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(54) Title: PROCESS FOR PURIFICATION OF WASTE WATER

(57) Abstract: The invention relates to a process for purification of waste water comprising a pretreatment to obtain a pretreated waste water, subjecting the pretreated waste water to a biological treatment in a biofilm reactor, followed by coagulation, flocculation and floc separation, said flocculation being induced by a coagulant in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety.



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Process for purification of waste water

The present invention relates to a process for purification of waste water comprising pre-treatment, biological treatment in a biofilm reactor, coagulation, flocculation and floc separation.

Many cities around the world are looking for compact wastewater treatment alternatives since space for treatment plants are becoming scarce. Acceptable removal efficiencies in compact plants can be achieved by chemical treatment combined with high rate separation processes like flotation, but the concentration of soluble organic matter may be too high to achieve secondary treatment standards. Therefore, biological treatment is also desirable in the process. Traditional activated sludge treatment requires much space and there is a need for more compact treatment concepts. Another consideration for the treatment process is sludge production. When metal salts are used for coagulation/flocculation, sludge production is normally high because of metal hydroxide precipitation.

The principle behind the high-rate treatment concept is that coagulation, flocculation and flotation is used to separate suspended and colloidal matter, including biomass, while a high-rate moving bed biofilm reactor (MBBR) is used for removing easily biodegradable, soluble matter, that produces biomass. Combined low doses of metal coagulant and cationic polymer added separately are used to achieve a cost effective particle separation process with minimal sludge production. Laboratory-scale experiments demonstrated that good particle removal from a high-rate MBBR effluent was achieved by flotation using a cationic polymer and iron added separately (Melin E. et al., Chemical Water and Wastewater Treatment VII, pp. 261-271, 2002, IWA Publishing, London).

GB 1 512 022 discloses a flocculating agent for water treatment comprising a concentrated aqueous solution of an inorganic flocculating agent and an organic cationic polymer. The inorganic flocculating agent comprises ferric sulphate, ferrous sulphate, aluminium chlorohydrate, aluminium sulphate or ferric chloride, and the organic cationic polymer is for example a polyvinyl pyridine, a polyamide, a polyamine or a polyalkyleneimine. The flocculating agent is fed into a stream of an aqueous suspension of solid material causing formation and precipitation of a hydroxide corresponding to the inorganic flocculating agent. In the concentrated aqueous solution the amount of the inorganic flocculating agent is equal to or

greater than the amount of the cationic polymer. The high amounts of the inorganic flocculating agent results in the formation of high amounts of sludge (iron or aluminium hydroxide) which is unfavourable in view of the further treatment of the sludge.

- 5 GB 2 322 128 A discloses a coagulant for clarifying drinking water. This coagulant is formed by the reaction of an inorganic coagulant with a cationic polymer at elevated temperature, typically at a temperature in the range of 45-65°C. The inorganic coagulant is aluminium sulphate, ferric chloride, aluminium polyhydroxy-chlorosulphate or ferric sulphate, and the cationic polymer is obtained by
10 polymerization of vinyl monomers such as diallyl dimethyl ammonium chloride. The amount of the polymer in relation to the inorganic coagulant is very small, and the amount of the polymer in the final product is also very small, typically 0.5% or 1% of the total weight of the final product. This coagulant is exclusively designed for the clarification of raw water (containing minor amounts of organic substances,
15 such as humic acids, and cations and anions) in drinking water treatment plants.

- KR 2000059008 A discloses combined removal agents for coloring agents and COD in dyeing wastewater using decoloration and agglomeration. These combined removal agents are composed of a cationic polymer decolorant, a stabilizing agent and a coagulant, such as Fe(III) and alum. The polymer is made
20 from dicyandiamide, ammonium chloride and formalin. According to this document there is no reaction between the cationic polymer and the inorganic compounds.

- GB 2 296 238 A discloses a composition for removal of dyes from textile industry effluents comprising a ferrous salt, a polyamine or a diallyldialkylammonium polymer (polydadmac) and a dicyandiamide-formaldehyde-ammonium chloride.
25 These three components are added either as a blend or individually. This composition is claimed to provide a synergistic effect, and removing the final brown colour from the effluent.

