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Influence of drying of biosludge on organochlorine compounds from pulp and paper industry

Author Details

S. Gupta	Thapar Centre for Industrial Research and Development, Paper Mill Campus, Yamuna Nagar - 135 001, India
M. Purwar	Thapar Centre for Industrial Research and Development, Paper Mill Campus, Yamuna Nagar - 135 001, India
S.K. Chakrabarti	Thapar Centre for Industrial Research and Development, Paper Mill Campus, Yamuna Nagar - 135 001, India
Satnam Singh (*Corresponding author*)	School of Chemistry and Biochemistry, Thapar University, Patiala - 147 004, India e-mail: ssingh@thapar.edu

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Abstract

Pulp and paper industry is one of the major sources of man-made generation of organochlorine compounds. During biological treatment of wastewater, part of organochlorine compounds is discharged with treated effluent and part is retained on biomass and disposed of as waste activated sludge. Due to presence of these compounds, the disposal of biosludge from pulp and paper industry has become an issue. The estimation of adsorbable organic halogen (AOX) compounds after drying and grinding resulted in 49% lower concentration of AOX due to stripping of purgeable compounds. These purgeable compounds are not released at 60°C in aqueous medium during estimation of purgeable organic halogen (POX) compounds. Dispersion of sludge by sonication overcomes the loss of POX compounds and results in higher concentration of AOX compounds. The drying of biosludge samples at 45, 100 °C and in presence of sun light resulted in 20.1, 49.0 and 29.6% removal of purgeable AOX compounds, respectively. The lab scale sorption study using dichloromethane (as volatile organochlorine compound) reveal that biosludge from pulp and paper industry is a good adsorbent of volatile organochlorine compounds and results in poor release of these compounds during estimation of POX compounds.

Key words

Adsorbable organic halogen, Organochlorine, Purgeable organic halogen, Biosludge, Pulp and paper industry

Introduction

Natural formation of organochlorine compounds is well documented and more than 1500 natural organohalogen compounds have been identified (Biester *et al.,* 2004). The effluent from pulp and paper industry is one of the major sources of organochlorine compounds (Zheng and Allen, 1996; Ali and Sreekrishnan, 2000). The organochlorine compounds are generated during bleaching of brown pulp by chlorine and its derivatives (Bajpai and Bajpai, 1997; Roy *et al.,* 2004). Organochlorine compounds in water and wastewater can be monitored by several techniques, among them; the one based on adsorbable organic halogen (AOX) parameter is the most commonly used (Zheng and Allen, 1996; Barroca *et al.,* 2001).

The removal of biodegradable organic substances in the effluent; both soluble and finely dispersed is accomplished by biological oxidation with the help of microbial consortia principally bacteria (Chakrabarti *et al.,* 2008). Aerobic biological treatment by activated sludge process (ASP) is the most widely used and proven process for treatment of pulp and paper industry effluent. In ASP microorganisms oxidize dissolved and particulate organic matter into simple end products with generation of additional biomass. An equivalent amount of produced biomass is separated and disposed of in a concentrated form called secondary sludge/ excess sludge/ waste activated sludge (WAS) (Gupta *et al.,* 2010). Biological treatment can generally achieve relatively high reduction of biochemical oxygen demand (BOD) and toxicity (Diez *et al.,* 2002).

Partial removal of AOX compounds in the biological system has also been well recognized (Reeve, 1991; Taghipour and Evans, 1996). The removal of these compounds is achieved through volatilization, biosorption and biological dechlorination. Some chlorinated compounds, especially chlorinated phenols, are poorly eliminated in the activated sludge process. The main removal process for chlorinated phenols has been found to be sorption into sludge (Leuenberger *et al.,* 1985). One to three percent of the incoming AOX compounds in influent are adsorbed on waste activated sludge (Chakrabarti *et al.,* 2009). Handling and disposal of WAS from pulp and paper industry is a source of problem throughout the world (Mahmood and Elliott, 2006). In India, AOX compounds bearing sludge from pulp and paper industry has been classified as hazardous waste (MoEF, 2008). Hence, the disposal of sludge in pulp and paper industry has become a cause of concern. Drying and grinding of sludge is required for estimation of AOX compounds in sludge (DIN, 1989). To evaluate the purgeable AOX compounds, which may be lost during drying of sludge, POX compounds are to be estimated. The method recommends adding the purgeable organically bound halogens amount to amount of AOX to compensate the loss of organochlorine compounds during drying and grinding.

