP	S41	277.16	Unsuitable	123.14	Unsuitable
29	Keshopura	HP	S42	80.245	VP	53.505	Poor
30	Kuthada Kalan	HP	S43	68.973	Poor	56.335	Poor
31	Lalgarh	HP	S44	131.98	Unsuitable	88.828	VP
32	Mundali	HP	S45	359.84	Unsuitable	477.01	Unsuitable
		TW	S46	297.49	Unsuitable	352.15	Unsuitable
33	Nagal Karna	HP	S47	370.28	Unsuitable	167.46	Unsuitable
		TW	S48	505.31	Unsuitable	286.99	Unsuitable
34	Parasoli	HP	S49	119.32	Unsuitable	137.63	Unsuitable
		TW	S50	197.94	Unsuitable	165.13	Unsuitable
35	Parempura	HP	S51	120.21	Unsuitable	88.47	VP
36	Patan	HP	S52	65.009	Poor	122.19	Unsuitable
37	Peepalabai	HP	S53	166.33	Unsuitable	52.83	Poor
		TW	S54	761.36	Unsuitable	452.44	Unsuitable
38	Peipura	HP	S55	127.99	Unsuitable	119.09	Unsuitable
		TW	S56	140.35	Unsuitable	123.45	Unsuitable
39	Rajwas	HP	S57	131.82	Unsuitable	128.82	Unsuitable
40	Ramser	HP	S58	326.39	Unsuitable	118.57	Unsuitable
		TW	S59	182.23	Unsuitable	103.09	Unsuitable
41	Ratanpura	HP	S60	101.89	Unsuitable	111.12	Unsuitable
		TW	S61	105.06	Unsuitable	236.81	Unsuitable
42	Roopura	HP	S62	128.8	Unsuitable	129.5	Unsuitable
		TW	S63	744.64	Unsuitable	728.18	Unsuitable
43	Sambhariya	HP	S64	15.25	Ex	197.83	Unsuitable
44	Shankarpura	HP	S65	359.35	Unsuitable	311.65	Unsuitable
45	Siya Ka Bas	HP	S66	85.941	VP	106.48	Unsuitable
46	Tehda	HP	S67	131.22	Unsuitable	141.3	Unsuitable
47	Tekchandpura	HP	S68	30.129	Good	33.43	Good

Global Journal of Science Frontier Research (B) Volume XV Issue VI Version I Year 2015

S. No.	Village	Source	Sample No.	Pre- Monsoon		Post- Monsoon	
				WQI Value	Quality Rating	WQI Value	Quality Rating
48	Tilpatti	HP	S69	89.386	VP	80.97	VP
49	Todabhata	HP	S70	181.07	Unsuitable	162.15	Unsuitable
50	Tunga	HP	S71	13.535	Ex	88.001	VP