- WO 03/029151 A1 discloses a composition for use as a coagulation and flocculating agent in the purification of waste water. The disclosed composition
30 consists of an aqueous solution of polyaluminium chloride as the main constituent, a magnesium or calcium compound and an organic polymer flocculating agent. The organic flocculating agent is a polyamine, a poly-diallyldimethyl-ammonium chloride, a polyethylenimine acetate or a polyethylenimine. The amount of the organic flocculating agent is preferably 20-25 parts by weight per 100 parts by
35 weight of aluminium.

US 4 891 422 discloses inorganic-organic alloy polymer adduct compositions for purification of potable water, paper mill effluent or industrial waste water. The adduct composition is made from an inorganic polymer in reaction with a guanidine polymer or an organic alloy thereof with a polyamine, polyquaternized
5 polymer, polyamide or polyamine-polyamide polymer. In the exemplified compositions the ratio of the polymer(s) to the metal(s) is typically very high, i.e. the amount of the metal is small in comparison to the amount of the polymer. The preferred metal component seems to be aluminium.

GB 1 424 702 discloses a method of decolorizing waste colored aqueous liquid
10 containing non-cationic coloring substance with a water-soluble organic coagulating agent or a metallized complex of said organic coagulant. The organic coagulant is a condensation product of for example a polyamine compound with an aldehyde, or an aromatic amino compound with an aldehyde or a mixture of two amino compounds with an aldehyde. Copper ion is most valuable in obtaining
15 the metallized coagulating agent.

Most of the above discussed documents relate to the purification of drinking waters and specific industrial waste waters, such as dyed waste waters and waste waters from paper industry. The present invention is focussed on the purification of municipal waste waters and normal industrial waste waters especially from food
20 industry or forest industry. The major part of the organic loading from municipal waste water is particulate organic matter having a specific particle size distribution. The soluble organic matter can be well represented by organic matter found in particle sizes less than 0.1 μm whereas the colloids and suspended solids typically have a particle size of above 0.1 μm . Additionally, the municipal waste waters
25 contain dissolved nutrients, for instance phosphorous that is of main interest.

The object of the present invention is to provide a compact, high-rate waste water treatment process, which provides a good purification efficiency, particularly with respect to suspended solids, organic matter and phosphorous, is easy to control and produces a low amount of sludge, particularly metal hydroxide sludge.

30 According to the present invention there is provided a process for purification of waste water comprising a pre-treatment to obtain a pretreated waste water, subjecting the pretreated waste water to a biological treatment in a biofilm reactor, followed by coagulation, flocculation and floc separation, said flocculation being induced by a coagulant in the form of a complex comprising an inorganic divalent
35 or trivalent metal moiety and an organic polymer moiety.

Said pre-treatment can be a physical (sieving, settling etc) or chemical or physical/chemical pre-treatment. Preferably the physical pre-treatment comprises removing large particles from the waste water by a sieve, preferably with sieve openings $< 0,5$ mm.

- 5 A preferred biofilm reactor comprises a high-rate biofilm reactor, preferably a moving bed biofilm reactor (MBBR).

The hydraulic retention time (HRT) in the MBBR is adapted so as to minimize the hydrolysis of particulate organic matter including colloids and solid substances, the HRT being preferably from 15 to 60 minutes, and more preferably from 30 to 45
10 minutes, when municipal waste water is treated.

In a preferred embodiment of the invention the soluble organic matter is removed by means of the biological treatment in the biofilm reactor, preferably in the MBBR, and particulate organic matter including colloids and suspended solids including biomass produced in the biological treatment is removed by means of said
15 coagulation/flocculation/separation. The soluble organic matter typically has a particle size of below $0.1\ \mu\text{m}$, and the particulate organic matter including colloids and suspended solids typically has a particle size of above $0.1\ \mu\text{m}$.

The process of the invention preferably includes a flocculation between the biofilm reactor and the floc separation. The flocculation is preferably carried out in a
20 flocculation tank. The hydraulic overflow rate is preferably from 5 to $20\ \text{m}^3/\text{m}^2\text{h}$, more preferably from 7.5 to $10\ \text{m}^3/\text{m}^2\text{h}$. The HRT in the flocculation tank is preferably from 5 to 15 minutes, more preferably from 7.5 to 10 minutes.