The present paper deals with the limitation of the protocol (DIN, 1989) for determination of AOX compounds in biosludge, effect of different drying conditions on release of POX compounds, and development of appropriate method for estimation of AOX compounds in biosludge from pulp and paper industry.

Materials and Methods

Biosludge samples were collected from the effluent treatment plant of an integrated wood base pulp and paper industry in North India having 220 ton average paper production per day and 100 m^3 effluent discharge per ton of paper. The wastewater is treated in activated sludge process and it generates 2.0-2.5 ton waste activated sludge (WAS)/ biosludge per day.

Adsorbable organic halogen content of liquid sample was estimated as per the procedure described in ISO 9562 (1989), using Thermo make total chlorine analyzer and p-chlorophenol (Merck, Germany) as standard. In case of sludge samples, moisture content of sample was measured by drying at 105±2°C till constant weight. For estimation of AOX compounds as per DIN (1989), the dried residue was ground and 50-100 mg sample was taken in glass beaker, dispersed in acidified water (1.5-2.0 pH using nitric acid), transferred to 100 ml volumetric flask and added acidified water up to the mark. Required volume of sample was taken in conical flask and diluted to 50 ml followed by addition of 10 ml nitrate stock solution and 50 mg activated charcoal. The sample was shaken in mechanical agitator at 200 rpm for 2 hr, filtered the suspension through quartz frits and filtered residue was washed with nitrate wash solution to make the residue free of halide ions. The quartz frit was placed in the boat of total chlorine analyzer and ignited at 950 °C in combustion tube. The flue gases were passed through scrubber containing concentrated sulfuric acid. Concentration of halides in flue gas was detected by microcoulometric titration.

For estimation of POX, 0.1 to 1 g (oven dried basis) wet sludge was taken in POX bottle and suspended in 80 ml water. The sample was heated for 30 min at 60 ^{0}C and stripped with oxygen at a flow rate of 150 ml min^{-1}. The gases were fed in to combustion apparatus and halides were detected by microcoulometric titration (DIN, 1989; EPA, 1982). Dichloromethane (DCM) was used as a standard for the determination of POX compounds. The POX content of biosludge was added to AOX content to compensate the loss of volatile compounds during drying.

To evaluate the effect of drying of biosludge on AOX compounds, wet sludge (50-100 mg on OD basis) was taken in glass beaker. The sludge was dispersed in acidified water (1.5-2.0 pH using nitric acid) and kept overnight. The sample was sonicated instead of drying and grinding for dispersion. Sonication was carried out with probe sonicator under ice bath for one-minute duration and process was repeated 3-4 times. Disintegrated sample was transferred in 100 ml volumetric flask and volume made up to the mark with acidified water. The sample was further processed for estimation of AOX compounds as per DIN (1989). To evaluate the loss of AOX compounds during drying of biosludge samples, sludge samples were dried at 45 and 100°C for overnight and in the presence of sun light (with an average temperature of 45-47°C) for 12 hr duration. The samples were analyzed in triplicate and ± values represent standard deviation (S.D).

Results and Discussion

The biosludge samples collected from the paper industry were characterized for various parameters and it contained 90.9% moisture, 72.5% organic content and 2231mg kg^{-1} AOX compounds. The concentration of AOX compounds in influent to activated sludge process and out-coming treated effluent were 8.45 and 5.09 mg l^{-1}, respectively. Accumulation of AOX compounds in biosludge was depended on the concentration of AOX compounds in influent to aeration basin (Gupta *et al.,* 2010). During drying of biomass, highest loss of AOX compounds was observed at 100 °C (49.0%). The extent of volatilization of AOX compounds at 45 °C and under sun light was 20.1 and 29.6%, respectively (Table 1). Volatilization of AOX compounds from biosludge was dependent on extent of temperature. Shomar (2007), reported reduction of AOX compounds up to 66% of its original concentration in the sludge exposed to the sunlight for three months.

