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Water pollution

NATURAL WATER RESOURCES CONTAMINATED BY CHEMICAL AND PETROCHEMICAL INDUSTRIES. QUALITY AND TREATMENT POSSIBILITIES

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Abstract. In terms of available natural water resources (surface and underground), Romania finds itself within the category of country with a limited potential. Regarding the quality of these resources, the formal statistics reflect their poor quality due to the impact of point emissions and diffuse emissions, typical for industrial and agricultural activities. It has to be mentioned that the underground water quality is seriously affected in areas where chemical and petrochemical units develop specific activities, especially for individual water consumers (rural households) which are not connected to a centralised drinking water system for treatment. The work presents the compliance evaluation of different water resources versus the applicable legal norms, the investigation being related to rural settlements for different sites in Prahova county (petrochemical industry) and Valcea county (chemical industry). Based on detailed analytical investigations, the following remarks are to be made: the nature and contamination level of organic pollution reflect the influence of petrochemical and chemical plants on the groundwater used as drinking water in surrounding rural settlements; aromatic hydrocarbons (BTEX) and phenolic compounds are present in concentrations over the legal regulations in the groundwater affected by the activity of a petrochemical plant; organohalogenated pesticides (HCH), phenolic compounds and volatile organic compounds (VOCs) were identified in natural resources located in the close proximity of a chemical plant; the associated inorganic pollution for these natural sources is due to the presence of iron, nitrates, phosphates ions. Based on each specific pollution profile the treatment flows for two locations are elaborated in order to assure the compliance of water quality with the enforced regulations.

Keywords: underground water, organic pollution, BTEX, HCH, VOCs, phenolic compounds, oxidation, adsorption/biosorption.

AIMS AND BACKGROUND

The production of drinking water in according to the quality standards is easy to assure in case of natural sources protected against pollution.

Today, it is unanimously recognised that drinking water resources are more and more polluted, due to the dispersion in aqueous medium of contaminants, some of them without natural equivalent. The discharge of sewage and industrial waste water insufficiently treated, the uncontrolled disposal of wastes, and the

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specific agricultural activities lead to the continuous degradation of surface and groundwater quality.

Among the pollutants with large frequency are: heavy metal ions, inorganic nitrogen compounds (ammonia, nitrites, nitrates), phosphates, sulphides, petroleum products, washing agents, phenolic compounds, pesticides a.s.o.

The sub-standard quality of drinking water is in direct relation with the quality of the resource used, the poor performance of classical treatment flow (coagulation-flocculation-sand filtration-chlorine disinfection), lack of process automation, the advanced worn-out of distribution system, inappropriate control equipment at the plant laboratories.

Due to increasing of raw water pollution, drinking water technology became very developed and lot of new processes were installed: modern oxidation processes like ozonation[1,2] and advanced oxidation (AOP)[3], adsorption technology[4,5] like activated carbon, new disinfection means.

EXPERIMENTAL

The main steps of the experimental study were:

- detailed analytical investigations of underground water located in two counties (Brazi/Prahova – 5 samples, Valcea – 3 samples) in order to assess the pollution profile/degree;
- selection of the representative underground sources, containing specific organic pollutants over the imposed limits by the enforced legislation;
- laboratory experiments for specific treatment flow sheets development (procedures steps succession, work conditions) in the case of two underground water samples, in order to assure the advanced removal of organic micropollutants.

Analytical methods used for water samples characterisation are standardised (the European standard adopted in Romania and/or Romanian effective standards). Also, the technique (experimental research methods) used for treatment technologies setting up, based on coagulation-flocculation, filtration, oxidation and adsorption are proceeded on process and technology type, in accordance with the implemented and certificated quality system SR ISO 9001:2001.

RESULTS AND DISCUSSION

DETAILED ANALYTICAL INVESTIGATIONS FOR UNDERGROUND WATER IN CONTAMINATED AREAS

An important step for water quality improvement consists of setting the real pollution profile and performance limits of selected treatment technologies versus the real pollution profile/level.