Where- VP = Very Poor, Ex = Excellent

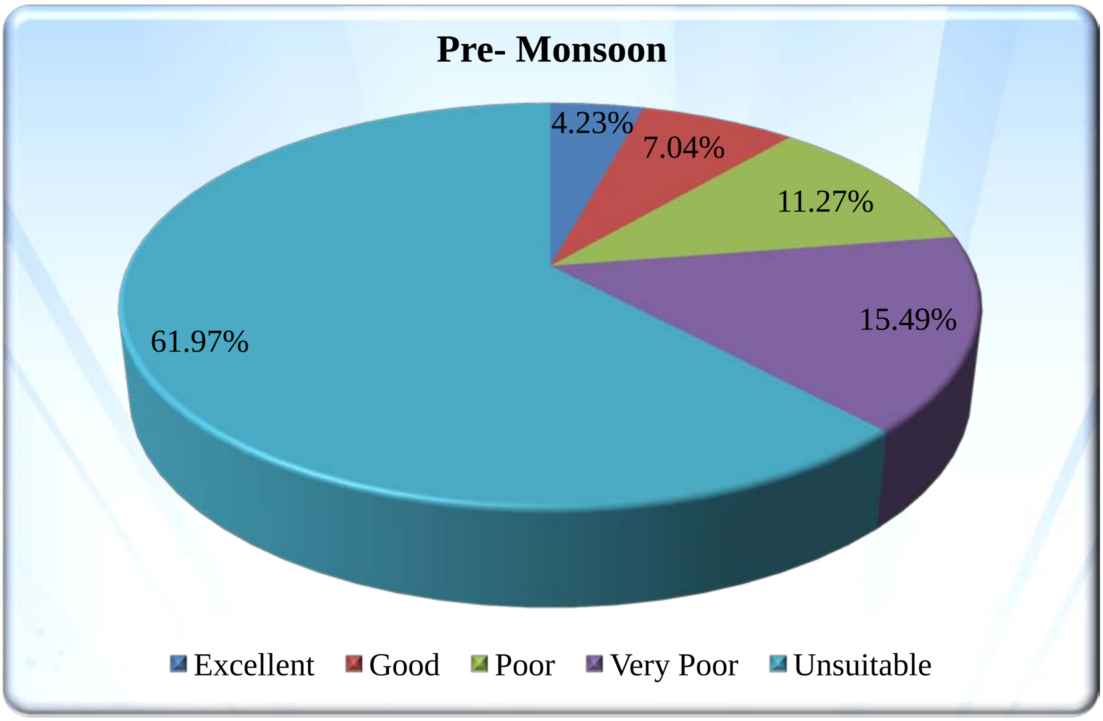

Figure 1 : Percentage representation of WQI classification in Pre monsoon season

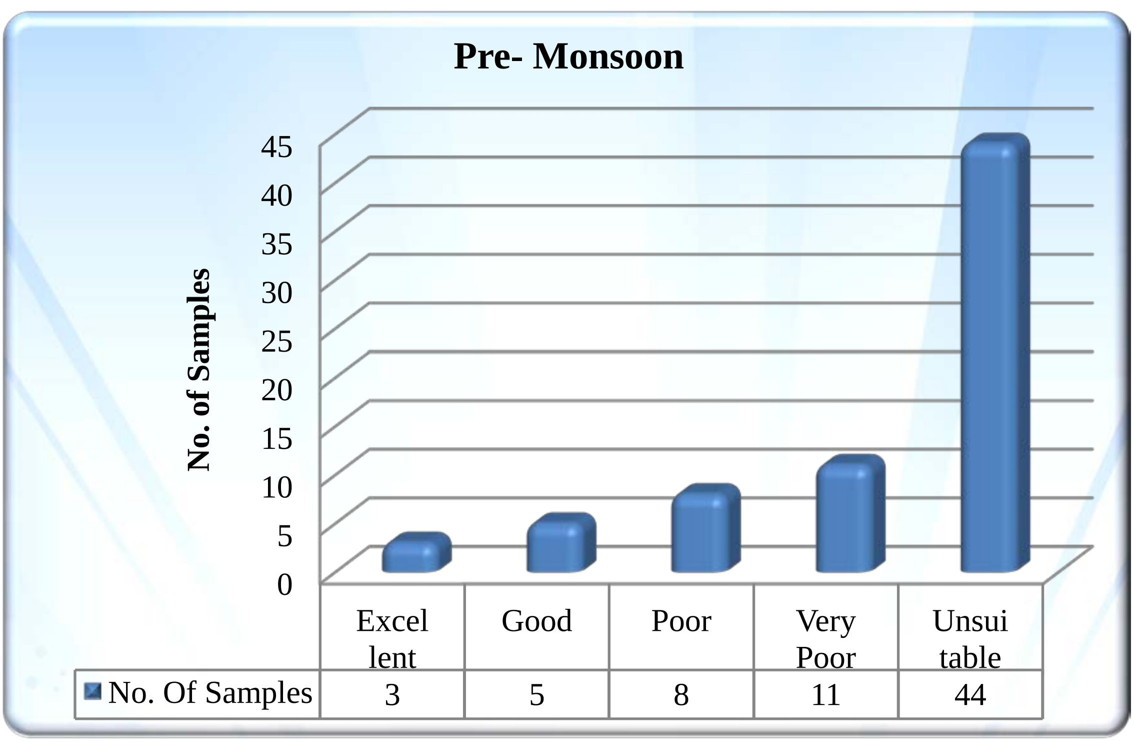

Figure 2 : Number of Villages classified on the basis of WQI values in Pre monsoon season

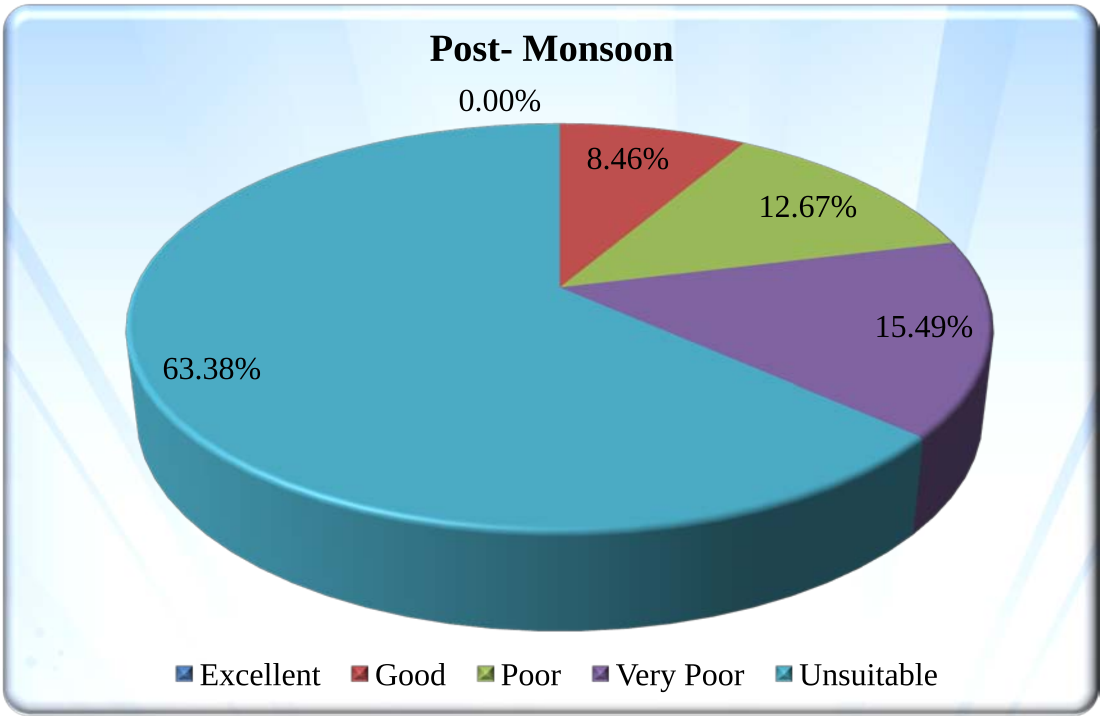

Figure 3 : Percentage representation of WQI classification in Post monsoon season

