ACTA UNIVERSITATIS AGRICULTURAE ET SILVICULTURAE MENDELIANAE BRUNENSIS

Volume LVIII 21 Number 5, 2010

RELATIONSHIP BETWEEN CENTRIFUGATION AND DRYING OF SLUDGE AND THE ORGANIC HALOGENS

K. Hrich, B. Groda

Received: May 12, 2010

Abstract

HRICH, K., GRODA, B.: *Relationship between centrifugation and drying of sludge and the organic halogens.* Acta univ. agric. et silvic. Mendel. Brun., 2010, LVIII, No. 5, pp. 185–190

This work is focused on determination of adsorbable organic halogens (AOX) concentration in the digested sludge from the sewage treatment plant and the losses of this component during dewatering and drying of sludge. Drying of the sludge from wastewater treatment plant is not extended too much in Czech Republic. In this work, the AOX are monitored, because AOX is one of the limits restraining use of the sludge on an agricultural land. Another reason is technological demand for using the sludge in cement processing, because chlorine in AOX can cause decrease in a heat transfer effect in a cement kiln. It is clear from the results that both centrifuged and dried sludge from the sewage treatment plant Brno fulfilled limits for using sludge on agriculture land. They can also be composted, in case they meet other requirements. If not, it is a possibility of co-incineration in cement kiln. In such case, limit for total chlorine including the AOX is required too. This limit was not exceeded. Another aim was to calculate a mass balance of AOX during the centrifugation and drying processes. It was found out, that after centrifugation the main part of AOX remained in the centrifuged sludge (96.4%). The rest was drawn-off with reject water. 60% of AOX in the reject water were dissolved compounds. A similar situation occurred during the drying process. More than 99% of AOX was bound in the dried sludge. The air and vaporised water contained such quantity of AOX, which corresponded with the amount of the dust in the air and the amount of particles of sludge in vaporised water.

adsorbable organically bound halogens, centrifugation, drying, sludge, waste water

Sludge is a mixture of water and solids separated from the waste water in various ways. Sludge is about 1–2% of the treated waste water; however, it contains 50–80% of the initial pollution in the waste water (Kutil, Dohányos, 2005; Malý, Malá, 2006). The ideal status would be to use all sludge as fertilizer for agricultural land to replace mineral fertilizers. However, sludge contains pollution originally present in the sewage. This limits its use on agricultural land, which is modified by regulation in Czech Rep. (corresponds with European regulation), specifying the concentration of heavy metals, PCBs, and AOX. Composting is another option for treating the sludge. The requirements on the sludge are similar. If the sludge contains the above pollutants, it is possible to dispose it in a hazardous waste landfill. In this case, the producer of sludge pays for it and therefore he looks for other choices. One of them is co-incineration of the sludge in the cement work. During the incineration process, chlorine from sludge reacts to chlorides and further with substances in the combustion gases. Arising products adhere to the furnace, cause deterioration of the heat transfer in the furnace, and reduce its effectiveness. Main part of this chlorine is of inorganic origin, but there are the adsorbable organic bound halogens – AOX, too. They are organic compounds containing halogen elements, usually chlorine atoms.

Many articles were published about AOX, but the majority is aimed at analysing concentration of AOX in industrial waste water and sludge. Commonly higher amounts of AOX are in effluents from textile or paper factories. These effluents are usually being treated directly in the own treatment plants. Content of AOX in sludge from urban waste water was mentioned in (Shomar, 2007), who studied the concentration of AOX in waste water and sludge in sewer system of Gaza Strip. It follows from this article that some AOX compounds can form directly during the treating process, especially in anaerobic tanks. Other authors focused rather at the methodology AOX analysis in the sludge (Krysell *et al.*, 2008) and the AOX concentration in rivers, such as (Kaczmarczyk, Niemiycz, 2005).

As already noted, this work was aimed on monitoring the AOX in the centrifuging and drying processes. Sampling was made at the municipal waste water treatment plant (WWTP) in Brno-Modřice, which has sludge treatment including centrifugation and drying. Its capacity is 400 thousand population equivalents (p. e.).

Sludge treatment at WWTP Modřice

Total volume of the digestion tanks is 14 960 m^3. They are equipped by gaseous seal laminated roof. Tank diameter is 20 meters with conical bottom with 8 m depth. Digestion tanks are fitted with a vertical, slow, normal stirrer. Heating of the tanks on temperature 35 °C is carried out by three heat-exchangers sludge/sludge and two heat-exchangers sludge/water.