Two counties, Brazi (impact of Petrobrazi plant-petrochemical industry) and Valcea (impact of Oltchim plant-chemical industry) were selected for analytical investigations, in order to assess the pollution degree of underground water from different sites:

- Prahova county: Negoiesti, Brazii de Sus, Brazii de Jos, Barcanesti, Romanesti;
- Valcea county: Stuparei, Stolniceni, Cazanesti.

Tables 1 and 2 emphasise those organic and inorganic pollutants that exceed the legal limits for Prahova and Valcea counties. Table 1 reflects the influence of Petrobrazi plant on the underground water used as drinking water in surrounding rural settlements. The following remarks are to be made:

- limits exceeded for the following indicators:
  - turbidity (20-21.6 FTU versus limit of 5 FTU),
  - COD-Cr (19.8-30 mg/l versus limit of 3 mg/l),
  - phenolic compounds (0.02-0.07 mg/l versus limit of 0.001 mg/l),
  - Fe_{total} (0.65-8.53 mg/l versus limit of 0.1 mg/l);
- presence of aromatic hydrocarbons (BTEX) in two of investigated sites:
  - benzene (0.13-0.22 mg/l versus limit of 0.001 mg/l),
  - xylene (0.14 mg/l versus limit of 0.03 mg/l).

Thus, it can be stated that the analysed water resource do not comply the drinking water quality and they can not be supplied without an appropriate treatment.

Table 2 reflects the influence of Oltchim chemical plant on the underground water used as drinking water in surrounding rural settlements. The following remarks are to be made:

- limits exceeded for the following indicators:
  - COD-Cr (3.9-8.5 mg/l versus limit of 3 mg/l),
  - phenolic compounds (0.017-0.032 mg/l versus limit of 0.001 mg/l),
  - HCH (0.0007-0.0009 mg/l versus limit of 0.0005 mg/l),
  - nitrate (95.3 mg/l versus limit of 45 mg/l),
  - phosphates (0.71-5.9 mg/l versus limit of 0.1 mg/l),
  - Fe_{total} (0.45 mg/l versus limit of 0.1 mg/l);
- presence of volatile organic compounds (VOCs), which include both aliphatic and aromatic compounds, at the maximum analysed concentration of about 0.26 mg/l.

If the emission source for some pollutants is disputable, HCH and the other chloro-organic compounds VOCs included are directly related to Oltchim impact on environment.

WATER TREATMENT TECHNOLOGIES

The drinking water quality can not be achieved by classical technological flow, when some toxic, chemically resistant compounds are present in the influent. Some of these compounds were detected and quantified in the investigated water re-

Table 1. Characteristics of underground water in Petrobrazi –Prahova area

No	Pollutant	Measured concentration					Analytical method used	Limits	
		Negoiesti	Brazii de Sus	Brazii de Jos	Barcanesti	Romanesti		(STAS 1342-91)	L 458/2002
1	Turbidity (NTU)	< 1	< 1	20.6	21.6	20	STAS 6323-88	5	≤ 5
2	COD-Cr (mgO_2/l) (homogenous)	2.5	3.99	19.8	3.8	30.6	STAS 3002-85 SR ISO 6060-96	3.0	5 (COD-Mn)
3	COD-Cr (mgO_2/l) (settled supernatant)	–	–	14.2	3.2	24.5	STAS 3002-85 SR ISO 6060-96	–	–
4	Fe_{total} (mg/l)	0.85	0.65	3.86	5.62	8.53	SR 13315-96	0.1	0.2
5	Phenolic compounds (mg/l)	0.025	0.02	0.066	0.066	0.07	SR ISO 6439-01	0.001	0.001 (NTPA013)
6	BTEX total (mg/l)	UDL	UDL	0.4	UDL	0.2	7 + 8 + 9 +10	not specified	–
7	Ethylbenzene (mg/l)	UDL	UDL	UDL	UDL	UDL	ISO 11423/2-00	not specified	–
8	Benzene (mg/l)	UDL	UDL	0.22	UDL	0.13	ISO 11423/2-00	not specified	0.001
9	Toluene (mg/l)	UDL	UDL	0.038	UDL	0.012	ISO 11423/2-00	not specified	–
10	Xylene (mg/l)	UDL	UDL	0.14	UDL	0.06	ISO 11423/2-00	not specified	–

Notes: UDL – under detection limit (0.001 mg/l for BTEX species); HG 351/2005 – Program for gradual removal of dangerous substances emissions, discharging; limits for fresh water: toluene: 10 μg/l; benzene – 1 μg/l; *o,m,p*-xylene – 10 μg/l/isomer.

