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A review on the occurrence and treatment of methylpyridine: An industrial solvent

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Methylpyridines are used as solvents and raw materials in preparation of various chemical products in the agro-chemical, pharma and textile industries. The excessive presence of alkylpyridines in aquatic ecosystems has led to serious concerns regarding their neurotoxicity. An increasing volume of 2-methylpyridine (2Mp) containing wastewater is let out as effluent by various industries due to poor regulations regarding its usage and production, especially in developing countries. This observation coupled with the refractory nature of 2Mp, mandate its complete removal from the environment. The present review consolidates the physical properties, occurrence scenarios, pathways to exposure and methods of removal of 2Mp from aqueous or simulated solutions. Industrial working environments, nearby surface water bodies, and contaminated surface and subsurface soil were found to be the pathways for human exposure to 2Mp. While conventional biological treatment was found to be slow and not as efficient, sorptive processes based on nanomaterial sorbents were found to have tremendous potential in 2Mp treatment over a wide range of concentrations.

Keywords: Exposure pathways, toxicity, methylpyridine biodegradation, graphene nanomaterial adsorbent, methylpyridine properties.

Introduction

Methylpyridines are volatile and toxic organics that are flammable with a pungent and unpleasant odour. Methylpyridine refers to three monocyclic isomers with a chemical formula C_6H_7N and a molar mass of 93.13 g/mol. 2-Methylpyridine (2Mp) is the most commonly detected variant with the methyl group attached to the alpha positioned carbon of pyridine. It is used in agro-chemical, pharma and textile industries in concentrations of 0–200 mg/L and passes through the activated biological treatment mostly without change[1]. The wastewater containing 2Mp is toxic to aquatic life and has harmful effects on the liver and the central nervous system of humans[2]. 2Mp is only partially bio-degraded naturally, is miscible with water and most organic solvents and bears no net charge, making its removal harder than anticipated[3,4]. Recurrent contact with even low doses of 2Mp could lead to liver and kidney damage, eventually ending in multiple organ failure[5].

Thus, the presence of this neurotoxin needs to be controlled prior to effluent discharge from the industry. While developed countries like the USA monitor the import, production and usage of 2Mp, developing countries do not have any such substantial framework in place. Very limited sources of concise information exist with regards to 2Mp, its exposure pathways and its lifecycle in the environment.

This review thus tries to analyse and compile studies pertaining to, (i) properties and production of 2Mp; (ii) effluent standards and toxicity limits for discharge in developed and developing countries; (iii) case studies that reported the presence of 2Mp and its pathways to human exposure; (iv) degradation of 2Mp in the natural environment and its treatment by biological and sorptive techniques.

Properties of 2Mp:

Methylpyridines are slower and less biodegradable than their other substituted counterparts like pyridine-carboxylic acid. 2Mp was the first pyridine compound reported to be isolated in pure form from coal tar. It is a yellowish liquid with an intensely disagreeable pungent odour.

While short term exposure in low concentrations is relatively safe, recurring exposure leads to its accumulation in one or many human organs. Liver and kidney damage may lead to mortality. 2Mp is partially polar due to its unsymmetrical structure. It is a good solvent for both polar and non-polar ingredients and is itself soluble in both water and alcohol. 2Mp is a flammable product (to be stored below 23°C). 2Mp is lighter than water with a density of 0.943 g/mL, a vapour density of 3.2 (vs air), vapour pressure of 10–12.6 mm Hg (24.4°C). The melting and boiling point of 2Mp is – 66.7°C (206.3 K) and 129.5°C (402.5 K) respectively[6]. It has a pKa of 5.9, making it a weakly basic compound. 2Mp at neutral and alkaline pH is poorly ionizable, leading to poor treatability. At pH values lower than its pKa, it undergoes protonation[7].

Occurrence of 2Mp

Production:

2Mp is a high production volume chemical. Trends in the US show a gradual overall increase in 2Mp import, production and usage throughout the country. Attempts have been made by their environmental protection agency (US-EPA) to curtail its usage over the years, but they seem to have succeeded only to a particular degree[8]. Reported annual usage changed from 8 million kg (1989), to an estimated quantity > 0.5 million kg (1994), to a wide usage range of 5–25 million kg (2006), to finally an undisclosed quantity (2012). No such data is reported in developing countries.

