CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci

Occurrence and removal of heavy metals from industrial and municipal wastewater: a comparison between MBR and conventional activated sludge processes (CAS)

Giacomo Carletti*[1], Paolo Pavan[§], David Bolzonella*, Cristina Cavinato*
* Department of Science and Technology, University of Verona, Strada Le Grazie 15, 37134 Verona.
[§] Department of Environmental Sciences, University of Venice, Dorsoduro 2137, 30123 Venice.
[1] Interuniversity Consortium "Chemistry for the Environment" (INCA), via delle Industrie 21/8 Marghera, Venice, Italy

The new challenge in wastewater treatment technologies is the removal of micropollutants to "zero discharge" levels. MBRs is one among the best available techniques to reach this target. In this study a comparison between two MBR and two CAS processes with different influent wastewater has been made in order to demonstrate the efficiency for heavy metals removal. The utilization of an automatic sampler, equipped with an ultrafiltration membrane, gives a deep knowledge of the solid-liquid portioning which is very important to understand both the main removal mechanisms that take place and the wastewater characteristics (industrial, municipal or mixed industrial/municipal). MBR processes were able to guarantee higher performances for Pb, Fe, Cd, Cu, Ni and Al removal (always >70%) that have been detected mostly in the bound matter, on the other hand some other compounds like As, Hg, Cr and Zn showed smaller removal percentages. A consequences of using MBR processes is the accumulation of metals in wasted sludge, however in this study the detected concentrations met the limits for agriculture applications.

1. Introduction

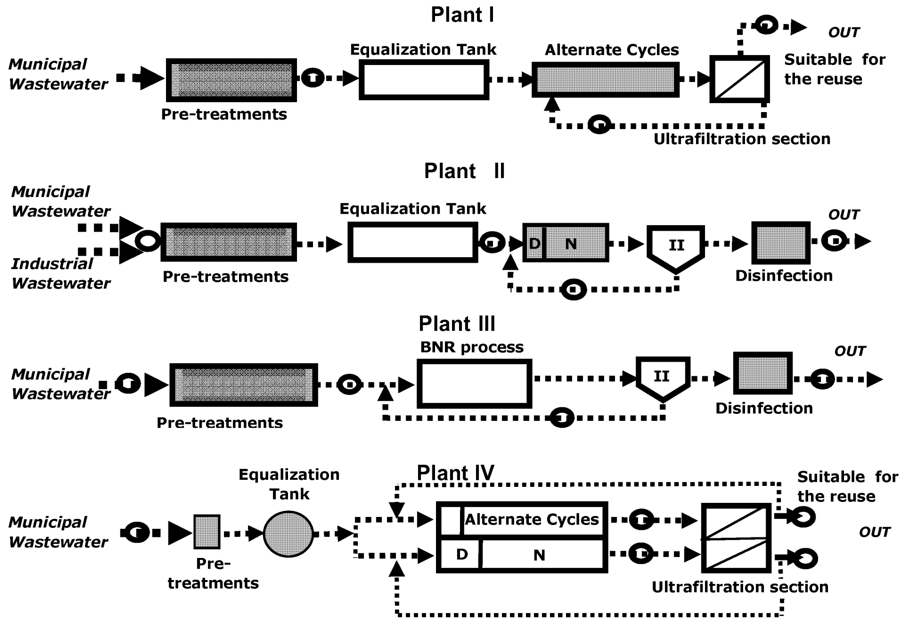
Metals are generally present in wastewaters both at trace and high levels. Although present at very low concentrations, metals, especially heavy metals, are very toxic for the environment and the aquatic life as well as human health, therefore they are particularly observed micropollutants. Furthermore one has to consider also that heavy metals are problematic for the activated sludge processes. In fact if these compounds are greater certain concentrations, some inhibitory effect on the activity of both heterotrophic and autotrophic biomasses can happen (Juliastuti et al., 2003).
The sources of heavy metals can be both the industrial and the municipal ones, however the WWTPs had to remove these influent concentrations in order to respect the always stricter law limits and sometime it happens that conventional activated sludge processes using secondary settler are not able to reach its. In recent years the research for the heavy metals removal has focused on new techniques and among these, MBRs are probably one of the more effective solution that can be adopted also in the optical of

wastewater reclamation and reuse. In this paper metal removal from municipal and industrial wastewater is discussed by means of the activated sludge system, both in conventional (CAS) and as membrane bioreactor (MBR) configurations. Two MBR and two CAS plants have been monitored and studied.

