



FLUORIDE CONTENT IN GROUNDWATER QUALITY OF SOME VILLAGES IN RAJASTHAN, INDIA

¹Kishan Gopal Jhanwar, ²Rajeev Mehta, ³Preeti Mehta
^{1,2,3}Department of Chemistry, Sangam University, Bhilwara-311001, Rajasthan

ABSTRACT

A study of the water quality condition of many villages in Rajasthan carried out to assess risk to human health. It was found that ground water of many villages of Rajasthan is contaminated with fluoride by naturally fluoride rich rock salt system. Physicochemical analysis has main consideration to assess the quality of water for its best utilization like drinking, irrigation. The result of this study helps in enhancing awareness of health hazards of contaminated water. Drinking water with excessive concentration of fluoride causes fluorosis which progresses gradually and becomes a crippling malady in the long run. It affects young, old, poor, rich, rural, and urban population. It has attained a very alarming dimension. Rajasthan suffers both the problems of quantity and quality of water. In most part of the state groundwater is either saline or having high nitrates and fluoride content. Obviously, groundwater is the major source of drinking water and over 94% of the drinking water demand is met by groundwater. Excess fluoride concentration in drinking water has deleterious effects on human health. All the districts in Rajasthan are engulfed by the clutches of fluorosis, to a varying degree. There being no perennial surface source for drinking water, the state is dependent chiefly on groundwater and its level is deeper year-by-year due to over exploitation. As the water table is receding more and more water sources are becoming prone to higher fluoride concentration. The pattern and prevalence of fluorosis in human population are determined by a number of epidemiological factors like water chemistry, demographic and nutritional profile of the community and high mean annual temperature of the area. UNICEF has taken definite steps in collaboration with Government and NGOs, to deal with the problem of fluorosis in Rajasthan. Beside, changing dietary habits, harvesting rainwater and promoting defluoridation of drinking water at household level can yield spectacular results in this regard. Different defluoridation techniques are being tried to make drinking water free from fluoride contamination. Awareness camps are being organized all over the state to make the masses aware of ill effects of fluoride problems. The state government has also taken up various programmed action plans such as artificial recharge of groundwater, rejuvenation of traditional baoris-kunds, RWH and judicious use of underground water for drinking and other purposes. Keeping in view the underground realities, this hydrotoxicants in water supplies of different locations and the people suffering from fluorosis and other ailments were identified in specified zonal localities. [1,2]

KEY WORDS: Fluorosis, ppm, Fluoride, Ion-Selective Electrode

INTRODUCTION

Water is one of the five elements described in "shastra" to life. Water is most useful matter on the earth for all lives. Significance of water as a natural agent is not only determined by its availability on the surface of the earth but also determined by its physical & chemical properties. High fluoride in drinking water is a problem found on both the ground & surface of water. Water is a universal solvent so it has the capability

to dissolve nearly all natural compounds. The chemical composition of natural water is developed as the result of many diseases in men. Fluoride is a natural component of the earth's crust and is also found in many minerals, like fluorite, fluoroapatite, etc. due to its high electronegativity. Only fluoride forms are found in water. Fluoride forms sparingly soluble compounds in natural water. It enhances the fluoride accumulation of high fluoride concentration in soil & water due to this accumulation of high fluoride



concentration lead health problem in live stock. It has been reported by health organization as an essential substance in water for building healthy teeth at level with in 1 mg/L concentration. The maximum permissible limit of fluoride in water is 1.5 mg/L by WHO & ICMR⁹. The effects of fluoride in drinking water have been studied. Consumers also exhibiting positive symptoms after taking such water.Effects of fluoride “fluorosis” were first introduced by schortt and it is reported in both human & cattle.High fluoride concentration has been found where fluoride rich volcanic rocks are common. The distribution of fluoride content in the ground water of state is reported on the based analysis of ground water quality monitoring data. Fluorosis is a most widespread

geochemical disease affecting more than 66 million people including million children under the age of 14 year . The first presentation of water quality slandered was made in 1914 by USPHS. The fluoride concentration laid down by USPHS (1962)³² WHO (1963)³³ and ICMR (1962) In India nearly 177 districts in 19 states have been confirmed to be fluoride affected. In Rajasthan out of 27 districts 16 districts have been confirmed fluoride affected area and have more than permissible limit concentration of fluoride but Tonk district is the most worst affected one. In Rajasthan 6000 villages out of 33000 have water with fluoride concentration exceeding the permissible limit and dental & skeletal fluorosis is wide spread in these villages . [3,4]