International standards and toxicity:

The typical concentration of pyridinic derivatives like methylpyridines in the effluent from the manufacturing plants is generally in the range of 0–200 mg/L. Studies by the US Environmental Protection Agency (US-EPA), UK and Russia have mandated certain industries to set 1 mg/L as the 2Mp threshold in effluent discharged[9]. The continuous dermal/ skin exposure standard is set at a limit of 15 mg/m^3 for industry workers. Whereas Central Pollution Control Board, India (CPCB) lists 2Mp as an odorous irritant[10]. Unpleasant odour is detectable at a concentration of 0.82 mg/L. Average 2Mp presence limit in edible fish and crabs is 0.2 mg/kg, while 0.5 mg/L makes it unpalatable[5,6,11]. According to the American Medical Association, oral toxicity in rat is, LD_{50} ~ 400 mg/kg and dermal toxicity through rabbit skin is, LD_{50} = 386.6 mg/kg[6].

Pathways of exposure:

There are two broad pathways of 2Mp exposure in humans. They have been discussed below.

Exposure to industry workers:

The first pathway is by means of working in an industry where 2Mp is synthesised or used as a chemical intermediate or solvent. Contact with 2Mp is via direct exposure to skin and by inhalation[12,13]. Persons exposed to 2Mp in industrial manufacturing and processing is estimated in excess of 1 in 99 (US-EPA, 2014). Till date 11,240 cases (1,234 female) of ailment due to 2Mp exposure have been reported in the US (National Occupational Exposure Survey, 2006)[14,15]. 2Mp is used as a solvent and a chemical intermediate in manufacture of timber products, organic chemicals, pharmaceuticals, and public owned treatment works and thus is found in these industry effluents. Picloram (herbicide) and amprolium (coccidiostat) use 2Mp as an ingredient in manufacture[16]. A case study is mentioned in Table 1, serial number 1.

Exposure to public:

(i) The second pathway involves exposure to 2Mp that has persisted in the industrial effluent even after biological treatment and has been released into the environment. The effluent 2Mp with its high mobility moves through soil and affects crops in neighbouring agricultural fields. 2Mp displays high to medium mobility with K_{oc} (soil adsorption coefficient) values ranging from 4–215 mL/g[13,17]. It also seeps through the soil to pollute groundwater at depths up to 6–10 m. A case study is mentioned in Table 1, serial number 6. In an aerobic sediment column study where subsurface sediment was leached with contaminated groundwater, 65% of the initially applied 2Mp was removed after 5 weeks of operation[18]. In anaerobic aquifer slurries, 2Mp remained even after 97 days[19].

(ii) Another portion of the effluent 2Mp reaches waterbodies in the vicinity of the industry, polluting the water. This water may be used by persons residing beside the waterbodies for various activities. Case studies are mentioned in Table 1, serial numbers 3–5.

2Mp has also been found to be affecting fisheries present in the waterbodies themselves. Meat from fishes and crabs in such lake polluted lakes has shown presence of 2Mp. This

Table 1. Case studies elucidating the different pathways of 2Mp exposure

Sl. No.	Type of pathway	Location/source	2Mp concentration	Comment	Ref.
1.	Industry workers	Shale oil processing wastewater	5–25 mg/L	It is used as a cleaning agent	27
2.	Fisheries	Korean fish pastes	146 μg/kg	Exceeds limits by a large margin	28
3.	Waterbodies	Coal gasification wastewater	3.71 mg/L	–	29
4.	Waterbodies	Low temperature carbonization wastewater	5 mg/L	Mean concentration from 10 samples	30
5.	Waterbodies	Tar plant drainage wastewater	54 mg/L	Highest concentration of 2Mp observed	7
6.	Sub-surface soil	Wood works wastewater	0.91 mg/L	At depth of 6 m	31

2Mp inadvertently enters humans on consumption of fisheries. A case study is mentioned in Table 1, serial number 2.

