Effect of Few Parameters on Removal of Atrazine from Waste Water

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Abstract: *Water has been contaminated due to modern agricultural practices, excessive use of pesticides and chemicals, mining and uncontrolled industrial activities. Wide range of chemicals and pesticides used for agriculture and other purposes have led to serious pollution of surface and groundwater. Atrazine, the second most widely used herbicide in world for controlling various weeds, has been found contaminating surface waters, soils and groundwater. Residual amounts of atrazine and its metabolites have been detected in the soil, water bodies, vegetables, grains and other foods products. It is extremely toxic to fish and aquatic invertebrates and it has been implicated increasingly in mammalian gonadal toxicity, genotoxicity and neurotoxicity. Conventional methods for the removal of pesticides are found to be either uneconomical or insufficient. The present study is directed towards the development of alternative technology based on biosorption for removing atrazine from wastewater environment.*

Thirteen different biosorbents were prepared from fungal cultures isolated from atrazine contaminated soil. These biosorbents were screened on the basis of growth of base strain,kinetics of atrazine removal and maximum atrazine uptake capacity. The biosorbent IITB-LP emerged out to be the best absorbent on all counts and was selected for detailed biosorption study. Sorption equilibrium studies were conducted to establish the biosorption uptake capacity of the biosorbent. The biosorption kinetics was studied at different initial concentrations of atrazine as 0.5 mg/L, 1 mg/L, 1.5 mg/L, 2 mg/L and 4 mg/L. The time required by atrazine to reach the equilibrium condition was determined using the kinetic profiles. The effect of biosorbent size on sorption kinetics was studied by taking three different size ranges viz. 0.2mm, 0.4 mm and 0.60 mm. The effect of agitation speed on removal of atrazine was studied for three different agitation speeds of 150 rpm, 200 rpm and 250 rpm.

The removal rate was found to be increasing with anincrease in the initial atrazine concentration and with decreasing biosorbent size. The reaction followed Lagergren's pseudo 2nd order reaction kinetics. The biosorption of atrazine ontobiosorbent followed Langmuir isotherm model. It was found that the biosorption process of atrazine was controlled by intra-particle diffusion, which was confirmed by various kinetic studies and interruption test.

Keywords: *atrazine, batch biosorption studies, biosorption.*

1. Introduction

Atrazine is a very popular, most frequently soil-applied, pre emergent and selective herbicide (USEPA, 2006). It is used for selectively controlling weeds in wide variety of crops, forestry cultivation; selective control of pond-weeds including submerged aquatic plants; and also in wood preservation, home gardening and tsetse fly control (Meister, 1998). As non selective herbicide, it is used for weed control along highways, on railroads, storage yards and industrial sites (Ribaudo and Bouzaher, 1994).

1.1. Environmental Contamination due to Atrazine and Need for Research

Atrazine is applied in field by different modes viz. spray, dust, smoke. Once applied, some atrazine may enter the air, some may enter surrounding areas including streams, lakes, or other waterways through washed-off from the soil by rainfall and some atrazine may enter the groundwater through its leaching from the upper soil surface to deeper soil layers. Atrazine gets accumulated in the plants by absorption via their roots and

translocated through xylem to leaf and stem of plants. It has been frequently detected in agricultural products such as fruits, milk, butter, sugar beet, etc (Krivankova et al., 1989).

Atrazine has a half life of several days to several months and in some situations, of a several years. However, in most cases, atrazine is broken down in the soil over a period of one growing season. Persistence of atrazine is moderate to high in surface water bodies (Thurman et al., 1992) while very high in deeper soils and aquifers (Assaf and Turco, 1994).

Atrazine had been reported as most commonly detected pesticide in water bodies in various countries such as Australia, Canada, China, Germany, France, the United States and other regions. This could be due to its high rate of use, moderate solubility, spillage, runoff and leaching (Silva et al., 2004).

Maximum contaminant level (MCL) for atrazine set by European Union in water is 0.1 μg L^{-1} and total pesticides as 0.5 μg L^{-1} (Carney, 1991) while in the United States and China the MCL is 3 μg L^{-1}. The European Union has banned the use of atrazine.