Fig.1. Map showing fluoride variation in Rajasthan

The presence of fluoride in ground water can be attributed to geological reasons . In recent years, great concern has been universally voiced regarding environmental pollution arising as a side effect of industrial and other human activities. In our own country, with the advent of industries, more and more toxic substances are either used as raw material or emitted during manufacturing processes in the form of dusts, fumes, vapours and gases. These pollutants ultimately dissipate in the working environment and pose occupational health hazards. Many of these chemicals are hazardous and impose chronic impact on organisms including human beings. By the very nature of their wide distribution, the halogen group of minerals, including fluorides, forms a natural part of our environment. In order to strike a balance between such an environment and general health of human population and live stock of any region, the level of fluoride concentration in potable water, food, soil and atmosphere needs to be an appropriate level. Fluorosis, though a common endemic problem of our country is more widespread and acute in Rajasthan. Defluoridation of contaminated water alone doesnt bring the fluoride content to safe limit It would be

necessary to overcome the toxicity of the remaining fluorides ingested other sources. This is achieved by effecting minor changes in the diet and dietary habits of the population compatible with their social system and available resources Since soil fluorides usually originate from micas are associated with clay-sized minerals, heavy soils tend to have substantially higher concentrations than sandy soils. Fluoride enters the soil through weathering of rocks, precipitation and impure water, mainly from waste run off and fertilizers.[5,6] Since much of our food is ultimately derived from plants often grown in contaminated areas, fluoride in soil is an important source of intake. Anti- oxidants possessing antagonistic effect play prophylactic role in preventing fluorosis. A malady- remedy analysis of the problem of fluorosis has to be holistic in character as the disease not only affects human beings but also plants and animals. Therefore , we need to have , as far as possible, an idea of the source of fluoride and its dispersion in the environment including land, water and air. Based on such study , an integrated approach has to be evolved to draw up a strategy for the control of this disease. In this manuscript clinical manifestations of various degrees of fluorosis and strategies concerning



to mitigation of fluoride content in water, have been delineated.[7]

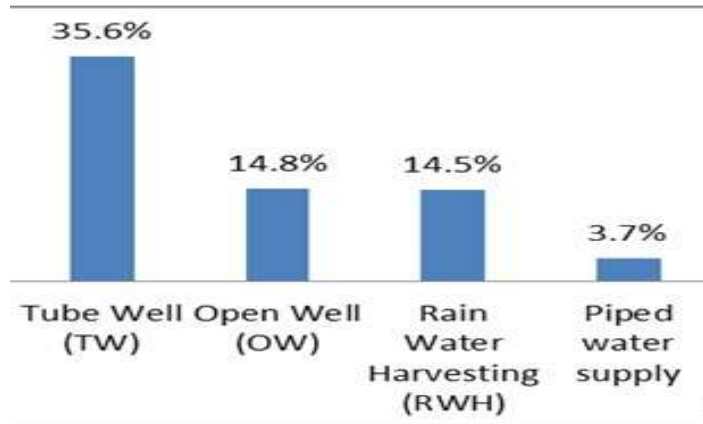


Fig.2. Fluoride in groundwater in Rajasthan

MATERIALS AND METHODS

Many methods have been suggested for the determination of fluoride ion in water given by official British and American compilation of Methods. The calorimetric & electrode method are the most satisfactory at the present time. Samples are collected in good quality polythene bottles of one liter capacity from different villages. Sampling has been carried out without adding any preservative in rinsed bottles directly for avoiding any contamination and brought to the laboratory. Fluoride concentration of sample was determined by ion electrode method.

Fluoride Ion-Selective Electrode Method:

Apparatus: Ion-Selective Meter, Fluoride Electrode, Magnetic Stirrer Reagent: Fluoride Standards of various ranges (0.2-20ppm)

Fluoride Buffer (TISAB-Total ionic strength adjustment buffer) Procedure:

Calibrate the instrument take 10ml sample in a beaker at 10ml buffer solution. Put stirring bar into the beaker immerse electrode & start the magnetic stirrer and wait until reading is constant withdrawal electrode rinse with distilled water. Fluoride contamination is a major Health hazard in many parts of the district. A few symptoms of Fluorosis types could be seen by naked eye and need not so many investigations. The 110 villages of Deoli Tehsil have high Fluoride concentration in water (i.e. >1.5 mg / lt). It has been observed people 58.19% villages of them have Fluoride concentration of water from 1.5 to 3.0 mg / Lt and 30% village have 3.0 to 6.0 mg / Lt of Fluoride, while 12% village have more than 6.0 mg/ l. of Fluoride. People of these villages are suffering from dental and skeletal Fluorosis. In Newai Tehsil almost 240 villages out of 269 villages

(considered 1.5 – 6.0 mg/lt) are affected by dental Fluorosis. While in Malpura Tehsil atleast 134 villages have Fluoride concentration 1.5 – 6.0 mg/lt and 42 villages have more than 6 mg/lt. concentration of Fluoride. The People of these villages are also affected by Dental Fluorosis. In Todaraisingh 79 (Fluoride concentration is more than 1.5 mg/lt) villages and habitants are affected by dental as well as minor skeletal Fluorosis out of 79 villages 70 have Fluoride concentration from 1.5 to 6.0 mg /lt. About 82 villages of Uniyara Tehsil are reported to have high concentration of Fluoride (>1.5 mg/lt.) in water and the many children and adults are affected by Dental and Skeletal Fluorosis. 330 Villages and habitants in Rajasthan state have Fluoride concentration in water more than 1.5 mg/lt. but of them 280 have 1.5 to 6.0 and 50 have more than 6 mg/lt Fluoride concentration. This high concentration reveals the dental as well as skeleton Fluorosis in the people.[8,9]

Many others symptoms of high take of Fluoride. Skeletal Fluorosis feeling of burning and tingling in the limbs, pain in the bones and joints, formation of gas in stomach, lack of appetite chronic fatigue and weakness of muscles are also reported by people. The people of this area have also compliant severe pain and stiffness in the neck, back bone and joints. So the more investigation and studies are needed.

DISCUSSION

Fluoride present in water is in a simple form and ingested fluoride is rapidly absorbed through gastro-intestinal tract and lungs. The peaks are reached after 30 min in blood. The rapid excretion takes place through renal system over a period of 4 to 6 h. in children (3 yrs of age only) about 50% of total absorbed amount is excreted, but in adults and children



over 3 years about 90% is excreted. Approximately 90% of the fluoride retained in the body is deposited in skeleton and teeth. The biological half-life of bound fluoride is several years. Fluoride also passes through the placenta and also appears in low concentration in saliva, sweat and lacteal secretion (milk). Fluorides

present other than in water are relatively less harmful. Fluoride ions from soluble inorganic fluoride compounds are rapidly absorbed. Fluoride sufficient in amount to cause mottling of primary dentition may reach through placenta.



Fig.3. Dental Fluorosis

Fluoride is mainly excreted in the faeces. Ingestion of fluoride causes decrease in the ionized calcium. This hypocalcemia leads to changes in internal milieu of the body to maintain the calcium levels and leads to secondary hyperparathyroidism. [10]

The increased activity of osteoblasts in bones by activating membrane bound 35 cycle AMP. This increased osteoblastic activity causes increase in citric and lactic acids released from ruffled border of osteoblasts. This causes increase in H⁺ ion concentration, and hence lysis of lysosomes takes place. Release of lysosomal enzymes viz acid protease, collagenase, hyaluronic acid in bones and other tissues of the body catalyses the reactions favouring the depolymerisation of the glycoprotein of bones and of

the cartilage. This causes breakdown of hydroxy proline, which is responsible for stabilisation of collagen triple helix. As the protein polymer deaggregates, and dissolves the mineral binding capacity (mbc), also get reduced and calcium is liberated, which helps in maintaining the serum calcium level. As a result the solubility of hydroxyapatite crystals also increases, causing its breakdown along with reduced laying down of collagen by reducing hydroxylation of proline and lysine. This event simultaneously led to the elevation of the serum mucoprotein or polysaccharide levels. The net result of degradation of ground substance in bones and other calcified tissues like teeth leads to symptoms of fluorosis like delayed eruption of teeth, dental fluorosis and premature ageing.[11]



Fig.4. Skeletal fluorosis causing deformed legs

RESULTS

In 1947, Ajmer-Mewar, was first reported as endemic region by Shourie. Voluminous work on the subject was done by workers like Kesliwal and Solomon (1950); Bhargava (1974) and Mathur (1977) on various aspects of fluorosis. Later on, zonal labs of National Environmental Engineering Research Institute, NEERI in Jai Pur, reported high fluoride

content in groundwater from different parts of Rajasthan. Geologically, there is a belt underneath Aravali range, beginning from Panch Mahal, Gujrat to Gurgaon (Harayana) and passing through southeast Rajasthan that is rich in fluorospar, cryolite and fluoroapatite. In Jarna-Khurd village 20km away from the city of Jai Pur, there are no youth. All 1200 people irrespective of age look old and have cracked teeth.