The sludge contained some volatile organically bound halogen compounds, which were stripped off during drying at different conditions (Table 1) but were not purgeable at 60 °C in aqueous medium. To elucidate the sorption behavior of organochlorine compounds in biosludge, 0.1 g sludge was dispersed in water and spiked with DCM solution containing 50 µg l^{-1} as POX compounds, the recovered concentration of DCM was 49.96 µg l^{-1}. Similarly 0.2, 0.35, 0.5 and 1.0 g biosludge was dispersed and spiked with standard dichloromethane solution containing 50 µg l^{-1} DCM as POX compound (Table 2). As the concentration of biosludge increased, there was higher sorption of DCM and the stripping of the same decreased (Fig. 1). The increase in sorption of DCM with

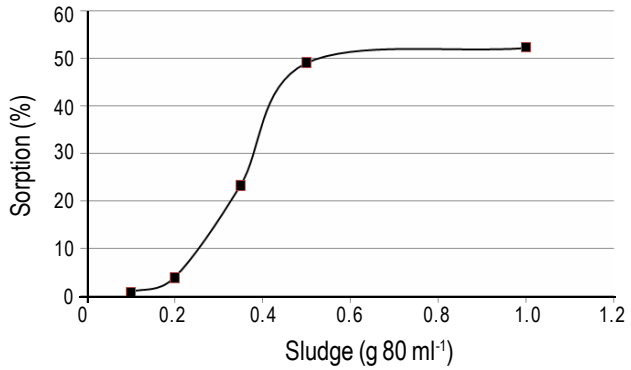

Fig. 1: Effect of biosludge concentration on sorption of dichloromethane (DCM) as POX compound

Table - 1: Effect of drying on concentration of adsorbable organic halogen (AOX) compounds in biosludge of pulp and paper industry

Drying temperature (^{0}C)	AOX (mg kg^{-1})	Reduction (%)
45 (overnight)	1782 ± 14	20.1
45-47 (12 hr sunlight)	1571 ± 36	29.6
100 (overnight)	1138 ± 47	49.0

Values are mean of three replicates ± S.D.

Table - 2: Effect of biosludge concentration on desorption of dichloromethane as POX compounds

Sludge dispersed (g 80 ml^{-1})	POX recovery concentration (µg l^{-1})	Recovery concentration (%) of standard POX
0.1	49.96	99.9
0.2	49.41	98.8
0.35	38.67	77.3
0.5	25.62	51.2
1.0	24.01	48.0

increase in biosludge concentration was due to equilibrium distribution between the solid sludge and aqueous phase. Recovery of the standard from water containing the same amount of DCM was 50.28 ± 0.09 µg l^{-1}.

Further to check the sorption behavior of biosludge, 0.35 and 1.0 g sludge were dispersed in water, spiked as earlier and shaked for 1.0 hr at 200 rpm. In case of 0.35 g sludge sample, sorption of DCM increased from 22.7 to 40.4% and recovery of DCM was 29.81 µg l^{-1}. Similarly in latter case, the sorption of DCM increased from 48.0 to 64.3% and recovery was 18.9 µg l^{-1}. Increased sorption of DCM with increased concentration of biosludge, agitation and time was due to attain equilibrium concentration (Leuenberger *et al.,* 1985).

Since biosorption was considered an important step in the removal of organochlorines in secondary treatment systems from pulp and paper mill effluent (Gloria *et al*., 1994). The volatile organochlorine compounds were adsorbed on biosludge during biological treatment. Other mechanisms such as Van der Waals forces, chemical binding or hydrogen bonding might also be involved (Juhasz *et al.,* 2002). These compounds were stripped off by application of higher energy *i.e.* heat for drying but were not purgeable in aqueous medium at 60 ^{o}C. The increases in temperature or added energy, enhanced cell wall passage for organochlorine compounds (Wandan *et al.,* 2006). The release of water vapour during the drying process facilitated the release of volatile compounds whereas desorption of volatile compounds could not be possible with lesser energy during POX estimation in aqueous solution. Negligible release of volatile compounds during POX estimation resulted in lower AOX content than actual concentration of the same. There was no loss of POX compounds during disintegration of sludge with probe sonication and gave higher AOX value than estimated as per DIN (1989).

In conclusion, the biosludge from pulp and paper industry is a good adsorbent of volatile organochlorine compounds and release of these compounds is poor during estimation of POX content at 60^{o}C in aqueous medium. These compounds are strongly adsorbed on sludge and can only be removed during drying of biosludge. The conventional method (DIN, 1989) requires drying and grinding of sludge prior to estimation of AOX compound which results in loss of volatile organochlorine compounds and fallout in low AOX content. Whereas, the suggested method (dispersion with sonicator) removes the deficiency of conventional method and gives the actual AOX content in the biosludge from pulp and paper industry.

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