Two parallel centrifuges Guinard D5LLC with capacity 36 m^3.h^{-1} per unit were used for dewatering of sludge. About 670 m^3.d^{-1} of sludge with 57 g.l^{-1} dried matter are processed on average. Drier NARA NPD14W type with indirect heating consists of horizontal case trough equipped with two hollow rotating spindles with hollow paddles. Hot oil (180–210 °C) flows inside the case, spindles, and paddles. Retention time of the sludge in the drier is about 4 hours. Steam with captured dust from the sludge (3.43 m^3.h^{-1}) is lead to a gas scrubber. Condensate with temperature of 85 °C is filled into sludge/water heat exchanger and serves as main source of heat for digestion tanks. Dried sludge of the amount 28 t.d^{-1} and 88–92 % dry matter is cooled to 40 °C and carried with the system of spindles out to prepared containers. Produced sludge is sampled and carried away for its final use. The whole production of dried sludge is used as an alternative fuel in a cement work. At the time of cement factory stoppages, centrifuged sludge is used as a material for industrial composts.

According to the values obtained from the WWTP operator, the average AOX concentration in raw waste water was 0.138 mg.l^{-1} in 2007. The concentration decreased to 0.050 mg.l^{-1} in treated water. The material balance was calculated on the basis of knowledge of water flow through the WWTP and it can be said that 59.6 % of AOX are captured in the sludge and 40.4 % remain in water. The daily quantity of AOX in sludge was 7359 g.

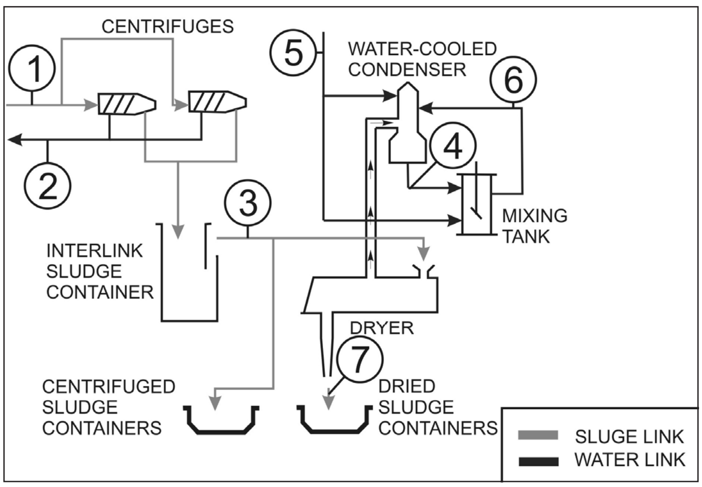
MATERIAL AND METHODS

Selection of sampling sites

Eight sites were selected (see fig. 1): (1) stabilized sludge entering the centrifuges, (2) water from centrifuges, (3) sludge entering the dryer (centrifuged sludge), (4) the cooling water entering the gas scrubber, (5) industrial water entering the gas scrubber, (6) the mixture of water and condensate leaving the gas scrubber, (7) dried sludge, (8) air in the dryer building before it enters the filters for deodorizing (not marked in the figure).

Concentrations of AOX were analysed immediately after sampling. In case this was not possible, the samples were frozen and analysed as soon as possible.

Air was sampled by the HS-SPME method (head space – solid phase micro extraction), in which the sampled air was caught into a prepared container and allowed to react on a fibre impregnated sorbent. The sample was then analysed by gas chromatography.



1: *Sampling sites in the centrifugation and drying processes*

Analysis of AOX

Analysis of aqueous samples was carried out according to ČSN EN 1485: Water quality: The determination of adsorbable organically bound halogens. The ECS 1200 Euroglas analyzer was used. In case of sludge samples treatment, the sludge is pre-dried to 130 °C, mixed with water and further treated similarly to aqueous samples.

