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CHEMICAL SPRAYS FOR CONTROLLING MALODOR AND PATHOGENS IN THE HOUSEHOLD AND PUBLIC TOILETS AND URINALS

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ABSTRACT

Stinking urinals and toilets are universal being common in the third world countries with prevailing mismanagement and poor funding to municipalities. This problem has been addressed in a sustainable manner. Our long term studies have revealed that bi weekly night spray of sodium hydroxide (0.5% in tap water) control malodor in the household toilets. The malodor in a public urinal and toilet (5 days study) was controlled after 5 sprays of NaOH (1%) in a day (at 3h intervals). Chemical spray also reduced frequency of water flushes after use; 3-4 /day in the houses but 10 flushes/day in the public urinals (2 flushes in between sprays; first flush after 10minutes of a chemical spray and second after 2h). In addition to regular water flush after toilet use, additional flush must follow after 10 minutes of every spray. Further, weekly combined spray of sodium hydroxide (1.0%) and hydrogen peroxide (0.05%) at night is recommended in the public facilities to oxidize recalcitrant malodor compounds to non odorous biodegradable compounds. However, concentration of H_2O_2 may be increased (maximum 0.5%) while time intervals between night sprays may be reduced considering malodor problems. These sprays may be useful in sanitizing toilets, urinals and washrooms in the hospitals during COVID pandemic.

Key words: Malodor, urinal, toilet, biofilm, sodium hydroxide, hydrogen peroxide

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Public toilets and urinals are the major source of foul odor in the urban areas. Malodorous compounds in the toilets are butyric acid, *p*-cresol (Burton and Camb 1891, Berthelot 1918), indole, skatole (Brieger 1878) and sulfur compounds mainly hydrogen sulfide and methyl mercaptan (Moore et al. 1987, Sato et al. 2001, 2002). Dimethyl mono-, di-, and trisulfide, in some conditions, can also contribute to the toilet malodors. In addition, ammonia and amines (methyl amine, dimethylamine, ethylamines and trimethyl amine) are important in the urinals (Perry and Schroeder 1963, Troccaz et al. 2013).

Genesis of Malodor

The biofilms (0.10mm thick) formed on the surface of pots and pipes etc. of urinals and toilets decompose organics of urine and fecal origin releasing malodorous compounds. Although urea is a very stable compound having a half life period of about 40 years at 25^0C (Shaw and Bordeaux 1955, Callahan et al. 2005) but urease released from microbial biofilm breaks into carbonic acid and ammonia.

Growth Limiting factor of Microbes

The medium pH affects microbial growth including their viability. The optimum growth of *E. coli* takes place between pH 5.5-8.5. Cell growth stop slowly at pH >5.5 while pH >8.5 not only stop cell growth but also kill (Source: Internet http://www.exptec.com.). pH > 9.0 also arrests other bacteria growth such as *Clostridium sporogenes*, *Erwinia caratovora*, *Psedomonas aeruginosa*, *Thiobacillus novellus* and *Streptococcus pnemoniae* (Kenneth Todar "Online Textbook of Bacteriology" http://textbook bacteriology.net/nutgro_4.html).

The pH also affects activity of urease enzyme for urea degradation. Michaelis constant (KM) and maximum reaction rate (vmax) of urease are dependent on the pH of medium and pH effects are much smaller on Km than V max. The reaction rate (Vmax) is almost nil in the acidic medium (pH = 4) but increases with pH becoming maximum at pH = 7. Further increase in pH value decreased reaction rate of urease becoming minimum at pH= 9 (Fidaleo and Lavecchia 2003).

Biocides

Sodium hydroxide (0.4%) kills 90% population of *Pseudomonas diminuta* ATCC 11568, *Pseudomonas alcaligenes* INCQS, *Pseudomonas aeruginosa* ATCC 15442, *Pseudomonas fluorescens* ATCC 3178, *Pseudomonas picketti* ATCC 5031, *Bacillus subtilis* ATCC 937 and *Escherichia coli* ATCC 25922 in 14.2 minutes (Mazzola et al. 2006). Sodium hydroxide not only damage cell wall and cell membrane of microbes (Guo et al. 2014) but also their nucleic acids (Gates 2009). Similarly viral caspids and nucleic acids (RNA/DNA) are damaged in the strong sodium hydroxide solution (Chen et al. 2012, Karissa et al. 2016). Thus strong sodium hydroxide solution is toxic to microbes including virus. Sodium hydroxide also stops malodor of unsaturated organic compounds (CPCB 2008).