Their shoulders, hips and ankles are swollen and ache all the time. It is painful to stand up, if they squat on the floor. In Jalore district of Rajasthan, the fluoride content in water has increased to 6.8 mg/l as against the permissible limit of 1.5 mg/l causing premature aging in the people. Nearly 120 out of 728 villages in the district are in the grip of fluorosis with some of the villages being the worst hit as identified by the European Commission (EC). Osteoporosis, bone deformation and yellowing of teeth are rampant. Even the unborn children are not safe. People are threateningly dependent on aquifers for their drinking needs. All over, in Rajasthan drills, borepipes, tubewells and handpumps are becoming the triphalistic instruments to extract water of varying fluoride concentration from the deep of the earth. The area 20 km away from famous marble city.

Makrana, having 60 villages has been known as Banka-Patti because most of the people of this fluorotic belt are facing skeletal deformities due to consumption of fluoride rich water. Most of the peoples of Tedhasar village of Churu district seem to be totally handicapped due to fluoride poisoning.

Mottling of teeth in children is one of the earliest and most easily recognizable feature of fluorosis. Beside a health problem, it is an aesthetic and social problem also. A yellow-white discoloration appears, which turns brown and presents itself in horizontal streaks, since new layers of matrix are added on horizontally during tooth development. In late stages, the teeth become black. They may be pitted or perforated and may even get chipped off. Lose of premature teeth (endentulous) is common in endemic areas.[12]

Severity of **dental fluorosis** in as group of children in fluorotic belt helps in determining the community fluorosis index (cfi), which depends on identifying the extent of dental fluorosis in an individual child. Deans classification is used in identifying the mild, moderate and severe fluorosis in the teeth and a numerical grading is given by very experienced eyes.

The skeletal fluorosis manifests initially at the beginning of adulthood and is progressive if persons continue to consume fluoride rich water. Maximum ill effects of fluoride are detected in the neck, spine, pelvic and shoulder joints. Early symptoms of skeletal fluorosis include pain and stiffness in the neck, back and major joints of the extremities. Restriction of movement commences. The stiffness steadily increases until the entire spine becomes one continuous column of bone, manifesting in a condition referred to as poker back. Finally, various ligaments of the spine become ossified. The stiffness that first appears in the spine

spreads to various joints of girdles and limbs. The involvement of the ribs gradually reduces the movement of the chest during breathing. The increasing immobilization of joints leads to deformities of hip, knee and other joints causing severe disability. Characteristic structural changes in a fluorosed bone as revealed in X-ray include increased bone mass density (BMD) and bony out growths. Skeletal fluorosis usually become crippling in people in the endemic regions. Symptoms developed due to pressure caused by osteophytes (bony outgrowth), narrowing of inter-vertebral space and increase in the size of vertebrae or narrowing of spinal canal lead to paralysis.

Non-skeletal fluorosis-The conventional belief that fluoride affects only bone and tooth has been negated in recent years as the evidences on the involvement of soft tissues/organs/system of the body are convincing. Involvement of skeletal muscles, red blood corpuscles, ligaments, blood vessels, spermatozoa and G-I mucosa has been documented so far. In animals involvement of kidney, liver adrenals and reproductive organs have also been reported. Direct involvement of skeletal muscles in fluorosis has now been scientifically proved. Fluorosed skeletal muscles show widespread destructive changes. The other symptoms include-

Gastro-Intestinal problems-G-I mucosa is involved in the early stage of fluorosis. The main complaints are nausea (flu like symptom), loss of appetite, acute stomach pain, bloated feeling, gas formation, constipation followed by intermittent diarrhoea and headache. These complaints are considered early warning signs of fluorosis.

Neurological problems-Nervousness, depression, tingling sensation in fingers and toes, excessive thirst and tendency to urinate frequently are some of the manifestations observed in fluorotic belt.

Allergic problems-It includes painful rashes on the skin prevalent in women and children, which clear up in 7 to 10 days.