The floc separation is preferably carried out by means of flotation. Dissolved air flotation is especially preferred. The hydraulic overflow rate in the flotation tank is
25 preferably from 5 to $20\ \text{m}^3/\text{m}^2\text{h}$, more preferably 7.5 to $10\ \text{m}^3/\text{m}^2\text{h}$. The HRT in the flotation is preferably from 10 to 30 minutes, more preferably from 15 to 25 minutes. It is also possible to carry out the floc separation by other per se known methods, such as sedimentation or filtration.

The waste water to be purified by the process of the invention can be industrial
30 waste water, for example from food industry or forest industry, or municipal waste water or a combination thereof.

The metal complexed polymer coagulant of the invention can operate at pH values between 2 and 9. The pH of normal municipal waste water is typically between 5 and 8.

5 The complexed coagulant is preferably added to the waste water after the biofilm reactor. It is also possible to add the complexed coagulant into or before the biofilm reactor.

10 The coagulant is preferably added in an amount of 100 to 600 mg/g SS (suspended solids), more preferably 200 to 350 mg/g SS in the waste water to be treated (preferably after the biofilm reactor), calculated on the basis of dry content of the coagulant.

If the amount of the coagulant is given based on turbidity of the waste water, the coagulant is preferably added in an amount per litre of 0.2 to 1.1 mg/NTU (Nephelometric Unit), more preferably 0.6 to 1.0 mg/NTU in the waste water to be treated, calculated on the basis of dry content of the coagulant.

15 Said organic polymer can be selected from the group consisting of
condensation products of alkylamines, polyalkyl amines, ammonia or a mixture thereof with polyfunctional aliphatic dihalides or halohydrins,
urea-formaldehyde condensation products,
melamineformaldehyde condensation products,
20 Mannich (co)polymers,
polymers based on dicyandiamide or polymers from reaction of dicyandiamide and formaldehyde and optionally an ammonium salt and/or an alkylene polyamine and/or urea.

25 Said organic polymer can also comprise the reaction or condensation products of two or more of these polymers or condensation products.

A preferred organic polymer comprises a polymer made from formaldehyde, dicyandiamide and ammonium chloride.

30 Said divalent or trivalent metal can be divalent or trivalent iron, trivalent aluminum or divalent copper, preferably trivalent iron.

A preferred metal complexed polymer coagulant is an Fe^{3+} -complexed dicyandiamide-ammonium chloride polymer.

In the coagulant the weight ratio of the organic polymer moiety to the inorganic moiety is preferably in the range from 7:1 to 3:1, more preferably from 6:1 to 4:1, for example about 5:1.

The metal complexed polymer coagulant is water soluble and cationic.

- 5 The metal complexed polymer coagulant is preferably added to the waste water in the form of an aqueous solution.

The metal complexed coagulant can be obtained by reacting an organic polymer capable of forming a complex with a divalent or trivalent metal, and a source of a bivalent or trivalent metal in an aqueous solution at a temperature of between 0°C and 45°C, preferably between 10°C and 30°C, and more preferably between 15°C and 25°C. In the production of the metal complexed polymer coagulant the manufacturing process is very simple and no heating is required. Furthermore the needed chemicals are inexpensive.

15 The source of the bivalent or trivalent metal can be a sulphate or chloride of said metal, for example ferric chloride, ferric sulphate, ferrous sulphate, aluminium sulphate (alum), aluminium chloride, hydroxyaluminium chloride, hydroxyaluminium sulphate, cupric sulphate or cupric chloride.

The above metal salts can be in solid form or in the form of an aqueous solution. The aqueous solution can be a concentrated solution of the metal salt.

- 20 The process of the present invention removes very efficiently organic substances and phosphorous present in waste waters. The soluble organic matter is removed by the biological treatment in the biofilm reactor and the particulate organic matter including colloids and suspended solids including biomass produced during biological treatment are removed by means of the treatment with the coagulant
25 followed by flocculation and floc separation.

As the hydrolysis of the metal complexed polymer coagulant used in the process of the invention has been found to occur at a pH of above 7, the formation of metal hydroxides, such as iron hydroxides (i.e. amount of sludge) during the purification of waste waters, such as municipal waste water is expected to be low.