Table 2. Characteristics of underground water in Oltchim–Valcea area

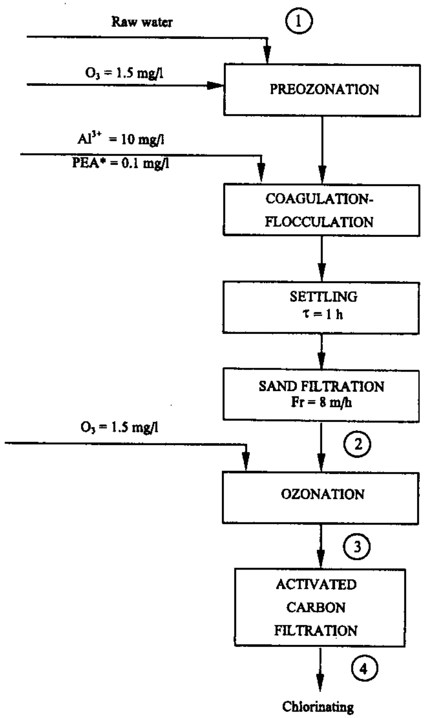
No	Pollutant	Measured concentration			Analytical method used	Limits	
		Stuparei	Stolniceni	Cazanesti		(STAS 1342-91)	L 458/2002
1	COD-Cr (mgO_2/l) (homogenous)	3.9	6.4	8.5	STAS 3002-85 SR ISO 6060-96	3.0	5(COD-Mn)
2	Phenolic compounds (mg/l)	0.032	0.008	0.017	SR ISO 6439-01	0.001	0.001
3	Ammonia (mg/l)	0.49	0.34	0.31	SR ISO 7150/1-01 (photometric) SR ISO 5664-01 (volumetric)	0.00	0.5
4	Nitrate (mg/l)	23.5	95.3	38.9	SR ISO 11048-01	45	50
5	Phosphate (mg/l)	0.09	5.89	0.71	SR EN 1189-00	0.1	–
6	Fe_{total} (mg/l)	0.2	0.45	0.1	SR 13315-96	0.1	0.2
7	VOCs (total) (mg/l)	0.26	0.012	0.0042	STAS 12997-91	not specified	–
8	HCH (total) (mg/l)	0.0009	0.0007	0.0001	SR EN ISO 6468-00	0.0005	0.0005

Notes: VOCs – volatile organic carbon (aromatic and aliphatic); HCH – hexachloro cyclohexane (total isomers).

sources: phenolic compounds, aromatic hydrocarbons and organo-halogenated pesticides.

Based on the following criteria:

- non-specific pollution profile as direct effect of the important industrial activities;
- water contamination induced by chemical and petro-chemical industries;
- inhabited areas in the neighbourhood of industrial units with significant environmental impact, two natural water resources were selected for further technological research. They belong to Brazi-Prahova (Brazii de Jos) and Valcea (Stuparei) areas and are both underground water.



No	Indicator	Concentration values (mg/l)				Efficiency (%)
		①	②	③	④	
1	turbidity	20.6 FTU	< 1 FTU	< 1 FTU	< 1 FTU	> 95
2	COD-Cr	19.8	10.1	4.3	< 1	94
3	Fe total	3.86	0.1	0.1	0.05	97
4	phenols	0.066	0.044	0.006	< 0.001	> 98.5
5	benzene	0.22	0.01	0.09	< 0.001	> 99.5
6	toluene	0.038	0.01	0.01	< 0.001	> 97.6
7	xylene	0.14	0.04	0.01	< 0.001	> 99.3