Hydrogen peroxide is another important ecofriendly biodegradable biocide for fungi, bacteria and viruses. Catalase from the microbes quickly breaks hydrogen peroxide to water and nascent oxygen oxidizing DNA, protein and membrane lipids *in vivo* (Liney et al. 2012). The diluted hydrogen peroxide in combination with sodium hydroxide form stronger oxidant (sodium peroxide) highly toxic to microbes.

Microbial decay of organics in the urine and fecal matter form malodorous compounds. We hypothesized that arresting microbial action using biocides (sodium hydroxide and hydrogen peroxide) will not only arrest malodor but also sanitize urinals and toilets.

Experimental studies

* Stock solutions of sodium hydroxide (2%) and hydrogen peroxide (0.5%) prepared using laboratory grade chemicals were stored in the cool dark place.
* Human urine samples (30mL) mixed with 1.0mL of sodium hydroxide (2%) remained malodor free for one week but samples without sodium hydroxide developed malodor.
* Human urine samples (30mL) mixed with 1.0mL of sodium hydroxide (2%) were inoculated on the nutrient agar medium in a pathological laboratory. The samples were sterile because of absence of microbial colonies in the culture plates.
* In another study, human urine sample was thoroughly mixed with saw dust containing urine and feces of Swiss albino mice (1g in 100mL urine sample). The mixture was divided into two sub-sample –a & b.
* Sub-sample-a was inoculated directly on the culture media (McCongy and Blood agar media) while sub-sample-b after adding 2.0mL of sodium hydroxide (2%). Microbial colonies present in the petri-dishes inoculated with sub-sample-a were absent in the sub-sample-b inoculated petri-dishes though few had some colonies similar to air exposed control plates.
* Microbial biofilms collected using sterile cotton swabs from toilet pots were transferred in the sterile 1% saline water (100mL), agitated vigorously and content was divided into A & B sub-samples. Sub-sample –A was inoculated directly on the nutrient agar medium while sub-sample-B after adding 2.0mL of sodium hydroxide (2%) + 0.5mL H_2O_2 (0.5%). After 48h of inoculation, colonies were noted in the culture plates inoculated with sub-sample-A but these were absent in the culture plates inoculated with sub-sample –B.
* We have tested efficacy of sodium hydroxide spray at the house hold level for >15years in KPS residence and for almost 5years in Dr. Shweta residence. Toilets normally used for urination and defecation in the small family households remained malodor free after bi weekly night spray (0.5-2.0%) of sodium hydroxide and response was dose dependent in terms of time scale. Chemical sprays also reduced frequency of water flushing to 3-4/day (beside after defecation); first flushing always after 10minutes of spray. Since malodor control is independent of NaOH concentration, we recommend **bi weekly 0.5% NaOH spray** for the household toilets which not only will reduce cost but also user safety due to NaOH dilution.
* Public toilets and urinals (for 15days) in the Botany Department, Univ. of Rajasthan, and a middle school toilet (Bal Kiran School, Langar ke Balagi, Jaipur) were malodor f**ree for entire day** after single application (morning) of 2% NaOH spray and 5-7 water flushing (first flush after 10minutes of spray).
* Public urinals in a shopping complex remained malodor free for entire day after **single spray each of NaOH (2%) + H_2O_2 (+ 0.05%) accompanied with 5-7 water flushing (first flush after 10minutes of spray)**.
* In another 5days study, 5 sprays of 1% NaOH (at 3h intervals) accompanied with 10 water flushes in a day

control malodor in a public urinal (2 flushes in between sprays; first flush after 10minutes of a chemical spray and second after 2h). 5 sprays of 1% NaOH (at 3h intervals) control malodor in a public toilet. In addition to regular flush after toilet use, one flush must follow after 10 minutes of chemical spray. Further, weekly combined spray of sodium hydroxide (1.0%) and hydrogen peroxide (0.05%) at night is recommended in the public facilities to oxidize recalcitrant malodor compounds to non odorous biodegradable compounds. However, concentration of H_2O_2 may be increased (maximum 0.5%) while time intervals between night sprays may be reduced considering malodor problems.