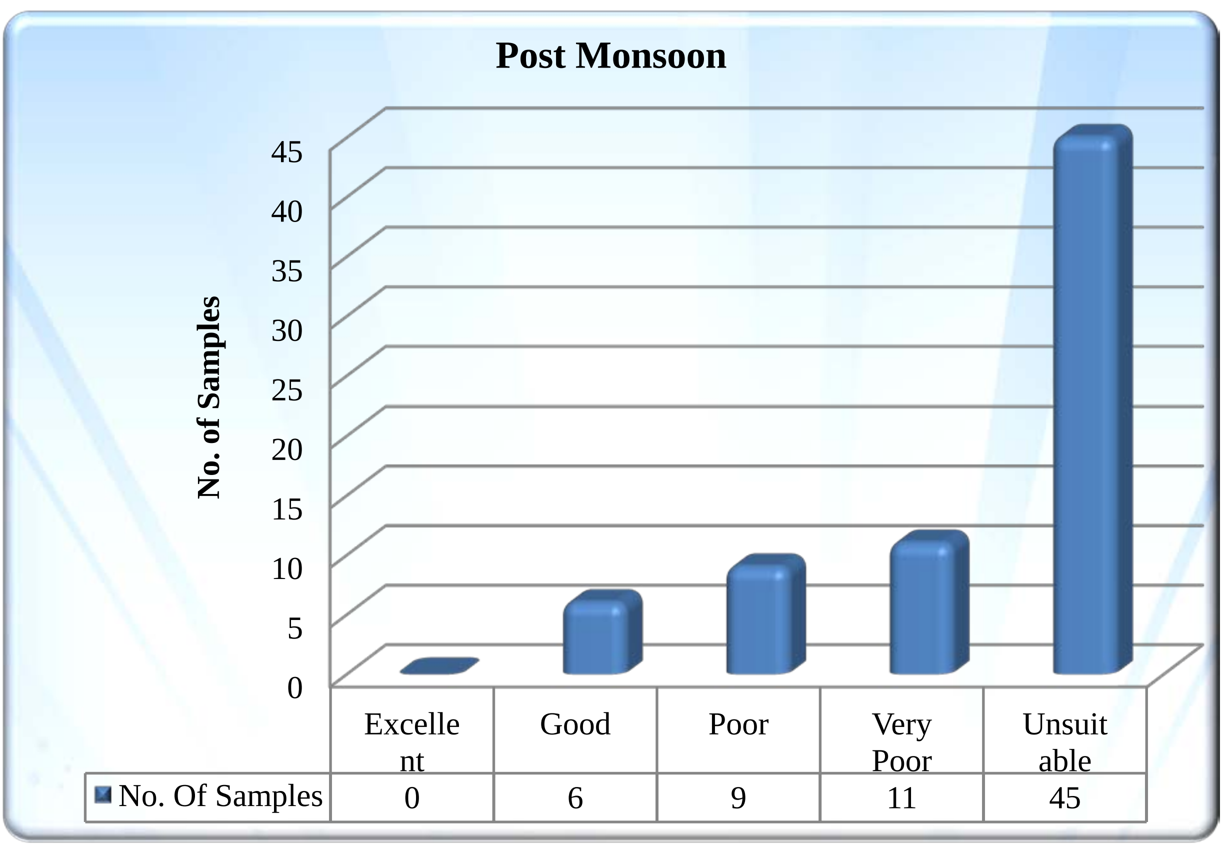

Figure 4 : Number of Villages classified on the basis of WQI values in Post monsoon season

ii. *Spatial Variation of WQI*

According to the results, it is revealed that in pre-monsoon season only three sampling sites namely *Ghasipura* (HP), *Sambhariya* and *Tunga* exhibit excellent groundwater quality for drinking, and five sampling sites namely *Bharampuri, Gudha Meena, Hans Mahal, Kaneta (HP)* and *Tekchandpura* indicate good ground water quality for drinking. The remaining 63 sampling sites are not directly suitable for potability because they are classified as poor, very poor and unfit categories as per the WQI ranges.

In post monsoon season there is not even a single sampling site under the excellent category and only six sampling sites namely *Charangarh, Gudha Meena, Jhar, Kaneta (TW), Kaneti,* and *Tekchandpura* fall in the category good for drinking. The rest 65 sampling sites are not suitable for potability as according to their WQI ranges they are classified as poor, very poor and unfit for drinking purposes. Graph (Figure 5) depicts the spatial variation of the WQI in the study area for the pre and post monsoon seasons both.

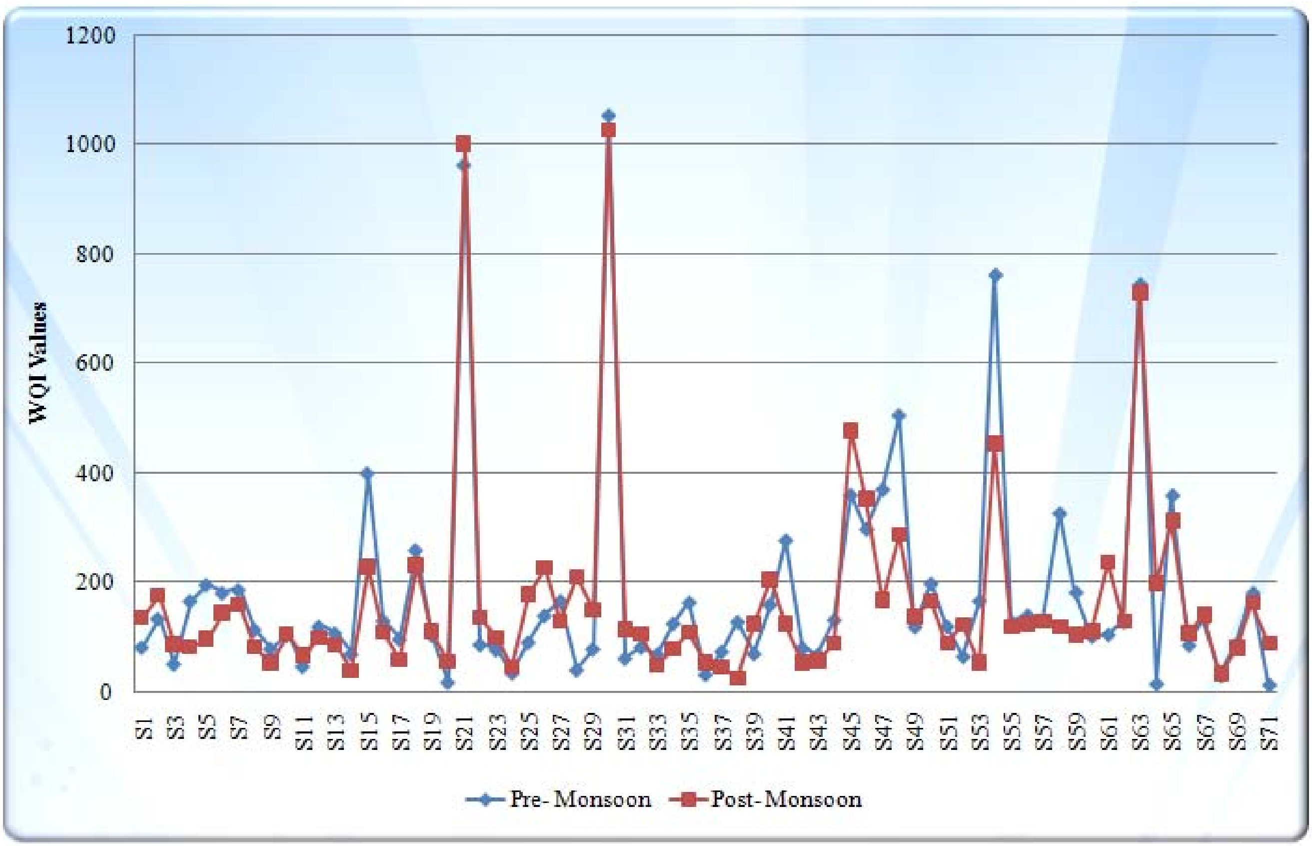

Figure 5 : Comparative graphical representation of WQI of groundwater at different Locations in the study area in pre and post monsoon seasons

Most of the stations are having groundwater of very poor and unsuitable categories with water quality ranging from 75 to 100 and >100 respectively. Table 9 and 10 contains the information about the various sampling sites in the study area with varying values of WQI in pre and post monsoon season respectively. These tables provide the appropriate information to take necessary steps in treatment of groundwater in the study area.