Treatment of 2Mp

2Mp remains rather neutral in an aqueous environment without undergoing hydrolysis because of absence of hydrolysing groups[20]. Various treatment techniques have been developed for the removal of 2Mp from water and wastewaters. 2Mp is partially degraded by *Actinobacteria*. It was biodegraded only 30% in 3 weeks under aerobic conditions and 10% in 3 months under anaerobic conditions, while using an enrichment culture obtained from sub-surface soil as an inoculum[21]. Another anaerobic study which used sludge from a wastewater treatment plant digester as inoculum found similar results[22].

Many researchers have studied the feasibility of using adsorption as a physico-chemical method for 2Mp uptake. A consolidated list of studies utilizing various sorbents in 2Mp removal, with optimal sorption equilibrium conditions is given in Table 2[23]. Nanomaterials like graphene oxide and sylopute (pure amorphous silica which is non-crystalline in nature) have shown a tremendous potential in 2Mp sorption over a broad 2Mp loading range. They seem to outperform activated carbons with their sorption capacity[7,24,25]. Graphene oxide has shown an ability to exist in the form of nanoparticles, which in effect allows it to exhibit high exposed surface area that can be investigated for sorption. Parameters that affect sorptive interaction between 2Mp and the adsorbents are initial 2Mp loading, pH, time of contact, adsorbent dosage and maintained temperature.

Observations:

Most studies that have been conducted have focused on using conventional adsorbents for uptake of 2Mp over very high 2Mp concentrations. This is in direct contradiction to 2Mp occurrence and exposure literature and has had led to poor understanding of 2Mp sorption at low concentrations. No focus is given to usage of 2Mp as a manufacture solvent (used to dissolve chemical ingredients), as used in the textile colouring industry (conc. 2.5–20 mg/L). This is a high volume, low concentration usage case. The problems relating to sorptive treatment were remediated by a study by Chatterjee and Majumder[7] which used a new age adsorbent, graphene oxide nanomaterial (GON) instead of conventional sorbents like soil, zeolites and activated carbons in 2Mp removal[3,4,26]. Graphene oxide nanomaterial was reported to have lower dosage requirements and a higher surface area. It is evident from Table 2 that as 2Mp concentration rises, the adsorption capacity also rises. GON is seen as having similar or better sorption capacity values when compared to other studies at comparable 2Mp loading (10 mg/L), but the dosage of GON (1.5 g/L) is much lower[3,4]. The adsorbent GON has a much faster rate of equilibrium attainment (1.5 h). Another new-age adsorbent used in 2Mp removal is sylopute[25]. It has shown good potential for usage at high 2Mp concentrations (up to 7000 mg/L). Such concentrations are not expected to be encountered even in the most critical of situations.

Table 2. Comparative studies of different adsorbents used in batch adsorption of 2Mp (C_0 – initial 2Mp concentration, q_e – adsorption capacity)

Sl. No.	Adsorbent	C_0 (mg/L)	Dose m (g/L)	pH	Time t (h)	Temp. T (K)	Best fit isotherm	q_e (mg/g) at corresponding C_0 (mg/L)	Ref.
1.	Graphene oxide nanocomposite	2.5–20	1.5	7	1.5	293–313	Redlich-Peterson	2.50 mg/g at 5 mg/L 4.76 mg/g at 10 mg/L 8.78 mg/g at 20 mg/L	7
2.	Commercial activated carbon	2.5–20	14	6.5	2	293–313	Langmuir	0.23 mg/g at 5 mg/L 0.45 mg/g at 10 mg/L 0.81 mg/g at 20 mg/L	7
3.	Coconut shells activated carbon (CS)	1–100	2	6	48	283–313	Langmuir	4.84 mg/g at 10 mg/L 24.81 mg/g at 25 mg/L 41.24 mg/g at 100 mg/L	3
4.	Acid activated CS	1–100	2	8	48	283–313	Langmuir	5.14 mg/g at 10 mg/L 24.84 mg/g at 25 mg/L 46.85 mg/g at 100 mg/L	3
5.	Jordanian zeolite-phillipsite	1–500	20	2	24	298 and 328	Brunauer-Emmett-Teller	0.35 mg/g at 10 mg/L 2.30 mg/g at 30 mg/L	4
6.	Jordanian zeolite-faujasite	1–500	20	2	24	298 and 328	Brunauer-Emmett-Teller	0.20 mg/g at 10 mg/L 1.20 mg/g at 40 mg/L	4
7.	Agro coal ash	50–300	2	6	7	283–303	Langmuir, Freundlich	1.87 mg/g at 100 mg/L	26
8.	Sylopute	0–7000	4	–	0.5	288–318	Langmuir	75 mg/g at 1000 mg/L 220 mg/g at 7000 mg/L	25