RESULTS AND DISCUSSION

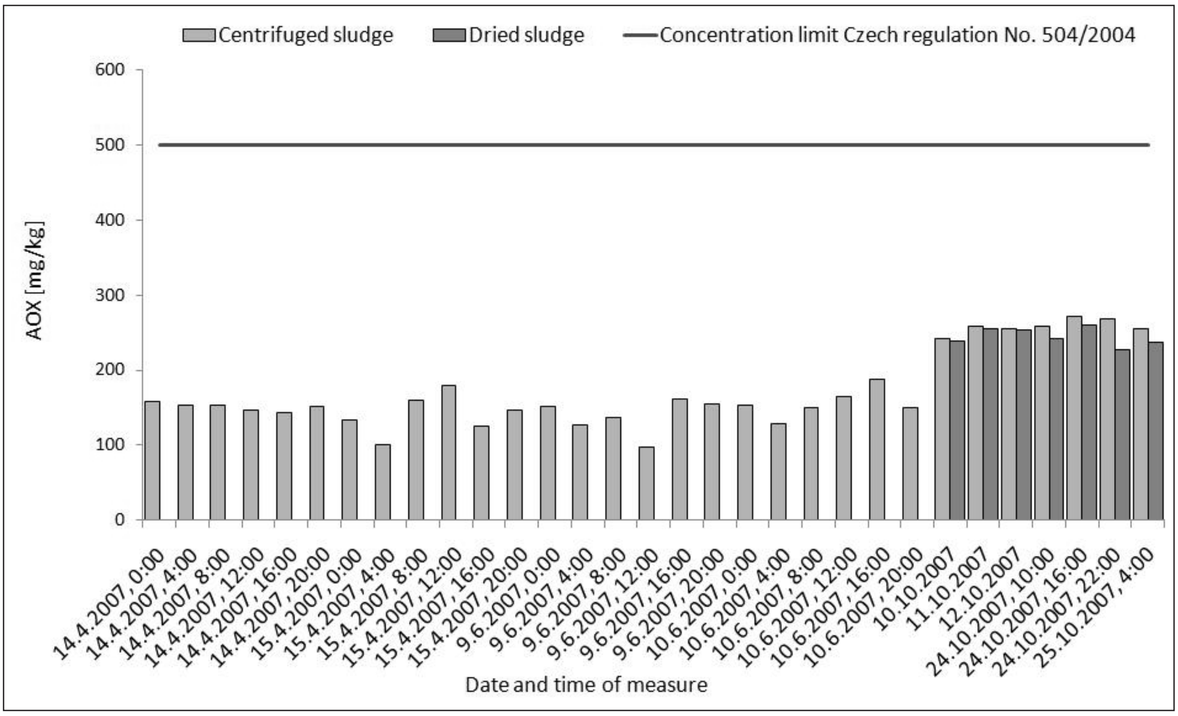
Results published in this work were measured during the year 2007. Daily average of stabilized sludge dry matter in measured samples ranged between 3.12 up to 3.57 % (table Ia and Ib) with the average of 3.38 %. The common value is not overreaches 10 % (Dohányos *et al.*, 2007), usually average dry matter in the sludge is 5.1 % (Malý, Malá, 2006). Higher dry matter content causes transport pipeline problems. Organic part of the dry matter in the monitored sludge was about 52.1 % (usually about 46 % – Chudoba *et al.*, 1991).

As shown in fig. 2, the AOX content in sludge is below the limit value for sludge disposal as fertilizer, and thus from the perspective of AOX content, the sludge can be used to fertilize agricultural land.

As already indicated, co-incineration in a cement furnace is possible. The cement factory is required to have a maximum total chlorine level which does not exceed 0.08 % wt. This is equivalent to 0.8 g total chlorine in one kilogram of dry matter. The measured samples of sludge were suitable for the cement factory. It corresponds with the data obtained from the WWTP operator: in 2008, the total chlorine level was usually only 0.052 % wt.

Data that represent the AOX way through centrifugation process are sorted in table Ia and Ib. Table II shows the values from sludge drying. During centrifugation, water was removed and the dry matter of sludge increased. The water content in dewatered sludge was between 72,6 % and 79,0 % (average 77,1 %). More than 99 % of dry matter remained in the sludge and 29.97 $m^3.h^{-1}$ centrifuged water flew off. The centrifuged sludge contained more than 96 % of AOX fed into the centrifuge. 99.6 % of AOX in the centrifuged sludge was bound in solid phase, while in case of stabilized sludge the percentage was only 96.8 %. Proportion of insoluble AOX in reject water was about 32 % of total AOX content. The average concentration of dissolved AOX in sludge was 242 $mg.m^{-3}$, the average concentration of AOX in sludge solids was about 260 $mg.kg^{-1}$, which corresponds with the literature data: 300 ± 162 $mg.kg^{-1}$ (min. = 68 $mg.kg^{-1}$, max. = 199 $mg.kg^{-1}$) (Malý, Malá, 2009). Adsorption capacity of solid sludge may cause the accumulation of certain substances contained in waste water, such as non-polar hydrocarbons, tensides, polycyclic aromatic hydrocarbons (PAHs), AOX, and heavy metals. Therefore, their proportion in solids of sludge is higher than in the aqueous phase. PAHs, AOX and PCB are not significantly decomposed.