Table 9 : Classifications of groundwater in the Study area with respect to WQI in Pre Monsoon Season

Name of the Sampling Site	No. of Samples	WQI Range	Quality Category
Ghasipura (HP), Sambhariya, Tunga.	03	0-25	Excellent
Bharampuri, Gudha Meena, Hans Mahal, Kaneta (HP), Tekchandpura.	05	26-50	Good
Anantpura (HP), Charangarh, Jhajhwar (HP), Jhar, Kaneta (TW), Kanota (HP), Kuthada Kalan, Patan.	08	51-75	Poor
Akhepura (HP), Bassi (TW), Danau Khurd (HP), Ghata (both), Gumanpura (HP), Hanumanpura (HP), Jhajhwar (TW), Keshopura, Siya Ka Bas, Tilpatti.	11	76-100	Very Poor
Akhepura (TW), Anantpura (TW), Banskho (HP and TW), Barala, Bassi (HP), Benada, Chainpuriya, Chapariya, Chatarpura, Danau Kalan, Danau Khurd (TW), Garh, Ghasipura (TW), Gumanpura (TW), Gwalini, Hanumanpura (TW), Kalyanpura (HP and TW), Kaneti, Kanota (TW), Kashipura, Lalgarh, Mundali (HP and TW), Nagal Karna (HP and TW), Parasoli (HP and TW), Parempura, Peepalabai (HP and TW), Peipura (HP and TW), Rajwas, Ramser (HP and TW), Ratanpura (HP and TW), Roopura (HP and TW), Shankarpura, Tehda, Todabhata.	44	Above 100	Unsuitable for Drinking

Table 10 : Classifications of groundwater in the Study area with respect to WQI in Post Monsoon Season

Name of the Sampling Site	No. of Samples	WQI Range	Quality Category
Nil	00	0-25	Excellent
Charangarh, Gudha Meena, Jhar, Kaneta (TW), Kaneti, Tekchandpura.	06	26-50	Good
Bassi (TW), Bharampuri, Chapariya, Danau Khurd (HP), Ghasipura (HP), Kaneta (HP), Keshopura, Kuthada Kalan, Peepalabai (HP).	09	51-75	Poor
Anantpura (HP and TW), Banskho (HP), Bassi (HP), Chainpuriya, Ghata (TW), Kalyanpura (HP), Lalgarh, Parempura, Tilpatti, Tunga.	11	76-100	Very Poor
Akhepura (HP and TW), Banskho (TW), Barala, Benada, Chatarpura, Danau Kalan, Danau Khurd (TW), Garh, Ghasipura (TW), Ghata (HP), Gumanpura (HP and TW), Gwalini, Hans Mahal, Hanumanpura (HP and TW), Jhajhwar (HP and TW), Kalyanpura (TW), Kanota (HP and TW), Kashipura, Mundali (HP and TW), Nagal Karna (HP and TW), Parasoli (HP and TW), Patan, Peepalabai (TW), Peipura (HP and TW), Rajwas, Ramser (HP and TW), Ratanpura (HP and TW), Roopura (HP and TW), Sambhariya, Shankarpura, Siya Ka Bas, Tehda, Todabhata.	45	Above 100	Unsuitable for Drinking

V. Conclsions

WQI values of groundwater samples analyzed for pre and post monsoon seasons depict that there exists an uncertain and narrow change in the WQI values which is not very significant with reference to potability and groundwater quality.

The results of current study revealed that ground water, used by the people residing in villages of Bassi Tehsil, is not suitable for drinking purpose. So, there is a need of continuous monitoring of water quality and proper environment management plan must be adopted to control drinking water pollution immediately. Based on these results and analysis of water samples, it is also recommended to use water only after boiling and filtering or by Reverse Osmosis treatment for drinking purpose by the individuals to prevent adverse health effects.

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Adsorption and Kinetic Study of Ni(II) Ions from Aqueous Solution using Natural Syrian Zeolite

By Dr. Ibrahim Raheb
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Abstract- Adsorption of Ni(II) ions from aqueous solution using natural Syrian zeolite has been studied. Batch shaking adsorption experiments were performed in order to determined the effects of contact time, pH and initial concentration on removal process. The experimental equilibrium data were tested for the Langmuir and Freundlish isotherms. It was determined that removal of Ni(II) ions was well fitted by pseudo-first order kinetic model. The adsorption involves a film diffusion, an intra-particle diffusion and a chemical ion-exchange between Na^+ ions of adsorbent and the Ni^{2+} ions. The adsorption is endothermic and spontaneous process under studied conditions.

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GJSFR-B Classification : FOR Code: 030703

ADSORPTIONANDKINETICSTUDYOFNIIIIONSFROMAQUEOUSSOLUTIONUSINGNATURALSYRIANZEOLITE

Strictly as per the compliance and regulations of :

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Abstract- Adsorption of Ni(II) ions from aqueous solution using natural Syrian zeolite has been studied. Batch shaking adsorption experiments were performed in order to determined the effects of contact time, pH and initial concentration on removal process. The experimental equilibrium data were tested for the Langmuir and Freundlish isotherms. It was determined that removal of Ni(II) ions was well fitted by pseudo-first order kinetic model. The adsorption involves a film diffusion, an intra-particle diffusion and a chemical ion-exchange between Na^+ ions of adsorbent and the Ni^{2+} ions. The adsorption is endothermic and spontaneous process under studied conditions.

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I. Introduction

Environmental preservation is nowadays mater of deep concern. Heavy metals release in wastewaters is on of most worrying pollution causes, as it effects on life may be particularly serious, either referring to plants and animals, or to man, reached indirectly by the toxic through food chain. Heavy metals are well-known toxic substances and therefore their removal from wastewater is require prior to discharge into receiving water[1,2].

Ions of heavy metals like copper, nickel, zinc, cadmium, lead, chromium and mercury as a significant impact on the environment since they are often detected in industrial wastewaters. Many techniques are using to removal of heavy ions. Conventional methods involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction biosorption, adsorption, etc [3-6].

Adsorption and ion-exchange methods are widely using for removal of the heavy ions from aqueous solutions because of simple and low coast of these methods.

Natural zeolite is generally regarded as the suitable material for using as a adsorbent and exchanger for wastewater treatment. Zeolites are widely used in ion-exchange applications, where they exchange cations from there structure with dissolved ones. The most important property of zeolite is the ion-exchange capacity expressing the ability of the material to take up cations. It also important that Zeolites are environmentally friendly materials[3,7,8].

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The present study discusses the possibility of the Syrian natural zeolite for removing nickel ions from aqueous solution. Also, the effect of different parameters on ion-exchange process were investigated. Some kinetic parameters were calculated for determination of adsorption mechanism. It is thought that results of this study can be useful for treatment processes of sectors containing heavy metal in their wastewaters.