WHO has classified atrazine as Class II pesticide (moderately hazardous to human health). It has been reported to be persistent, toxic, mutagenic, carcinogenic and tumorogenic. Acute and chronic effects of atrazine have been reported by many researchers. It causes various health problems in animals, aquatic life and human beings and other habitat.

Exposure to atrazine may take place by various possible routes like, by contact with skin, inhalation, or ingestion of contaminated food or water. Diversified application and non degradability of pesticides results in their residual effects through food chain. Prolonged exposure may reduce nervous breakdown (Tomlin, 1994).

Atrazine exposures have also produced tumour, weight change and liver and heart damage (Rita, 1998). Atrazine is toxic to animals, aquatic life and birds also (Pathak and Dikshit, 2011a). It can also cause gastrointestinal disorders, weight loss, muscle weakness and a lack of coordination. It is not bio acumumulated however it is rapidly transformed to nontoxic metabolites which are excreted through urine.

Though atrazine is reported to play a key role in sustainable agriculture (Pathak and Dikshit, 2012 b), It is associated with a lot of other problems like birth defects, low birth weights and menstrual problems. It has been reported to cause a significant inhibition of specific binding of various types of proteins like estrogens and progesterone receptors.

It has also induced DNA damage (Clements et al., 1997). Atrazine is reported to be a suspected carcinogen and possible endocrine disrupter (Takacs et al., 2002). Potential effect of atrazine on pregnant women and young children has been also reported (Gammon et al., 2005). It has a long-term effect on hormones, the immune system and reproduction. Exposure to high concentrations of atrazine for long time periods has shown signs of liver, kidney, lung, or cardiovascular damage in laboratory animals. Atrazine pose a threat to human health and the environment (Pathak and Dikshit, 2011b).

1.2. Atrazine: Synthesis and Discovery

Atrazine was first synthesized in 1948. Gaseous cyanogen chloride was trimerized to cyanuric chloride in presence organic solvents like carbon tetrachloride, ethyl ether or benzene. Hydrogen chloride was used as a catalyst (Pearlman, 1948). Currently atrazine is synthesized by reaction given in Figure 1. Cyanuric chloride (A) and isopropyl amine are reacted under basic conditions to form 2, 4-dichloro-6-isopropylamino-s-triazine (B). The intermediate (B is further reacted with monoethylamine in presence of dilute caustic soda to form atrazine (C). The reaction is performed in xylene or toluene in presence of water (Izmerov, 1982).

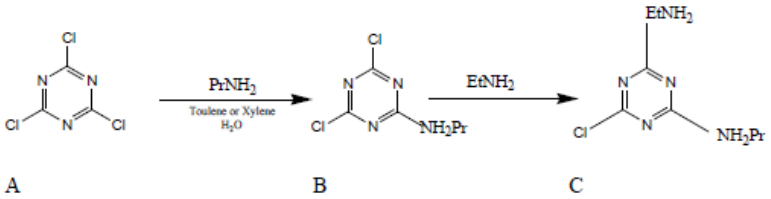

Fig.1: Synthesis of atrazine (Izmerov, 1982)

1.3. Chemical Identity

Atrazine is a selective and systematic chloro-s-triazine herbicide. The chemical structure of atrazine is shown in Figure.2.

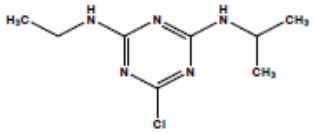

Fig.2: Structure of atrazine (Donnelly et al., 1993)

Recommended purity of commercial atrazine is at least 92% by food and agricultural organization. Most products are about 95% pure (ATSDR, 2003). Common impurities present in technical atrazine are sodium chloride, simazine and propazine (WHO, 2003), hexa chlorobenzene (PMRA, 2007), dichlorotriazines, hydroxytriazines and tris (alkyl) aminotriazines (EPA, 1983).

1.4. Physical and Chemical Properties

Technical atrazine is a white, odourless, colourless, crystalline, non-combustible and noncorrosive powder (HSDB, 2002). It has low vapour pressure and moderate lipophilicity (Edginton and Rouleau, 2005). Various forms in which atrazine is sold are, liquid, flowable liquid, water dispersible granular and wettable powder and dry flowable formulations (Meister, 1992).