Conclusion

2Mp was found from literature to be abundantly present in wastewaters from multiple industrial sources. Standards for 2Mp treatment in developing countries were found to be inadequate, while developed countries were found struggling to keep its usage in check. 2Mp was found to affect industrial workers by workplace exposure and other human beings mainly by surface water pollution (water and fisheries) and land pollution (leading to groundwater pollution). Due to the poor biodegradability of 2Mp, both aerobic and anaerobic treatment processes used in conventional treatment effluent plants were found not yielding suitable results in a short period of treatment. To remediate this, traditional adsorbents with poor sorption capacities have been used in the past two decades for uptake of 2Mp. These traditional sorbents require high dosages in application and their exhaustion results in a landfill hazard. The necessity for mass production and application of enhanced sorbents like graphene oxide nanomaterials with better capacity, regenerability and mechanical ruggedness was observed. A few studies successful in addressing these issues in 2Mp removal were reported.

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References

1. R. Chatterjee and C. Majumder, *J. Indian Chem. Soc.*, 2020, **97(4)**, 501. https://www.researchgate.net/publication/346470812_Process_optimization_of_2-methylpyridine_removal_by_graphene_nanoparticles.
2. ILO Content Manager. Chemical Neurotoxic Agents, http://iloencyclopaedia.org/component/k2/item/289-chemical-neurotoxic-agents (accessed January 11, 2020).
3. D. Mohan, K. P. Singh and D. Ghosh, *Environ. Sci. Technol.*, 2005, **39(13)**, 5076. https://doi.org/10.1021/es048282g.
4. Z. Rawajfih, H. A. Mohammad, N. Nsour and K. Ibrahim, *Microporous and Mesoporous Materials,* 2010, **132(3)**, 401. https://doi.org/10.1016/j.micromeso.2010.03.019.
5. R. A. Pandey and S. Sandhya, *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology,* 1997, **32(5)**, 1325. https://doi.org/10.1080/10934529709376612.

6. 2-Methylpyridine – The Good Scents Company – Aromatic/Hydrocarbon/Inorganic Ingredients Catalog information. http://www.thegoodscentscompany.com/data/rw1180531.html (accessed November 22, 2020).

7. R. Chatterjee and C. Majumder, *Journal of Water Process Engineering,* 2021, **39**, 101686. https://doi.org/10.1016/j.jwpe.2020.101686.

8. F. Ullmann, W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn and J. F. Rounsaville, "Ullmann's Encyclopedia of Industrial Chemistry", 5th ed., VCH Publishers, Deerfield Beach, FL, 1993, Vol. A1.

9. Y. Bai, Q. Sun, C. Zhao, D. Wen and X. Tang, *Appl. Microbiol. Biotechnol.,* 2010, **87(5)**, 1943. https://doi.org/10.1007/s00253-010-2670-8.

10. CPCB: "Environmental Standards for Ambient Air, Automobiles, Fuels, Industries and Noise", Pollution Control Law series; Central Pollution Control Board, 2000.

11. European Food Safety Authority – Trusted science for safe food. https://www.efsa.europa.eu/en (accessed November 22, 2020).

12. PubChem: 2-Methylpyridine. https://pubchem.ncbi.nlm.nih.gov/compound/7975 (accessed November 22, 2020).

13. PubChem: Hazardous Substances Data Bank (HSDB) : 101. https://pubchem.ncbi.nlm.nih.gov/source/hsdb/101 (accessed November 22, 2020).