II. Eperimental

a) *Materials*

All chemicals used in this study were analytical grade reagents. The natural zeolite ore using in this work collected from Omm'Ozen region in Syria. It was crushed and then sieved to different fractions, of which 100-200μ, was used in this study. This adsorbent is containing different zeolite phases (analcim, philipsite and shabazite) [9]. A certain amount of natural zeolite washed with distilled water tree times to avoid any effects from dissolved salts in the equilibrium solution. The adsorbent was then dried at 120°C for 24h and named Z. Modified zeolite with Na ions was prepared as following: 20g of Z sample was added to 500ml of NaCl(1M) solution, agitated at room temperature for 24h filtrated and washed by distilled water and then dried at 120°C for 24h.and named Z-Na sample. The stock solution of Ni(II)(1000mg/l) was prepared by dissolving a weighed quantity of $NiCl_2.6H_2O$ salt in bi-distilled water. The stock solution was used to prepare different solutions with Ni(II) concentration ranging (100, 200, 400, 700, 1000mg/l). Before adding the adsorbent, the pH of each solution adjusted to the required value by adding (0.1 M NaOH or 0.1 M HNO_3).

b) *Equilibrium Studies*

The batch ion-exchange experiments performed in a wide variety of conditions including contact time, pH, temperature and initial concentration. Effects of each factor were determined keeping other variables constant. In the experiments 0.3g of adsorbent was added to 50ml of Ni(II) solutions. Solutions were shacked for predetermined period. At the end of the experiment, solution filtrated and the metal contents in solution determined by Atomic Absorption Spectroscopy method. In these experiments, the averages of three tested samples reported.

c) Isotherm Studies

The adsorption capacity was calculated using following formula:

$$q_e = (C_0 - C_e).\frac{V}{m} \qquad (1)$$

Where q_e(mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration(mg/L), respectively, V(L) is the volume and m(g) is the amount of the adsorbent.

The nickel removal percentage was calculated using the formula:

$$\mathrm{Re}\,moval(\%) = \frac{C_0 - C_e}{C_0}.100 \qquad (2)$$

The data obtained were applied to Langmuir isotherm using the following liner expression of this model [10]:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}.K_L}.\frac{1}{C_e} \qquad (3)$$

Where q_{max}(mg/g) and K_L(L/mg) the Langmuir constants related to the ion-exchange capacity and energy of ion-exchange, respectively. Another isotherm, the Freundlish isotherm also used, which expressed as follows [10]:

$$Log\ q_e = Log\ K_f + \frac{1}{n} Log\ C_e \qquad (4)$$

Where K_f and n are the Freundlish constants.

d) Kinetic and Thermodynamic studies

Kinetic experiments were performed by using 50ml of nickel solution of various concentrations (100, 200, 400mg/L). To these solutions, we added 0.3g of modified zeolite Z-Na and shacked. Samples were taken at different time intervals (0-480 min) and different temperatures (298,313, 333 K) and remaining metal concentrations were determined. The rate constants were calculated using tow reaction-based kinetic models, the pseudo-first rate equation whose integrated form is given by formula [11].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (5)$$

Where q_e and q_t are the amount of Ni(II) adsorbed(mg/g) at equilibrium and at the time t, respectively, and k_1(min^{-1}) is the rate constant. The integrated form of the pseudo-second order rate reaction also was used [11].

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where k_2($g.mg^{-1}.min^{-1}$) is the rate constant of the pseudo-second order adsorption.

The effect of the temperature on the removal of Ni(II) by Z-Na adsorbent was studied and the activated energy was calculated using Arrhenius equation:

$$Ln\ k = Ln\ A - \frac{E_a}{R}.\frac{1}{T} \qquad (7)$$

Thermodynamic parameters such as enthalpy ΔH^0, entropy change ΔS^0 and Gibbs free energy ΔG^0 for the adsorption of Ni(II) were calculated using the equations[12]:

$$Ln\ K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (8)$$

$$\Delta G^0 = -RT\ LnK_d \qquad (9)$$

Where R is the general gas constant, 8.314 J/mol.K and T is the adsorption absolute temperature, K_d(ml/g) is the distribution coefficient which is obtained by the following equation:

$$K_d = \frac{q_e}{C_e} = \frac{C_0 - C_e}{C_e}.\frac{V}{m} \qquad (10)$$

III. Results and Discussion

a) Effect of contact time

Due to equilibrium nature of the removal process of Ni(II) by the modified zeolite Z-Na, it seen that the contact time affect the removal efficiency of the used adsorbent. Hence, the effect of contact time on the removal of Ni(II) by the Z-Na was studied in the batch experiment. The corresponding results are given in Fig.1. It cam be seen that the removal of Ni(II) ions from aqueous solution using The Z-Na increased during time and reached to nearly constant amount at equilibrium conditions after 360min. This obtained time was selected for the next adsorption experiments. The variation in the time of adsorption may also be due to the fact that initially all sites on the surface of Z-Na were vacant and the Ni(II) ion concentration gradient was relatively high. After 360min the adsorbent surface becomes saturated with respective metal and the removal efficiency becomes almost constant.

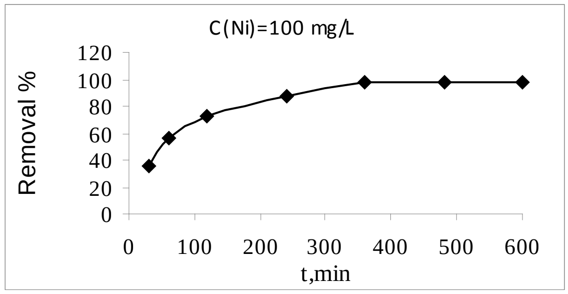


Fig.1 : Effect of contact tine on Ni(II) removal by Z-Na

$C_{Ni(II)}$=100mg/L, V=50mL, m=0.3g, T=298K, pH=6

b) Effect of pH solution

The effect of pH on the ion-exchange of Ni(II) by the Z-Na is presented in Fig.2. The pH of aqueous solution was an important parameter that controlled the ion-exchange process.