* Anionic polyelectrolyte

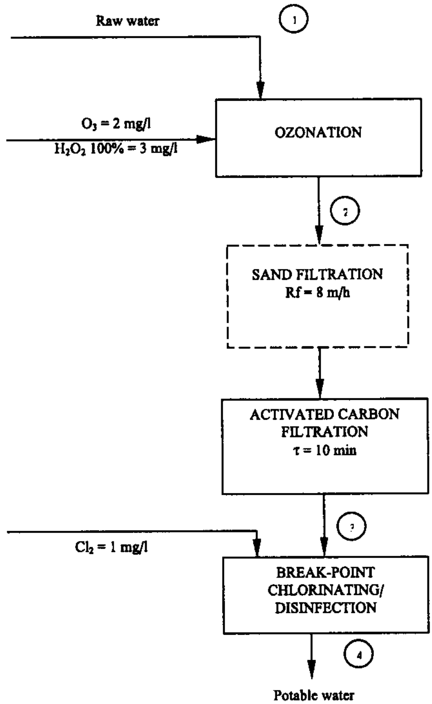
Fig. 1. Underground water treatment flow sheet from Brazi area (Prahova) – Brazii de Jos

Based on each specific pollution profile (organic and inorganic), the research results lead to specific technological flow (Figs 1 and 2, respectively).

To the classical treatment flow, some other technological operations were added, when influents containing organic pollutants and turbidity were to be treated:

• oxidation using ozone (± H_2O_2 activator), one or two stages for breaking the colloidal systems and organic pollutants (phenolic compounds, aromatic hydrocarbons, pesticides) oxidation, respectively;

• adsorption using activated carbon, for the removal of both oxidation products and micropollutants resistant to oxidation.



No	Indicator	Concentration values (mg/l)				Efficiency (%)
		①	②	③	④	
1	ammonia	0.49	0.4	< 1	< 0.05	> 91.6
2	COD-Cr	3.9	3.6	< 1	< 1	> 74
3	phenols	0.032	0.003	< 0.001	< 0.001	> 90.6
4	VOCs	0.26	0.01	< 0.001	< 0.001	> 99.6
5	HCH_t	0.0009	0.0005	< 0.0001	< 0.0001	> 88.9
6	Fe_t	0.2	–	0.03	–	> 88.9

Fig. 2. Underground water treatment flow sheet from Valcea area – Stuparei

Brazi. Figure 1 presents the final result of the experimental research work (Brazii de Sus–Prahova location) in order to set:

- the succession of unitary technological operations;
- the operation parameters at each treatment step;
- the residual concentration after each treatment step in relation with the influent specific pollution profile.

Some remarks are to be made:

- ozonation ensures the advanced iron precipitation, due to its de-complexation;
- two-stage ozonation avoids flotation at the coagulation-flocculation step, due to repartition of the total ozone dose;
- ozonation allows also the activated carbon filter to work as bio-filter. Its bio-regeneration has a direct result in a prolonged operating life.

Valcea. Figure 2 presents the final result of the experimental research work (Stuparei–Valcea location) in order to set:

- the succession of unitary technological operations;
- the operation parameters at each treatment step;
- the residual concentration after each treatment step in relation with the influent specific pollution profile.

The following remarks are to be made:

- oxidation using ozone and H_2O_2 simultaneously ensures destruction of HCH, phenols and the remaining VOCs;
- filtering using activated carbon can work also as a bio-filtration step;
- final chlorination is being conducted to the 'breaking point', thus ensuring ammonia oxidation and also disinfection.

CONCLUSIONS

Laboratory research work was carried for water treatment according to the pollution profile and to achieve the drinking water quality imposed by the Romanian legislation.

Some criteria were set in order to select priority sites:

- non-specific pollution profile as direct effect of the important industrial activities;
- water contamination induced by chemical and petro-chemical industries;
- inhabited areas in the neighbourhood of industrial units with significant environmental impact.

Brazi (impact of Petrobrazi plant) and Valcea areas (impact of Oltchim plant) were selected.

Based on the experimental results, different technological flows were set in which both the unitary processes and their sequential train were determined by pollution profile/level.

Compared to the classical treatment, new, modern processes were added as the specific conditions required:

– oxidation using ozone, one or two stages, for breaking the colloidal systems and organic pollutants (phenols, aromatic hydrocarbons, pesticides) oxidation, respectively;

– adsorption, using activated carbon, for the removal of both oxidation products and micropollutants resistant to oxidation, which can work also as bio-filter.

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