- 30 An advantage of the metal complexed polymer coagulant used in the process of the invention is that due to the optimal proportion of the polymer and metal in the complexed polymer coagulant, the amount of the metal hydroxide sludge will be

very small and the precipitated sludge will have good dewatering ability facilitating the further treatment of the sludge, including for example dewatering and burning. Upon burning the sludge the ash content will be low. The sludge is also suitable for composting or as a land filling substance. Also the flocs are densely packed in
5 the sludge whereby the volume of the sludge is small.

As compared to the separate addition of a polymer and a metal coagulant or to the combined addition of these two chemicals, the metal complexed coagulant used in the process of the present invention provides the advantages of being easier to handle, dose and control.

10 In the following the invention will be illustrated by means of examples and the enclosed drawing wherein

Fig. 1 shows results of sedimentation tests obtained by using an Fe^{3+} -complexed DCD polymer coagulant of the invention and a reference DCD polymer coagulant.

15 **Example 1**

An aqueous DCD polymer solution (prepared from formaldehyde, dicyandiamide and ammonium chloride) was used as starting material.

The Fe^{3+} -complexed DCD polymer coagulant is made by adding grinded $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 g) gradually into the DCD polymer solution (2g) and stirring the
20 solution for 30 minutes as the iron dissolved at room temperature. A portion of the obtained coagulant (0.2 g) dissolved in 30ml distilled water was titrated by concentrated NaHCO_3 solution and the pH was monitored. A precipitate was formed at pH~6.8-7.0. From a pure Fe(III) solution iron hydroxide precipitates at pH<4. The complex formation between the trivalent iron and the DCD polymer
25 prevents the precipitation of iron hydroxides below pH~7. As compared to the DCD polymer the Fe^{3+} -complexed DCD polymer of the invention has an increased cationic charge density in the molecule.

Example 2

Municipal waste water was subjected to sedimentation tests in order to evaluate
30 the effect of the Fe^{3+} -complexed DCD polymer. Four different samples of the same waste water were treated with different doses of the Fe^{3+} -complexed DCD polymer (DCD+Fe) prepared in Example 1. The turbidity, total phosphorous (tot P) and

chemical oxygen demand (COD) were measured. The results of the sedimentation tests are shown in Table 1 below.

Table 1

Test No.	Coagulant	Composition		$\mu\text{l/l}$	Polymer mg/l	Metal mg/l	T $^{\circ}\text{C}$	pH	Turbidity (NTU)	Tot P mg/l	COD mg/l
		Polym er % weight	Metal % weight								
Initial							16	7.37	137	6.05	342
4	DCD+Fe	33.6	6.8	40	13.4	2.7			7.73	0.746	89.5
2	DCD+Fe	33.6	6.8	60	20.2	4.1	16	7.09	3.72	0.452	83.4
1	DCD+Fe	33.6	6.8	80	26.9	5.4	15	6.96	3.61	0.192	78.1
3	DCD+Fe	33.6	6.8	120	40.3	8.2	16	6.97	1.85	0.084	81

5

The above results show that the best turbidity was achieved with the highest dose (120 μl) of the coagulant, but also lower doses gave excellent results for e.g. turbidity and total phosphorous (tot P).

Example 3

- 10 Municipal waste water was subjected to sedimentation tests. In the first test the waste water sample was treated with pure DCD polymer, and in the second test the waste water sample was treated with the Fe^{3+} -complexed DCD polymer prepared in Example 1. By complexation it is possible to achieve much higher charge density in the molecule. The results of the sedimentation tests (turbidity vs. dose) are shown in Fig. 1.
- 15

The test results show that the turbidity decreases noticeably, when the waste water is treated with the Fe^{3+} -complexed DCD polymer of the invention. This is due to the increased cationic charge density in the molecule. The reference DCD polymer was much less effective.

20 Example 4

Municipal waste water was taken from a pilot plant influent. The Fe^{3+} -complexed DCD polymer (DCD+Fe) prepared in Example 1 was tested at different doses.

The tests were carried out using a laboratory-scale flotation tester.