2. Materials

Various materials used for the current research have been described in this section. They have been sub classified as glass wares, chemicals, media, cultures and wastewater

2.1. Glassware

All the experimental work was performed using 'Borosil' glassware (M/s Borosil Glass Works Ltd, Mumbai, India). The glass wares washed and sterilized as per protocol.

2.2. Chemicals

All chemicals and reagents used for experimental work were of Analytical Grade. Atrazine (technical grade, 95.5% pure) used in this study was obtained from M/s Vijayalakshmi Insecticides and Pesticides Limited, Ethakota, India.

2.3. Media

Various media used in the study were potato dextrose agar (PDA), corn meal agar (CMA) and Czapak-Dox agar (CDA). Rose Bengal dye (1 mg/L) was added to the above medium for arresting growth of bacteria. Nutrient broth was prepared by dissolving 13 g powder in 1000 mL ultrapure water, while nutrient agar was prepared by dissolving 26 g powder in 1000 mL of ultrapure water.

2.4. Cultures

Fungal cultures used in this study were prepared by isolating the strains from soils precontaminated with atrazine. The cultures were routinely sub cultured on nutrient agar slants as per standard methods and stored at 4oC in refrigerator. They were further grown on PDA media whenever required.

2.5. Wastewater

Ultrapure water was used for making synthetic samples of atrazine for all experimental works. Working standards of atrazine for calibration were made using technical grade atrazine (95.5% pure), acetone and ultrapure water as solvents. Stock solution (1000 mg/L) was made according to the Standard Methods (APHA-AWWA-WPCF, 2005). Whenever required the stock solution was diluted by calculated quantity of ultrapure water to give desired concentration of atrazine in synthetic wastewater.

3. Methods

All the initial experiments on screening of fungi isolated from soil were performed in triplicate. All remaining experiments were performed in duplicate. Wherever and whenever, observations or results were found to be doubtful, one more duplicate set of those specific experiments was re performed.

3.1. Collection of Soil Samples

Soil samples were collected in sterile containers from specific locations in Dahanu, India where atrazine was used frequently. These locations were chosen as these were reported rich in the atrazine residues, so the probability of isolation of atrazine sorbing microorganisms was maximized. Apart from these locations, samples were also collected from 3 different areas of a company named Meghmani Dye-chemical Ltd, Ahmedabad India, namely outside the plant, the effluent exit area and the central effluent treatment plant. The soil samples were collected at depth of 20 cm in each case.

3.2. Isolation of Fungal Strains from Soil

The various strains to be used in this study were isolated from soil samples as per standard methods.13 isolates were separated, characterized and screened.

3.3. Preservation of Fungal Cultures

The isolated fungal culture should remain viable for longer time without any morphological, physiological and genetic alterations. These cultures were preserved and maintained under three types of preservation methods: slant, spore suspension and cryo storage

3.4. Preparation of Biosorbents

The dry mass of fungal biosorbent prepared by above process were pulverized in a laboratory grinder (Jyoti Mixer, India) and sieved to three different size ranges viz. 0-0.2 mm, 0.2-0.4 mm and 0.4-0.6 mm. Pulverized mass was washed with distilled water to remove any foreign materials. It was done by keeping the mixture in 100 mL flask at 150 rpm in a mechanical shaker for 3 hrs. After washing, the mass was dried for 2 days in sunlight. Then, it was oven dried at 50-60oC for 5 hrs to remove any trace of moisture present in the pores. Dried mass was cooled to room temperature, sieved to its original size and stored in 125 mL airtight bottles. Biosorbents were prepared for each of the 13 isolates and were named as biosorbent A to biosorbent M.

3.5. Effect of Biosorbent Dose

Effect of dose of biosorbent was studied at four doses of 500, 600, 700 and 800 mg/L. All other conditions were same as section 3.5.2. Samples were withdrawn at 0.5, 1, 1.5, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 20 and 24 hrs and analysed for residual atrazine concentration. The percentage removal of atrazine was plotted with time.