14. N. NOES, N. National Occupational Exposure Survey, Estimated Numbers of Employees Potentially Exposed to Specific Agents by 2-Digit SIC. https://web.archive.org/web/20110717195709/http://www.cdc.gov/noes/noes1/agtindex.html (accessed November 22, 2020).

15. NOES, N. CDC – NIOSH – National Occupational Exposure Survey (1981-1983). https://www.cdc.gov/noes/default.html (accessed November 22, 2020).

16. E. F. V. Scriven, R. Murugan, "Pyridine and Pyridine Derivatives", in: 'Kirk-Othmer Encyclopedia of Chemical Technology', John Wiley & Sons, Inc., Hoboken, NJ, USA, 2005, p 1625180919031809.a01.pub2. https://doi.org/10.1002/0471238961.1625180919031809.a01.pub2.

17. E. Bi, T. C. Schmidt and S. B. Haderlein, *Environ. Sci. Technol.*, 2006, **40(19)**, 5962. https://doi.org/10.1021/es060470e.

18. Z. Ronen and J.-M. Bollag, *International Journal of Environmental Analytical Chemistry,* 1995, **59(2-4)**, 133. https://doi.org/10.1080/03067319508041323.

19. M. N. Naik, R. B. Jackson, J. Stokes and R. J. Swaby, *Soil Biology and Biochemistry,* 1972, **4(3)**, 313. https://doi.org/10.1016/0038-0717(72)90027-2.

20. W. J. Lyman, W. F. Reehl and D. H. Rosenblatt, "Handbook of Chemical Property Estimation Methods", Washington, DC, American Chemical Society, 1990, **4**.

21. J.-P. Kaiser and J.-M. Bollag, *Soil Biology and Biochemistry,* 1992, **24(4)**, 351. https://doi.org/10.1016/0038-0717(92)90195-4.

22. Y. Hongwei, J. Zhanpeng and S. Shaoqi, *Ecotoxicology and Environmental Safety,* 2006, **63(2)**, 299. https://doi.org/10.1016/j.ecoenv.2004.12.016.

23. R. Chatterjee and C. Majumder, *J. Indian Chem. Soc.,* 2019, **96(4)**, 499. https://www.researchgate.net/publication/336128736_Modelling_of_adsorption_process_in_industrial_ wastewater_treatment_-A_review.

24. S. Chaudhuri, R. Chatterjee, S. K. Ray and C. Majumder, *J. Indian Chem. Soc.*, 2020, **97(4)**, 541. https://www.researchgate.net/publication/343179974_Removal_of_cadmium_ions_from_water_by_using_aluminum_functionalized_ graphene_oxide.

25. J.-W. Yang and J.-H. Kim, *Korean Chem. Eng. Res.,* 2019, **57(2)**, 210. https://doi.org/10.9713/KCER.2019.57.2.210.

26. G. B. Daware, P. V. Vijay Babu and B. L. Pangarkar, *Desalination and Water Treatment,* 2014, **52(31-33)**, 6263. https://doi.org/10.1080/19443994.2013.819152.

27. S. B. Hawthorne, R. E. Sievers and R. M. Barkley, *Environ. Sci. Technol.*, 1985, **19(10)**, 992. https://doi.org/10.1021/es00140a018.

28. F. F. V. Chevance and L. J. Farmer, *J. Agric. Food Chem.*, 1999, **47(12)**, 5151. https://doi.org/10.1021/jf990515d.

29. M. F. Giabbai, W. H. Cross, E. S. K. Chian and F. B. Dewalle, *Int. J. Environ. Anal. Chem.,* 1985, **20(1-2)**, 113. https://doi.org/10.1080/03067318508077050.

30. R. A. Pandey, N. M. Parhad and P. Kumaran, *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering,* 1989, **24(6)**, 603. https://doi.org/10.1080/10934528909375505.

31. D. F. Goerlitz, "A Review of Studies of Contaminated Groundwater Conducted by the US Geological Survey Organics Project, Menlo Park (CA), 1961–1990", Groundwater contamination and analysis at hazardous waste sites, Marcel Dekker, New York, 1992.