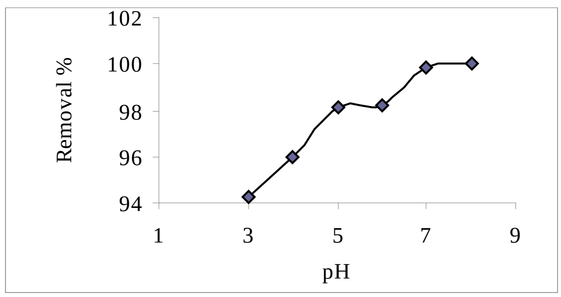


Fig.2 : Effect of pH on the removal of Ni(II)

$C_{Ni(II)}$=100mg/L, V=50mL, m=0.3g, T=298K, t=360min

Adsorption of Ni(II) increased with increasing pH to a pH in range 5-6, then increased up to pH 7-8 where beginning the precipitation process. Under acidic conditions the Z-Na surface will be completely covered with H^{+} ions and the Ni(II) ions cannot compete with them. However, with increasing pH, the competition from the $H^{=}$ ions decreases and the positively charged Ni(II) ions can be exchanged and be also adsorbed at the negatively charged sites on the Z-Na. At pH higher 8 the precipitation process $Ni(OH)_2$ will accurse[13]. Based on these results, Z-Na exhibited a good capacity for removing Ni(II) from solution at a range of pH values from 5-8. The maximum removal about 98% was at pH=5.

c) Adsorption isotherm

Adsorption equilibrium measurements were used to determine the maximum adsorption capacity and the obtained data were formulated into the most commonly models include Langmuir and Freundlish isotherms[14].

The adsorption capacity was calculated using formula (1). Fig.3 shows the adsorption isotherm for Ni(II) on adsorbent Z and Z-Na zeolite.

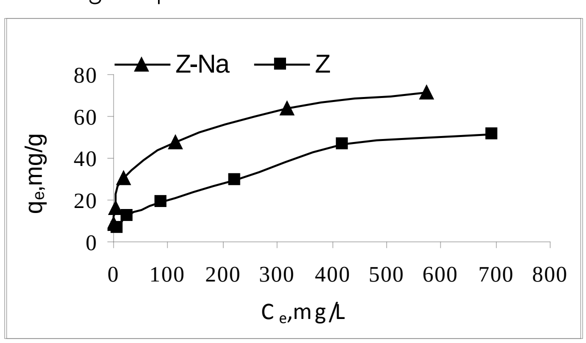


Fig.3 : The adsorption isotherm for Ni(II) on Z and Z-Na zeolite

V=50mL, m=0.3g, T=298K, t=360min

It is seen from Fig.3 that the adsorption capacity of both Z and Z-Na zeolite increases with the Ni(II) solution concentration. The equilibrium data from Fig.3 have been analyzed according to equation (3) and (4).

The Langmuir isotherm is a commonly applied model for adsorption on a completely homogeneous surface. The model assumes uniform adsorption energies onto the surface. The Freundlish model is shown to be consistent with exponential distribution of active sites, characteristic of heterogeneous surfaces. The values of the Langmuir constants K_L and q_{max} and Freundlish constants K_f and n were determined from the slope, intercept in Fig.4(a) and Fig.4(b) respectively and the results presented in table (1).

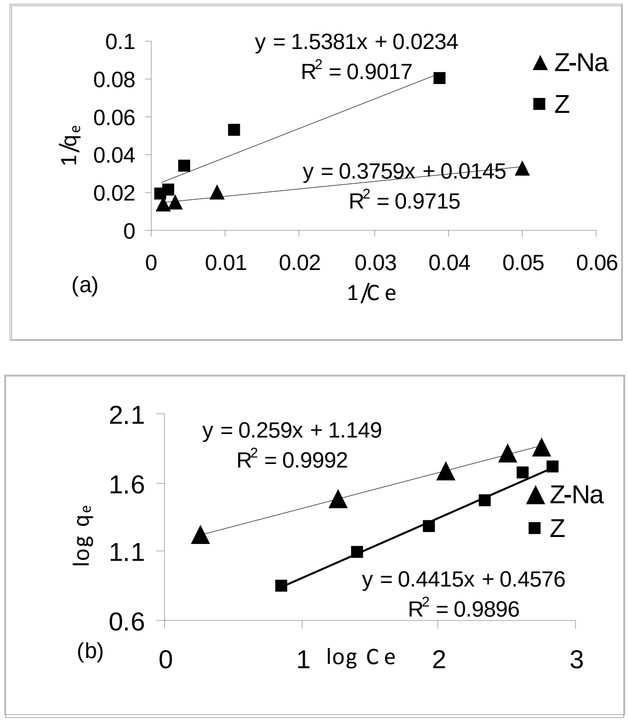


Fig.4 : Langmuir (a) and Freundlish (b) adsorption isotherms of Ni(II)

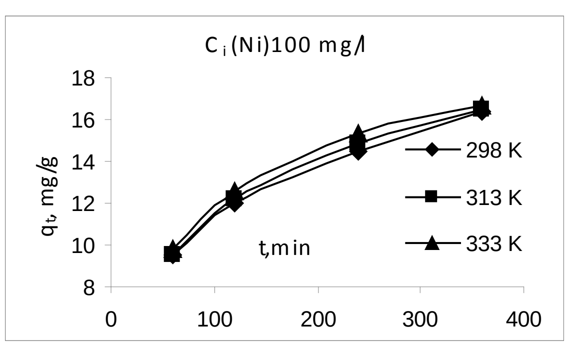
Table(1) : Isotherm Parameters Calculated for Ni(II) Removal on Adsorbent Z and Z-Na

	Langmuir model			Freundlish model		
	q_{max}	K_L	R^2	K_f	n	R^2
Z	43.48	0.0149	0.901	2.86	2.27	0.989
Z-Na	71.43	0.0373	0.971	14.1	3.86	0.999

Comparing of R^2 values of tow isotherm models, confirms that the Freundlish model is the best to describe the adsorption data. On the other hand, a competitive adsorption of Ni(II) accurse on the surface because the value of n>1. From the Langmuir isotherm, the maximum ion-exchange capacity q_{max} was 43.48 and 71.43 mg/g for Z and Z-Na adsorbents, respectively. It was seen the important of the modification process of zeolite for the removal of heavy metals ions from the aqueous solutions.

d) kinetic studies

In order to determined the ion-exchange kinetics of Ni(II) on the modified Z-Na, the pseudo-first order and pseudo-second order kinetics models were examined. On the other hand some of the thermodynamic parameters were determined. The Ni(II) adsorption dependence on time was studied at 298, 313, 333K for solutions with C_0=100,200 and 400mg/L. The uptake values for removal of Ni(II) from solution are shown in Fig.5.