The situation during the drying is a similar as in case of the centrifugation. The majority (about 99 %) of AOX contained in centrifuged sludge remains in the dried sludge. A negligible amount is retained in vaporised water. These AOX are probably dis-



2: *Concentration of AOX in centrifuged and dried sludges: comparison with the Czech regulation No. 504/2004 Coll.*

solved, just like in the reject water. Higher quantities than in vaporised water are contained in the air outflow. This is caused by high concentration of dust in the air outflow. The daily production of dust is on average 120 kg. About 17 g AOX escape into the air with the dust every hour. This dust is separated in a gas scrubber and thus the air in the dryer building meets the permissible exposure limit (PEL) for dust specified in Government Decree No. 361/2007 Coll. (the AOX limit is not set).

I: *Centrifugation process*

Date	04/14	04/15	06/09	06/10	10/10	10/11	10/12	10/13	10/14	10/15	10/16	10/ 24–25
Interval [h]	**20**	**20**	**20**	**20**	**24**	**24**	**24**	**24**	**24**	**24**	**24**	**20**
Stabilized sludge, inlet to the centrifuge												
Quantity [m^3]	829	825	808	806	734	723	739	720	821	755	795	716
Dry matter [kg.m^{-3}]	30.4	32.1	39.3	35.7	33.8	35.4	33.3	34.6	31.2	33.0	32.0	34.9
AOX [mg.kg^{-1} d.m.*]	186	202	300	189	253	279	274	246	281	256	285	321
AOX [g]	4687	5349	9526	5438	6277	7141	6743	6128	7198	6378	7250	8021
Centrifuged sludge												
Dry matter [%]	21.0	22.3	27.4	25.4	22.9	22.3	23.2	23.4	22.6	23.0	23.9	24.4
AOX [mg.kg^{-1} d.m.*]	151	141	138	156	242	259	255	235	268	246	273	312
AOX [g]	4255	4628	9331	5213	6131	7006	6581	5990	7043	6239	7061	7826
Reject water												
Quantity [m^3]	710	708	693	694	626	609	633	614	709	648	690	614
Suspended solids [g.m^{-3}]	395	493	542	447	380	450	300	290	450	500	580	475
AOX [mg.m^{-3}]	609	1020	282	325	233	222	256	225	219	215	274	319
AOX [g]	432	722	195	225	146	135	162	138	155	139	189	196

* d.m. – dry matter

II: *Drying process*

Date	10/10	10/11	10/12	10/13	10/14	10/15	10/16	10/24–25
Interval [h]	**24**	**24**	**24**	**24**	**24**	**24**	**24**	**20**
Centrifuged sludge, inlet to the drier								
Quantity [t]	107	114	105	106	112	107	104	101
Dry matter [%]	22.9	22.3	23.2	23.4	22.6	23.0	23.9	24.4
AOX [mg.kg^{-1} d.m.*]	249	276	269	242	278	253	281	316
AOX [g]	6131	7006	6581	5990	7043	6239	7061	7826
Dried sludge								
Dry matter [%]	91.4	91.5	91.7	92.1	91.5	92.3	91.9	90.8
AOX [mg.kg^{-1} d.m.*]	239	256	253	231	264	241	269	300
AOX [g]	5833	6458	6148	5677	6660	5892	6622	7390
Vaporized water								
Quantity [m^3]	80.2	85.9	78.6	79.0	84.4	80.4	77.2	73.7
AOX [μg.m^{-3}]	0.110	0.136	0.178	0.114	0.146	0.167	0.165	0.269
AOX [g]	8.84	11.70	13.99	8.99	12.34	13.44	12.75	19.80
Air from drier								
Quantity [m^3]	31104	31104	31104	31104	31104	31104	31104	31104
Dust in air, dried matter [kg]	118	97	106	124	72	121	132	174
AOX [mg.kg^{-1} d.m.*]	239	256	253	231	264	241	269	300
AOX [g]	28.2	24.8	26.8	28.7	19.0	29.1	35.6	52.3

* d.m. – dry matter

CONCLUSIONS

The average content in solids of digested sludge in waste water treatment plant Brno is about 260 mg.kg^{-1}.The most of AOX (96.8 %) is bound in suspended parts of sludge during the centrifugation and. 3.2 % of AOX remains in reject water, 68 % of total amount in form of dissolved substances. During the drying, 99 % of AOX remained in dried sludge. The rest (1 %) was divided between vaporised water and dust in outflow.

From AOX concentration point of view, both centrifuged and dried sludge fulfils the legal requirements set for their use on agricultural land, into compost, and co-incineration in cement works.