2. Materials and methods

In order to evaluate all the possibilities that can underline the differences between CAS processes and MBR processes, in heavy metals removal, four different plants have been chosen. Three of these are real WWTPs operating in the centre-north of Italy and one is a large demonstration plant (V_{MBR}=22m^3) continuously fed from a full scale plant.
The flow-schemes, the main project data and operational conditions of the examined plants are summarized in Table1.

Table 1. Characteristics of the studied WWTPs



Plant	E.I.	Influent flow (m^3/d)	Effective E.I.	Municipal rate (%)	Industrial rate (%)	SRT (d)	HRT (h)	MLSS (g/l)	MLVSS/ MLSS (%)
I	25000	4700	23000	100	0	20	11,2	7,7	76,5
II	350000	118000	315000	63	37	24	10,5	4,9	65
III	70000	15000	14000	100	0	9	14,4	5,6	63
IV*	-*	36	-*	100	0	20	7,3	9	70

* pre-industrial plant (no scale-up problems).

Wastewater sampling was conducting for a term of 18 months (2005-2006) with daily campaigns made always in the same sections, noting always about the weather conditions (dry or rainy) to evaluate the possible rainfall runoff impact. In order to obtain two simultaneous 24 hours average sampling, it had been utilized both a

conventional sampler and an automatic sampler equipped with an ultrafiltration membrane module for a reliable analysis on the solid fraction (figure 1).
This last device is able to collect the suspended particulate; in this way the retained is considerated a reliable and significant composite daily averaged sample on the dry content. The sampler is able to filtrate 350÷450 L per day of wastewater. As far as the membrane O&M, the filtration cycle can be set by a timer, but the usual values were: permeation (60 seconds)/strong backwashing (15 seconds). Since the membrane underwent to quick initial conditioning fouling, the possible organic layer over the whole sampling period was considered almost stable as well as the molecular weight cut off (MWCO) of the system, that marked the border line between liquid and particulate phase. At the end of each sampling operation, the membrane was cleaned using both hypochlorite solution and citric acid so to re-establish the original conditions.
Heavy metals have been investigated using EPA methods.

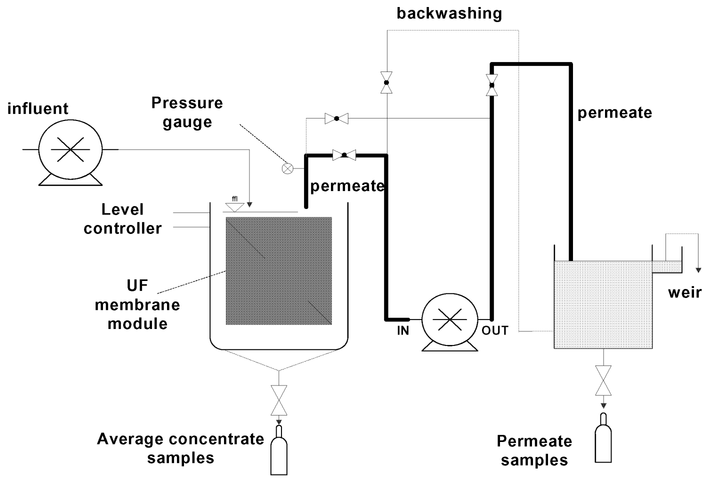


Figure 1. Automatic Membrane sampler

3. Results and discussion

The research has attested what literature says: the detected metals are generally present in the particulate form, in other word metals are usually bound to suspended solids (Gromaire-Mertz et al., 1999). Zn, As, Cd and Hg are found also in the soluble phase. Moreover our data processing has demonstrated that standard deviation of solid phase is smaller than the same calculated on the total or liquid fraction (SD of Cu in total phase is 15,56 and in the solid phase is 3,97; SD of Pb are 7,12 and 2,69; SD of Cd are 0,22 and 0,14; SD of Ni are 5,41 and 0,53; SD of Cr are 14,78 and 1,35). As a consequence of this metals linked to the solids fraction are less variable and so more reliable.
Thanks to this evidence we can identify as a first step, the kind of the influent wastewater. Municipal and industrial wastewater seem to have always the same behaviour as showed in Figure1 and Cr, Cu, Cd and Pb are some examples. It can be seen in the figure below that in industrial wastewater the solid phase is not so influenced by the TSS concentration like in the municipal wastewater on the contrary civil wastewater is more influenced by the seasonal changes. One can observe in fact that, if

the wastewater is almost municipal, metal contents associated to the suspended particulate has vertical trend, on the contrary an horizontal trend is determinable if industries are present in the catchments area. As a consequence: urban sources are already associated to suspended particulate before the discharge into the sewers system and do not depend on the solid content; industrial sources are discharged from industries in liquid phase and adhere to the particulate matter in the sewers pipelines. So, we can say that if the metals into the solid phase increase and the total suspended solids are almost steady, we are treating an industrial wastewater, the opposite is valid for municipal wastewater (Figure 2).