Urinary-Tract problems-Urine may be much less in volume; yellow-red in colour, and itching in urinary region.

Other Troubles-Radiographical studies show that ligaments and blood vessels get calcified. Erythrocytes (RBCs) are also affected in fluorosis. Fluoride is accumulated on their membranes, which lose in turns their calcium content. Attached red blood corpuscles do live their full life span and are likely to be eliminated by the system. Thus patients suffer from anaemia. Sperm abnormality in fluorosis results in male infertility. Oligospermia (deficiency of sperms), azoospermia (absence of sperms) and low testosterone levels in blood is very common in persons residing in endemic area consuming high fluoride in drinking



water. Weakness, stiffness and pain are included in muscular manifestations.

Fluoride can damage a foetus if the mother consumes water and food with high fluoride concentration during pregnancy. It can adversely affect the IQ of children.

The above-mentioned symptoms can also be due to other reasons. Therefore, the challenge before the medical officers is to differentiate and distinguish the symptoms due to fluorosis from other reasons. Non-skeletal fluorosis can be reversed within a short span of time, if a person starts taking low/nil fluoride water.[13]

CONCLUSION

According to W.H.O. the safe limit of fluoride in drinking water is 1-1.5 ppm. Hence it is concluded that

44.93% area are effected by 1.5-3.0 ppm fluoride and 40.63% area have been effected by 3-6 ppm fluoride and 7.55% area effected from 6-8 ppm fluoride and 3.63% area effected by 8-10 ppm fluoride and 3.25% area of Rajasthan is effected by more than 10 ppm fluoride. Fluoride is mainly found in groundwater in which the solvent action of water on the rocks and soil of earths crust derive it from the adjacent soil. The porosity of the rocks or soil through which water passes and the speed with which water flows, the temperature of the interaction of the rock and water, the hydrogen and calcium ion concentration, determine the fluoride content of the drinking water. Hodge and Smith (1965) have related the concentration of fluoride to the following well-established biological effects.

Table.1:- Fluoride Concentration And Related Effects

Concentration	Source	Malady
2 ppb	Air	Injury to vegetation
2 ppm or more	Water	Mottled enamel
8 ppm	Water	10% Osteo- sclerosis
20-80 mg/day	Water / Air	Crippling fluorosis
50 ppm	Food / Air	Thyroid changes
10 ppm	Food / Air	Growth retardation
>125 ppm	Food / Air	Kidney changes
>5 gms	Acute dose	Death

In fluorotic zones males suffer more than females. In India, this is mainly attributed more to migration of females after marriage. Irrespective of to and fro migration, there is always a likelihood of women getting less victimized. There is also a hypothesis of higher consumption of drinking water by man doing strenuous physical work but women are more affected during pregnancy and breast-feeding, due to lack of sufficient calcium in the body

Plan for an effective low cost defluoridation

Defluoridation is the process of removal of excess fluoride ion from water. So in regarding this several methods have been suggested for removing excessive fluoride from water depending on their mode of action. The defluoridation techniques could be divided into three groups –

- Based on chemical reaction with fluoride
- Based on absorption process

- Based on ion exchange process In this the quick reverse osmosis and electro dialysis are costly and not suitable in rural area.

The Nalgonda technique is an economical way for defluoridation. The Nalgonda techniques using alum and lime is easily applicable at both domestic and community level and treated water contains permissible amounts of fluoride

Approaches to be made are

- Health Education
- Treatment of the Disease
- Preventive Measures
- Health Education

Creating disease awareness: Creating awareness about the disease should be in the form of graphic presentation of the final consequences of the disease to the extent possible. If required, live presentations of the patients who are suffering from the severe form of the



disease in areas where the gravity of the problem has not reached to that extent. It may be of use to demonstrate the most severe extent of the disease and to motivate them to use the preventive or therapeutic measures. Creating awareness about the sources of the fluoride: The creation of awareness will help in implementing the need based preventive measures in the affected community.[12]

Treatment of the Disease

Vitamin C and D, salts of Ca, Mg or Al were prescribed in an attempt to reverse these effects. Published results were, however, inconclusive and largely negative. Recent studies conducted in Rajasthan under Raj DST sponsored studies indicated that fluorosis could be reversed, at least in children by a therapeutic regimen (Nutritional prophylaxis), which is cheap and easily available. The choice of the reported therapy was logical. The presence of calcium in gut directly affects the absorption of fluoride ions and also improve serum levels as observed by Teotia et. al (1995). Vitamin D3 in low doses enhances Ca absorption and retention without causing hypercalcemia and thus directly affects the absorption of fluoride ions. It also inhibits the excessive release of parathyroid hormone there by preventing excessive activation of osteoblasts thus preventing hyperosteoridosis and osteopenia. Ascorbic acid controls collagen formation, maintains the teeth structure and bone formation. The structures are adversely affected by higher fluoride intake.