- 25 Clarified water was analysed for suspended solids (SS) using GF/C filter, turbidity, chemical oxygen demand (COD), and filtered COD (FCOD) (filtered through GF/C

filter having nominal pore size of 1.2 μm). Dry solids (DC) and volatile solids (VS) were analysed from the sludge samples.

The analytical results from the tests are shown in Table 2 below.

Table 2

	Waste water	DCD+Fe		
		10 $\mu\text{l/l}$	30 $\mu\text{l/l}$	50 $\mu\text{l/l}$
SS (mg/L)	113	40	3	3
Turbidity (NTU)	62.5	23.1	1.16	0.29
COD (mg/L)	308	197	136	130
FCOD (mg/L)	157	140	132	129
Sludge DS (mg)		83	143	156
Sludge VS (mg)		64	110	119
pH	7.07			

The above test results show that the removal efficiencies were good in all cases.

Example 5

Tests were carried out in order to investigate a compact waste water treatment process. The process combines a moving bed biofilm reactor (MBBR) with low-dose coagulation and flocculation/flotation.

Waste water was taken from Ladehammer waste water plant in Trondheim, Norway. The plant receives both municipal and food industry waste water. The waste water was taken from the pilot plant influent. The Fe^{3+} -complexed DCD polymer (DCD+Fe) prepared in Example 1 was used as coagulant.

Large particles were removed from the raw waste water in a sieve before the water was pumped into the MBBR. To the effluent from the MBBR the coagulant was added under rapid mixing which continued for about 45 seconds (400 rpm). The water was then flocculated for 30 minutes while mixing with 80 rpm. The flotation was carried out in a laboratory-scale flotation tester, where distilled water saturated under 5 bar pressure was used as dispersion water. A volume of 0.15 l dispersion water was added to 1 l sample. The concentrations in the clarified water are corrected for dilution by distilled water. Samples from clarified water were taken 7 minutes after the addition of dispersion water. Sludge samples were taken by draining out the water from the bottom of the jars. The sludge layer stayed in the jar and was then washed out by distilled water into sample bottles.

The coagulant (DCD+Fe) was tested at doses of 75, 125 and 200 µl/l. The doses are given as pure product but the dosing solution was diluted 1:10 since the sample had quite high viscosity.

- 5 The process performance was evaluated by taking samples from raw waste water (after sieve), MBBR effluent and flotation outlet. The samples were analysed for suspended solids (SS) using GF/C filter, turbidity, chemical oxygen demand (COD), and filtered COD (FCOD) (filtered through GF/C filter having nominal pore size of 1.2 µm). Dry solids (DC) and volatile solids (VS) were analysed from the sludge samples.

- 10 The analytical results from the tests are shown in Table 3 below.

Table 3

	Waste water	MBBR effluent	DCD+Fe		
			75 µl/l	125 µl/l	200 µl/l
SS (mg/L)	205	162	3.5	3.5	13.8
Turbidity (NTU)	72.4	61.3	0.27	0.64	3.46
COD (mg/L)	443	206	34.7	36.3	47.8
FCOD (mg/L)	208	46.1	35.8	36.7	38.4
Sludge DS (mg)			214	230	245
Sludge VS (mg)			165	175	184
pH	7.50	7.63			

- 15 The above test results show that the removal efficiencies were good in all cases. COD and FCOD values are almost the same, showing that particulate matter was removed.

- 20 New tests with lower coagulant doses was carried out. Otherwise the tests were carried out as described above. The results from the tests are shown in Table 4 below.

Table 4

	Waste water	MBBR effluent	DCD+Fe		
			10 µl/l	30 µl/l	50 µl/l
SS (mg/L)	113	158	23	4	1
Turbidity (NTU)	62.5	70.8	8.5	0.94	0.29
COD (mg/L)	308	247	68.1	39.9	35.0
FCOD (mg/L)	157	50.7	42.2	36.7	36.6
Sludge DS (mg)			134	175	192
Sludge VS (mg)			104	135	147
pH	7.07	7.52			

The above test results show that the removal efficiencies were good in all cases.

- 5 COD and FCOD values are almost the same in the tests with 30 and 50 µl dosage, showing that almost all particulate organic matter was removed.