* Decomposing wastes (especially animal origin) stuck in the gully trap of a drain is often a source of malodor in the house, particularly in the kitchen. As and when this problem arises in my house (KPS), application of 2% NaOH at night in the gully trap via sink outlet not only control malodor instantly but also remove blockage, if any.

Mechanism of Malodor Control

Ammonia & Amines

Sodium hydroxide sprays kills microbes (biofilm) releasing urease and thereby arrest urea degradation.

H2S

Microbial degradation of protein products (of urine and excreta) in the absence of oxygen lead to formation of hydrogen sulphide gas. *Psedomonas*, *Citrobacter*, *Aeromonas*, *Salmonella* and *Escherichia coli* present in the biofilm on surface of urinal and toilet pots are the most common species of hydrogen sulphide producing bacteria.

Nascent oxygen released by catalase action on hydrogen peroxide kills microbes.

Catalase (Biofilm) + $H_2O_2 \rightarrow H_2O$ + O (nascent oxygen)

Nascent oxygen also reacts with hydrogen sulphide to form water and sulphur.

$$O + H_2S \rightarrow H_2O + S$$

Strong alkali (NaOH) also kills micro-organisms associated with hydrogen sulphide production. Alkaline conditions also increase hydrogen sulphide solubility forming more soluble bisulphide ion (HS^-) that does not escape from solution to the atmosphere.

$$H_2S + NaOH \rightarrow NaSH + H_2O$$

$$NaSH + NaOH \rightarrow Na_2S + H_2O$$

Alkaline pH = 10-11 conditions give fast reaction with removal efficiencies 97-99.9%. Thus sodium hydroxide and hydrogen peroxide spray not only kills microbes associated with H_2S production but they also react chemically arresting its release in the surroundings.

Mercaptans

Mercaptans dissolve in sodium hydroxide solution.

$$RSH + NaOH \rightarrow RSNa + H_2O$$

Alkyl disulphide is oxidized in presence of hydrogen peroxide and sodium hydroxide.

$$2RSNa + H_2O_2 \rightarrow RSSR + 2NaOH$$

(dialkyl disulfide)

$$RSSR + 5\ H_2O_2 + 2NaOH \rightarrow 2RSO_3Na + 6\ H_2O$$

Thus sodium hydroxide and hydrogen peroxide sprays oxidize mercaptans to non odorous compound that degrade fast in the Sewage Treatment Plant. The application of these chemicals is superior to conventional ones as they are odorless, quick in action and eco-friendly as they react and transform recalcitrant organic compounds into non-odorous compounds degrading fast in the STP. Their use also reduced number of water flushes.

Precautions: The preparation of concentrated sodium hydroxide and hydrogen peroxide solutions and their dilutions should be made by a qualified chemist in the municipalities, hospitals, shopping malls etc. The spray workers must cover their face with mask and wear chemical proof coats, hats, boots and goggles. The aluminum surfaces should be protected from contact. The product will also remove paint.

Conclusion: Based on 15years of application at the household level (KPS) and limited application at the public facilities, we recommend bi weekly spray of 0.5% sodium hydroxide solution in the households (at night before going to bed) and for 5 times/day (1.0%) in the public urinals and toilets for controlling malodor, more so in the hospitals where toilets, urinals and wash rooms also harbor pathogenic microbes and viruses. Combination of hydrogen peroxide (0.05-0.5%) and sodium hydroxide may be used at weekly intervals in the public facilities depending on the number of users/day. Based on our experiences, we also recommend application of 0.1% sodium hydroxide + 0.05% hydrogen peroxide for floor and tile cleaning in the hospitals during COVID pandemic.

We understand that this novel finding has potential for patent but publishing for the welfare of mankind.

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