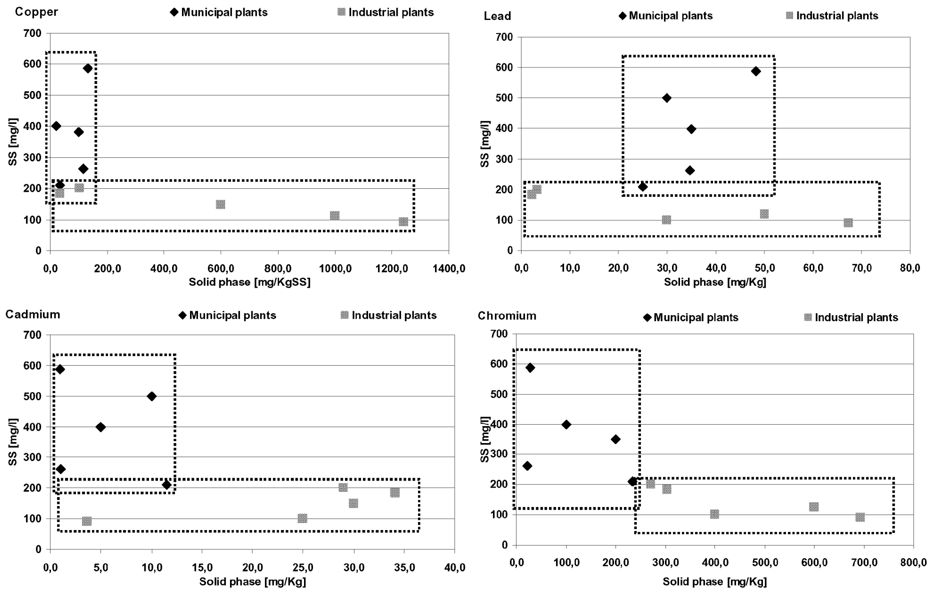


Figure 2. Tendency of particulate phase vs. TSS in municipal and industrial WWTPs

In order to obtain the real efficiency of the activated sludge processes in heavy metals removal, it's necessary the determination of the mass balances. Thanks to these values a reliable comparison between MBR and CAS processes has been made, but also some effective hypothesis about removal mechanism are possible. Table 2 shows the results.

Table 2. Mass balances, removal efficiencies and typical literature values

	IN (g/d)				OUT (g/d)				Total Removal (%)				Typical Values*
	I	II	III	IV	I	II	III	IV	I	II	III	IV	
As	n.d.	314	71	0,076	12,5	189	28,4	0,049	**n.d.**	**40**	**60**	**36**	–
Hg	40,4	236	61,1	0,951	3,29	159	8,53	0,082	**92**	**33**	**86**	**91**	57÷92
Cu	265	6650	1282	1,48	26,3	1789	8,10	0,122	**90**	**73**	**99**	**92**	54÷82
Pb	78	7285	578	0,573	20,7	1939	128	0,015	**74**	**73**	**78**	**97**	68÷100
Cd	n.d.	214	14,2	0,012	n.d.	11,8	n.d.	n.d.	**n.d.**	**94**	**n.d.**	**n.d.**	25÷74
Ni	40,9	3275	255,8	0,330	11,4	844	55,4	0,025	**72**	**74**	**78**	**92**	43÷95
Cr	46	4485	230	0,640	12,7	1651	98	0,085	**72**	**63**	**57**	**87**	68÷85

Zn	1698	62627	11766	12,8	545	38400	10466	1,7**	**68**	**39**	**90**	**87**	87÷88
Fe	5795	284506	59469	65,2	613	62838	6476	1,7**	**89**	**78**	**89**	**97**	67÷90
Al	9118	293737	104663	74,5	981	65697	58783	1,7**	**89**	**78**	**44**	**98**	70÷80

n.d. = not detectable

* Rogers, 1996; Chipasa, 2003; Katsoyannis and Samara, 2004.

** The values are the superior instrumental limits.

The interaction of living organisms with metal ions in aquatic systems can be divided into two main mechanisms. Biosorption, that represents the sum of all passive interactions of the cell wall with metal ions. These are adsorption reactions, ion exchange reactions with functional groups at the cell surface and surface complexation reactions.

The second mechanism is bioaccumulation, this interaction leads to an enrichment of metal ions in the interior of the cell, but while biosorption processes take place within a time scale of minutes, bioaccumulation is being performed on a longer time scale. This is the reason why the major process acting in activated sludge is biosorption. All these evidences are demonstrated by the results showed in table2. CAS processes have a removal efficiency similar to literature values, on the contrary MBR processes is able to guarantee higher performances for Al, Fe, Zn, Cu, Hg and Cr removal.