SOUHRN

Vztah mezi odstřeďováním a sušením kalu a organickými halogenidy

Tato práce byla zaměřena na zjišťování koncentrace adsorbovatelných organických halogenidů (AOX) v kalu z čistírny odpadních vod a hodnocením koncentračních změn AOX ve vyhnilém kalu při jeho odvodňování a sušení kalu. V České republice není sušení čistírenských kalů příliš rozšířeným způsobem. Jedním z důvodů, proč byly sledovány AOX v kalu, byl ten, že koncentrace těchto látek je jedna z limitujících hodnot při využití kalu na zemědělské půdě. Obdobně je tomu u použití kalu do zakládek kompostu. Sušený kal může být docela dobře spolu-spalován v cementářském procesu. I zde však je z technologického hlediska omezeno množství celkového chloru, respektive AOX obsaženého v kalu. Na celkovém chloru v kalu se podílejí vedle AOX i anorganické chloridy. Chlor se při spalování přeměňuje na takzvané „nálepy" a zhoršuje přestup tepla přes stěny pece. Pro vypočítání bilančních rovnic pro odstřeďování a sušení bylo zvoleno sedm odběrných míst, tak, aby byly pokryty všechny vstupy a výstupy z těchto procesů. Vzorky vody a kalu byly podrobeny analýze na přístroji ECS Euroglas 1200. Dále byla získána provozní data, jako množství vody a kalu, které procházelo procesy. Z výsledků analýz je jasné, že odstředěný a sušený kal splňuje limity AOX pro použití kalu na zemědělské půdě. Mohou být tedy i kompostovány, pokud splňují ostatní požadavky. Z hlediska obsahu chloru, respektive AOX, je možné využít kal při spolu-spalování v cementárně. Z bilančních výpočtů vyplynulo, že během odstřeďování zůstává většina podílu AOX v kalu (96,4 %). Zbytek je odstraněn v odstředěné vodě. Přes 99 % pevných částic zůstává v odstředěném kalu. V procesu sušení zůstává v sušeném kalu přes 99 % AOX. Zbytek je rozdělen mezi ostatní výstupy (odpařená voda, odváděný vzduch). V odstředěné vodě tvoří hlavní podíl rozpustné formy AOX. Podobně tomu bude i v odpařené vodě. AOX v ovzduší odváděném ze sušárny jsou vázány na prachové částice.

adsorbovatelné organické halogeny, odstřeďování, sušení, kal, odpadní voda

REFERENCES

DOHÁNYOS, M., KOLLER, J., STRNADOVÁ, N., 2007: Waste water treatment. VŠCHT, Praha (in Czech).

GOVERNMENT DECREE No. 361/2007 Coll., kterým se stanoví podmínky ochrany zdraví při práci (in Czech).

CHUDOBA, J., DOHÁNYOS, M., WANNER, J., 1991: Biological waste water treatment. SNTL Praha (in Czech).

KACZMARCZYK, A., NIEMIYCZ, E., 2005: Adsorbable Organic Halogens (AOX) in Polish Rivers – Levels and Changes. Acta hydrochim. hydrobiol. 33: 324–336.

KRYSELL, M., BECKER, R., WEGENER, J. W., BUGE, H. G., 2008: Certified reference materials for organic contaminants in sewage sludge: a feasibility study. Accred Qual Assur, 13: 553–562.

KUTIL, J., DOHÁNYOS, M., 2005: Efficient use and disposal of sewage sludge. Biom.cz [online]: Available from WWW: http://biom.cz/cz/odborne-clanky/efektivni-vyuziti-a-likvidace-cistirenskych-kalu-2 (in Czech).

MALÝ, J., MALÁ, J., 2006: Chemistry and technology of water. ARDEC Ltd., Brno (in Czech).

MALÝ, J., MALÁ, J., 2009: Waste water treatment. Tribun EU s. r. o., Brno (in Czech).

REGULATION No. 504/2004 Coll., kterou se mění vyhláška Ministerstva životního prostředí č. 382/2001 Sb., o podmínkách použití upravených kalů na zemědělské půdě (in Czech).

SHOMAR, B., 2007: Sources of adsorbable organic halogens (AOX) in sludge of Gaza. Chemosphere, 69: 1130–1135.

Address

Ing. Karel Hrich, Fakulta stavební, Ústav chemie, Vysoké učení technické v Brně, Žižkova 17, 602 00 Brno, Česká republika, e-mail: hrich.k@fce.vutbr.cz, prof. Ing. Bořivoj Groda, DrSc., Ústav zemědělské potravinářské a environmentální techniky, Mendelova univerzita v Brně, Zemědělská 1, 613 00 Brno, Česká republika, e-mail: borivoj.groda@mendelu.cz