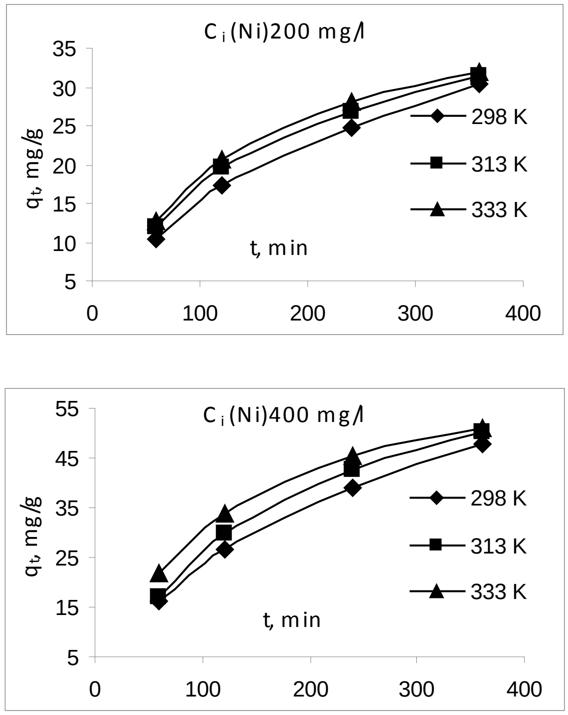
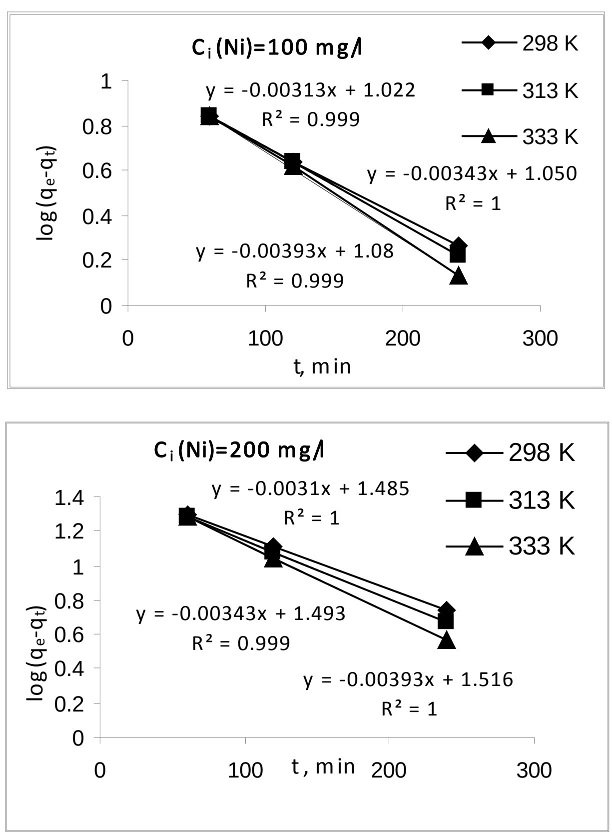


Fig. 5 : Adsorption kinetics for Ni(II) on Z-Na for different initial Ni(II) concentrations

It is seen from the Fig.5 that the adsorption takes place in tow steps. The first step accurse at the beginning stages(i.e. apporx. in the first 50-250 min), when the Ni(II) uptake increases. After these periods adsorption process exhibit slower rate and reach equilibrium after 360min. Similar behavior was found in other systems[15]. The data from Fig.5 were analyzed using (5,6) equations and presented in Fig. 6 and 7. Calculated rate constants $k_{1,}$ k_2 and correlation coefficients R^2 were summarized in table 2.



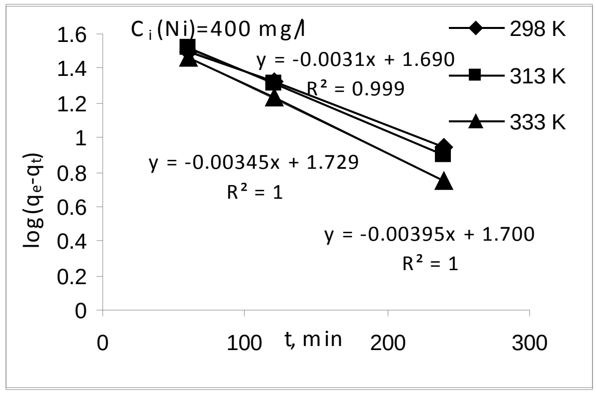


Fig.6 : Pseudo-first order reaction kinetics for the adsorption of Ni(II) onto Z-Na

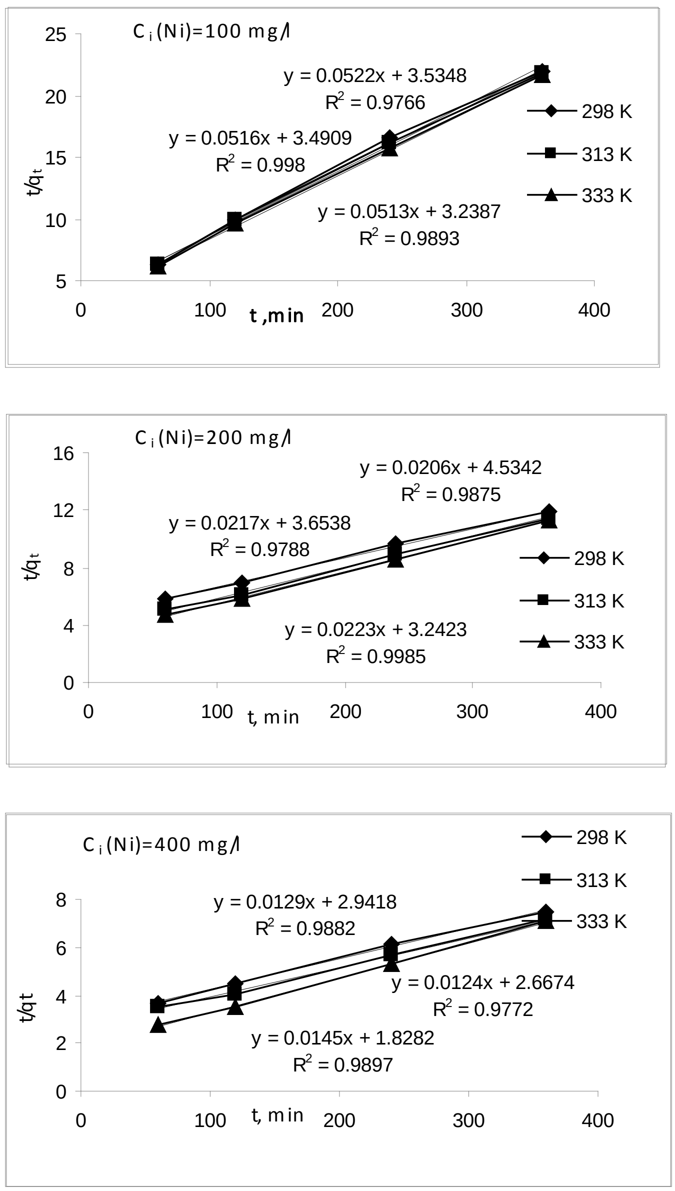


Fig.7 : Pseudo-second order reaction kinetics for the adsorption of Ni(II) onto Z-Na