PREVENTIVE MEASURES

Providing Defluoridated Water for Drinking Purpose

Methods of defluoridation recommended so far are aimed at bringing the fluoride levels to the **WHO standards**. Desirable characteristics of defluoridation process, cost effectiveness, easy to handle, (operation by rural population) – the major sufferer – independent of input fluoride concentration, alkalinity, pH, temperature, no effect on taste of water, no addition of other undesirable substances (e.g. Al salts) to treat water, all these parameters must be considered for adopting any of the defluoridation process/technique.

Changing the Dietary Habits

Defluoridation of drinking water alone shall not bring the fluoride level to safe limit. It would be necessary to overcome the toxic effects of the remaining fluoride ingested through other sources. This can be done by effecting minor changes in the diet and dietary habits of the population compatible with their social system and available resources. The main aim must be to

- Restrict use of fluoride rich food
- Avoiding use of fluoride rich cosmetics
- Use of food rich in Calcium, Vitamin C and antioxidants
- Rain Water Harvesting: (Alternative water source)

Fluoride affects the people and the animals as well. Therefore it is desirable that the animals should also be provided with fluoride free water for maintaining their longevity. Defluoridation of drinking water for animals will be too costly and not feasible and therefore the only solution of this problem is water harvesting. The water harvesting technology should be aimed not only to provide fluoride free water to human beings but also to animals. Rainwater storage can be a major source of fluoride free drinking water for the animals. These three-pronged attacks can prove to be a blessing for the population especially for the younger generation living in fluoride rich areas having no choice except to drink the water contaminated with fluoride and suffer the inevitable consequences including permanent deformities.[13]

REFERENCES

1. *Fluorine and fluorides (Environmental Health Criteria-36)*. WHO, Geneva 1984, pp 93.
2. R. Maheshwari, and N. Bansal, *Excess fluoride in groundwater: Its clinical manifestations, preventive measures and preventive processes*, Proceedings of National Conference on Environmental Conservation, pp. 113-1120, . pp.113-120, 1-3 September 2007.
3. R. Maheshwari and B Rani, B. N. Gupta, *Fluoride Toxicity, Everything About Water, No.7, pp.31-37. 2006.*
4. Maheshwari, R. (2007). *Fluoride Toxicity: An Alarming Threat, Proceedings of International Conference on Toxicology, Toxicogenomics and Occupational Health, Jiwaji University, Gwalior, MP.*
5. R. Maheshwari, *Fluoride Distribution: Recent advances in Mitigation Strategies for Sustainability of Modern Styled Era, Proceedings of International Conference on Recent Advances in Environmental Protection, St Jonhs College, Agra, pp. 45-38.2007.*
6. Mittal, N. Trivedi, S.K. Gupta, S. Kumar, and R. K. Gupta, *Radiological Spectrum of Endemic Fluorosis: Relationship with calcium intake, Skeletal Radiology, vol. 22. no. 4, 2pp.57-66, 1993.*
7. A.K.Susheela: *A treatise on fluorosis*. Edi. A.K. Susheela, F.R.R.D.F., New Delhi, India(2001).
8. J.D.Sharma, M.K.Sharma, P.Jain and D.Sohu, *Asian J. Exp. Sci., 19(2), 113-118(2005).*
9. Babulal Das, Jitu Talukdar et.al., *Current Science, 85(5), 659-661(2003).*



-
10. Gita Seth, A.Kumar, M.K Samota, *Trade Science Inc.*, 2(6), 191-193(2005).
 11. *Standard Methods for the Examination of water and Waste Water*, Am. Pub. Health Assoc., New York, 15th Ed. (1981).
 12. W.G Nawlakhe., D.N.Kulkarni, B. N.Pathak , K.R.Bulusu, *Indian J. Environ. Health.*, 17, 26-65(1975)
 13. B.K.Shrivastava ,*Asian J. Exp. Sci.*, 23(1), 269-274(2009)