From the results of Tables 3 and 4 it can be concluded that the best results were obtained with doses 50-75 µl/l.

Example 6

- 10 Pilot-scale studies were carried out in order to investigate a compact wastewater treatment process. The process combines a moving bed biofilm reactor (MBBR) with low-dose coagulation and flocculation/flotation. A combined iron and cationic polymer coagulant in the form of a complex is used.

Materials and methods

- 15 The pilot-plant was located in the Ladehammeren wastewater treatment plant in Trondheim, Norway. The treatment plant receives both municipal and food industry wastewater.

- Large particles were removed from the raw water in a sieve having mesh size of 0.8 mm (Salsnes filter) before the water was pumped into the MBBR. The MBBR had a total volume of 5 m³. The bioreactor contained Kaldnes K1 biofilm carriers occupying 50% of the reactor volume. This gives an effective surface area of 250 m²/m³ reactor volume. The MBBR effluent flowed into flocculation tank through an overflow tank. The Fe³⁺-complexed DCD polymer (DCD+Fe) prepared in Example 1 was used in the test as 5:8 dilution (5 parts product and 3 parts water) and dosed with an in-line mixer. The flocculation consisted of two chambers fitted with turbine mixers and had a total volume of 2.5 m³. The flocculation tank was

connected to a 1.4 m³ flotation unit (surface area of 1 m²). The flow to flotation was initially 5 m³/h but was decreased to 4 m³/h for documentation period resulting in 20% and 30% recycle ratios, respectively. The plant was equipped with on-line sensors for suspended solids measurement from the MBBR and flotation effluents.

- 5 Since the standard flocculation tank in the pilot plant was larger than required, some experiments were carried out with a more compact flocculation unit. In these experiments, a pipe flocculator was installed inside the standard flocculation tank. The compact flocculation had a volume of 0.44 m³ and had 300 vertical pipes with inner diameter of 28 mm and length of 1 m.
- 10 The process performance was evaluated by taking composite samples over 24 hours period from raw water (after sieve), MBBR effluent and flotation outlet. The samples were analysed for suspended solids (SS), chemical oxygen demand (COD) filtered COD (FCOD), biological oxygen demand (BOD5), filtered BOD5 (FBOD5) and total phosphorus. GF/C filters with nominal pore size of 1.2 µm were
- 15 used in SS, FCOD and FBOD analyses. In some tests, composite samples taken over shorter periods of time were also analysed to study the effect of wastewater variation on the process.

The sludge formation studies were carried out over a two hours period. The floating sludge was removed at 30 min intervals and collected into a sludge tank.

- 20 The volume of the sludge was measured together with dry solids (DS) content. During the experiment, SS samples were collected from the MBBR and flotation effluents. The specific sludge production $SS_{removed}/DS_{formed}$ could then be calculated for the chemical treatment of the MBBR effluent.

The MBBR was operated with a HRT of 60 minutes.

- 25 Table 5 shows the average and max/min influent waste water quality in the tests.

Table 5

Influent waste water	BOD mg/l	FBOD mg/l	COD mg/l	FCOD mg/l	SS mg/l	tot-P mg/l
Average	213	111	330	145	162	3.1
Maximum	370	324	832	512	510	5.1
Minimum	103	43	74	26	52	1.8

Results

5 The SS concentration in flotation effluent was below 15 mg/l and SS-removal efficiencies above 92 % at a dosing range from 22 to 89 μ l/l. Good removal efficiencies were achieved demonstrating that regulating the coagulant doses improved the treatment results.

10 At the same dosing range as given above, the total COD concentration in flotation effluent was between 40 mg/l and 125 mg/l when FCOD concentration in MBBR effluent was between 30 mg/l and 150 mg/l, respectively. The results show the importance of soluble organic matter concentrations in the MBBR effluent to the total organic matter removal efficiency in the process. The results demonstrate that good removal of particulate COD and BOD₅ was achieved from the MBBR effluent and some FCOD was also removed. The COD and BOD₅ removals in the
15 whole process are therefore mainly affected by removal of soluble fractions in the MBBR.