3.6. Effect of Initial Atrazine Concentration

Effect of initial atrazine concentration of atrazine was studied. Biosorbent dose was 600 mg/L, size was 0.2 mm and agitation speed was 250 rpm for different atrazine concentrations. The different concentrations tried for atrazine removal were 0.5, 1.0, 1.5, 2 and 4 mg/L. The temperature was maintained at 30oC and the study was performed for 8 hrs.

4. Results

4.1. Isolation and Growth of fungal Strains

Fungal strains were isolated from soil collected from different locations at Dahanu and Meghmani Dye-Chem Ltd, Ahemedabad. The results have been discussed in following subsections.

4.2. Optimum Dose of Biosorbent

Optimum dose for biosorption of atrazine was determined as method discussed in section

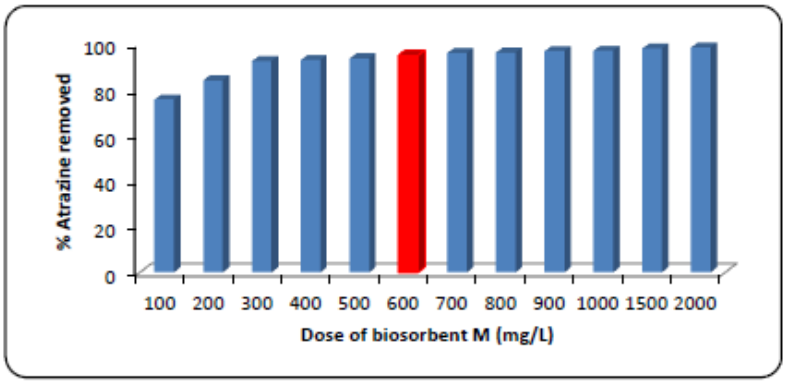

Fig.3: Optimum dose of biosorbent IITB-LP

Figure3 shows the percentage of removal of atrazine at different doses (100- 2000 mg/L) after contact time of 8 hrs. There was no significant improvement in removal after 500 mg/L. The optimum dose was found to be 600 mg/L for biosorbent IITB-LP, which was maintained in all further xperiments for initial atrazine concentration of 1 mg/L. It is expected that the optimum biosorbent dose will change with the initial atrazine concentration.

4.3. Effect of Biosorbent Dose

For more precise observation, the previous experiment was repeated at the dose ranging from 500 to 800 mg/L keeping all other conditions constant. However, this time, kinetics was measured by standard methods . The percentage removals of atrazine at different doses are plotted and are shown in Figure 5..

The removal of atrazine increased with increase in biosorbent dose. Till first 6 hrs, the difference could be observed significantly from the Figure 4. After 8 hrs, there was no appreciable difference for the removal of atrazine at any dose of 600 to 800 mg/L. Therefore, 600 mg/L was selected as optimum dose in further studies.

5. Conclusion

Effect of various parameters were studied and result is shown and discussed at appropriate sctins. There is need to study more parameters for abatement of atrazine pollution

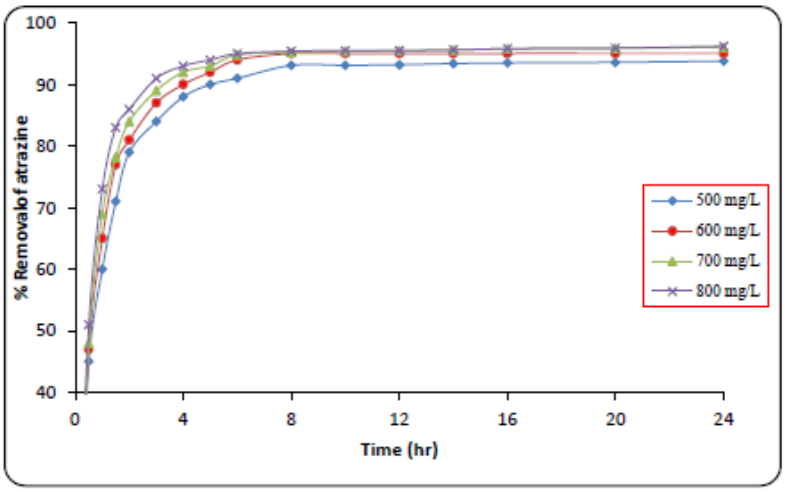

Fig.4: Effect of dose of biosorbent IITB-LP

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