Table 2 : Rate constants and R^2 values for the pseudo first-and second order reaction kinetics and activation energy of the removal of Ni(II) onto Z-Na

C_0,mg/L	T,K	$k_1.10^3$ min^{-1}	R^2	$k_2.10^3$ g/mg/min	R^2	E_a kJ/mol
100	298	7.2	0.999	0.765	0.976	5.32
	313	7.8	1	0.745	0.998	
	333	9	0.999	0.803	0.989	
200	298	7.1	1	0.088	0.987	5.64
	313	7.8	0.999	0.120	0.978	
	333	9	1	0.149	0.998	
400	298	7.1	0.999	0.049	0.988	5.62
	313	7.9	1	0.054	0.977	
	333	9	1	0.107	0.989	

As seen from table 3 the values of correlation coefficients for pseudo-first order are higher than R^2 for pseudo-second order and the k_1 rate constant increases quite slightly with temperature. The k_2 rate constant variables when initial concentration is increasing. The studied adsorption is better described by the pseudo-first order model. From the results in table 3 we can say, that the process accurse according to the film diffusion and interaction particles diffusion mechanisms[16].

The variation of k_1 with temperature in the 298-333K region was used for the calculation of the activation energy(E_a) of the adsorption. The activation energy was calculated using Arrhenius equation(7) as shown in Fig.8.

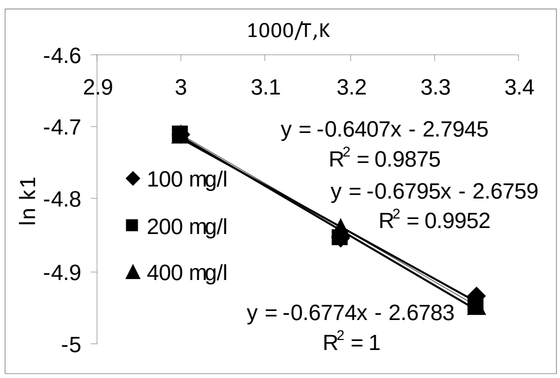


Fig. 8 : The Arrhenius plot using rate constant values from table 3 for the pseudo-first order

The values of the activation energy in table 2 are quite small and change only slightly for different initial concentrations. In general a low E_a value means that the adsorption involved is physisorption[17].

The data obtained from the adsorption experiments at 298, 313 and333K and the initial Ni(II) concentrations of 100, 200 and 400 mg/L, were used for the calculation of thermodynamic properties using (8-10) equations. The plot of ln K_d vs 1/T in Fig.9. gave a strait line, and the values of ΔH^0 and ΔS^0 can obtained from the intercept and slope, respectively. The thermodynamic parameters are presented in table 3.

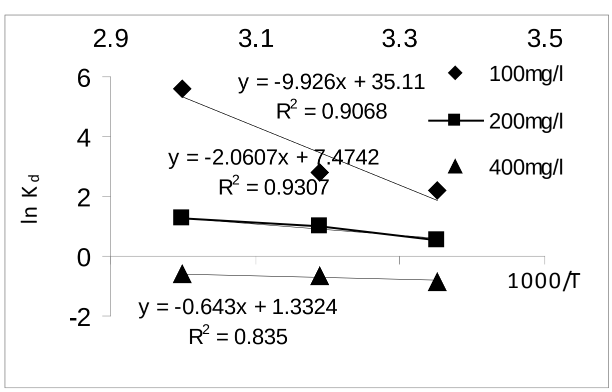


Fig. 9 : The plot of ln K_d vs 1/T for different initial Ni(II) concentrations

Table 3 : Thermodynamic parameters for the Ni(II) adsorption on Z-Na

C_0 mg/L	T,K	LnK_d	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 $J/K.mol$	R^2
100	298	2.207	-5.48	82.4	291.4	0.906
	313	2.803	-7.29			
	333	5.626	-15.50			
200	298	0.509	-1.26	17.12	62.14	0.930
	313	1.014	-2.64			
	333	1.240	-3.43			
400	298	-0.853	2.11	5.34	11.07	0.835
	313	-0.661	1.72			
	333	-0.623	1.72			

The ΔG^0 values in table 4 show that, the adsorption of Ni(II) on Z-Na accurse spontaneously in the 298-333K temperature range and the spontaneity slightly decrease with temperature. The Ni(II) adsorption is endothermic($\Delta H^0 > 0$). It is also evident that the spontaneity as well as the ΔH^0 and ΔS^0 values all decreases as the initial Ni(II) concentration increases. The similar behavior has also been reported for so0me other adsorbents[18]. The positive ΔS^0 values reflect the fact that the adsorption involves the liberation of tow Na^+ when one Ni^{2+} ion is bound to the adsorbent.

IV. Conclusion

The Syrian natural zeolite is effective in removing the nickel(II) ions from aqueous solutions by adsorption.

The Ni(II) ions distributed inside the Z-Na adsorbent indicating that the removal process from water solutions is mainly an ion-exchange. The adsorption kinetics is described by the pseudo-first order model. The activation energy ~ 5kJ/mol. The adsorption involves a combination of the film and interaction particle diffusions, and chemical cation-exchange between Na^+ ions of zeolite and the Ni^{2+} ions. The process is endothermic and spontaneous in the 298-333K temperature range.

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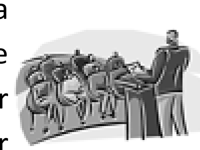

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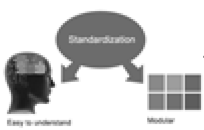

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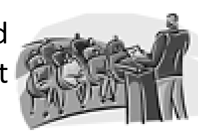

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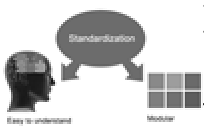

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References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

Index

A

Acetonitrile · 3, 4
Arrhenius · 27, 30

B

Biases · 11

C

Chlorobutane · 3, 4, 5
Cholinium · 8

F

Freundlish · 25, 27, 29

H

Halide · 1

I

Imidazolium · 1, 5, 8, 9

L

Langmuir · 25, 27, 29

M

Methylimidazolium · 1, 3, 8

P

Pseudo · 25, 27, 29, 30, 31

T

Thawed · 2, 4
Toluene · 2, 4

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