There are several reasons that can explain this fact, first of all the possibility to work at high concentrations of biomass in the MBR reactors, with the consequence of aiding the biosorption and bioaccumulation mechanisms, the second reason is the barrier made by the ultrafiltration section with the consequence of the total absence of suspended solids in the permeate flow. The removal of compounds like As, Zn and Cd is lower because this elements are detectable not in trace levels, even in the liquid phase. Also the conventional pre-treatments are very important and efficient in order to remove heavy metals, in fact the calculated performances are always near to 100% (the worst result is Hg with 98,4%).

The last important consideration about heavy metals removal rises from figure 3 and is that metals are present in influent wastewater stream and become concentrated in the sludge and disposal of heavy metal-laden sludge could represent an environmental hazard. As a consequence, considering that the metals content into the sewage sludge are of particular interest for the possible application on land for agriculture, they must be often monitored. Data processed from plants I, II and III, equipped with anaerobic digesters, show that levels of metals, before the dewatering, met the limits for agriculture application (EU Directive 86/278/EEC).

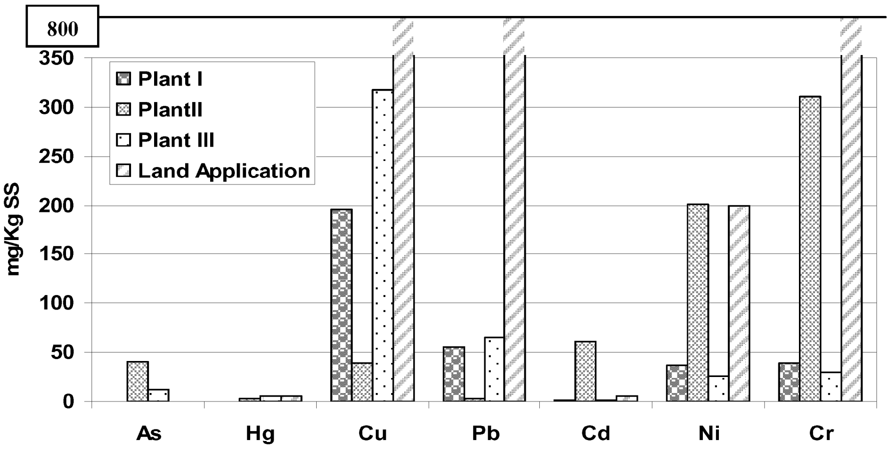


Figure 3. Out of Anaerobic Digester of plant I, II and III and limit for Land Application

4. Conclusions

The study has demonstrated, thanks to the automatic sampler equipped with an ultrafiltration membrane, that the metals linked to the solid fraction are more reliable.

The data processing let us understand if the plant receives municipal or industrial wastewater studying the influence of TSS concentration.

Generally it's possible to assert that total occurrence of heavy metals is Cd<Pb<Cu<Zn<Fe<Al, while Cd<Pb<Cu<Zn<Al are present in the suspended particulate phase.

Comparing the performances of CAS and MBR processes it's possible to observe that the use of ultrafiltration technology is one of the best possible choice in order to obtain high heavy metals removal.

MBR technology concentrates heavy metals into waste sludge, however the plants studied are able to guarantee sewage sludge useful for land application.

5. References

F.Fatone, D.Bolzonella, P.Battistoni, F.Cecchi. (2005)"Removal of nutrients and micropollutants treating low loaded wastewater in a membrane bioreactor operating the automatic alternate-cycles process". Desalination 183,395-405.

Innocenti L., Bolzonella D., Pavan P., Cecchi F. (2002). "Effect of sludge age on the performance of a membrane bioreactor. Influence on nutrients and metals removal". Desalination, 146 (1-3), 467-474.

Gromaire-Mertz M. C., Garnaud S., Gonzalez A., Chebbo G. (1999). "Characterisation of urban runoff pollution in Paris". Water Science and Technology, 39 (2), 1-8.

Chipasa K.B. (2003): "Accumulation and fate of selected heavy metals in a biological wastewater treatment system", Waste Management, 23, 135-143.

M. Karvelas, A. Katsoyiannis, C. Samara, "Occurrence and fate of heavy metals in the wastewater treatment process". Chemosphere 53 (2003) 1201-1210

Juliastuti S.R., Baeyens J., Creemers C., Bixio D., Lodewyckx E., The inhibitory effects of heavy metals and organic compounds on the net maximum specific growth rate of the autotrophic biomass in activated sludge, Journal of Hazardous Materials, B100, (2003) 271-283.