20 When the Fe-DCD coagulant of the invention was used, the average sludge production was very small, about 1 g DS_{produced}/g SS_{removed}. The iron doses used in the process were low enough to prevent significant excess sludge production due to precipitation. The average dry solids concentration in the sludge was 25 g/l. The results of dewatering tests showed good dewaterability and indicated that about 40 % dry solids content could be reached in dewatered sludge.

Claims

1. A process for purification of waste water comprising a pre-treatment to obtain a pretreated waste water, subjecting the pretreated waste water to a biological treatment in a biofilm reactor, followed by coagulation, flocculation and floc separation, said flocculation being induced by a coagulant in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety.
2. The process according to claim 1 wherein the pre-treatment comprises a physical or chemical or physical/chemical pre-treatment.
3. The process according to claim 2 wherein the physical pre-treatment comprises removing large particles from the waste water by a sieve.
4. The process according to any of claims 1 to 3 wherein the biofilm reactor comprises a high-rate biofilm reactor, preferably a moving bed biofilm reactor (MBBR).
5. The process according to claim 4 wherein the hydraulic retention time (HRT) in the MBBR is adapted so as to minimize the hydrolysis of particulate organic matter including colloids and solid substances, the HRT being preferably from 15 to 60 minutes, and more preferably from 30 to 45 minutes in municipal waste water.
6. The process of any of claims 1 to 5 wherein soluble organic matter is removed by means of the biological treatment in the biofilm reactor, preferably in the MBBR, and particulate organic matter including colloids and suspended solids including biomass produced in the biological treatment is removed by means of said coagulation, flocculation and separation.
7. The process of claim 6 wherein the soluble organic matter has a particle size of below 0.1 μm , and the particulate organic matter including colloids and suspended solids has a particle size of above 0.1 μm .
8. The process according to any of claims 1 to 7 wherein the process includes a flocculation between the biofilm reactor and the floc separation, the flocculation preferably being carried out in a flocculation tank, the hydraulic overflow rate being preferably from 5 to 20 $\text{m}^3/\text{m}^2\text{h}$, more preferably from 7.5 to 10 $\text{m}^3/\text{m}^2\text{h}$ and the

HRT being preferably from 5 to 15 minutes, and more preferably from 7.5 to 10 minutes.

9. The process according to any of claims 1 to 8 wherein the floc separation is carried out by means of flotation, the hydraulic overflow rate being preferably from 5 to 20 m³/m²h, more preferably from 7.5 to 10 m³/m²h and the HRT being preferably from 10 to 30 minutes, and more preferably from 15 to 25 minutes.

10. The process according to any of claims 1 to 9 wherein the waste water comprises industrial and/or municipal waste water.

11. The process according to any of claims 1 to 10 wherein the coagulant is added to the waste water after the biofilm reactor.

12. The process according to any of claims 1 to 11 wherein the coagulant is added in an amount of 100 to 600 mg/g SS (suspended solids), preferably 200 to 350 mg/g SS in the waste water to be treated, calculated on the basis of dry content of the coagulant.

13. The process of any of claims 1 to 12 wherein the organic polymer is selected from the group consisting of

condensation products of alkylamines, polyalkyl amines, ammonia or a mixture thereof with polyfunctional aliphatic dihalides or halohydrins, urea-formaldehyde condensation products,

melamineformaldehyde condensation products, Mannich (co)polymers,

polymers based on dicyandiamide or polymers from reaction of dicyandiamide and formaldehyde and optionally an ammonium salt and/or an alkylene polyamine and/or urea, and

reaction or condensation products of two or more of these polymers or condensation products.

14. The process of any of claims 1 or 13 wherein the organic polymer comprises a dicyandiamide-formaldehyde-ammonium chloride polymer.

15. The process of any of claims 1 to 14 wherein the divalent or trivalent metal is divalent or trivalent iron, trivalent aluminum or divalent copper.

16. The process of any of claims 1 to 15 wherein the divalent or trivalent metal comprises iron, preferably trivalent iron.

17. The process of any of claims 1 to 16 wherein in the coagulant the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from 7:1 to 3:1, preferably from 6:1 to 4:1.

5 18. The process of any of claims 1 to 17 wherein the coagulant is in the form of an aqueous solution.

19. The process of any of claims 1 to 18 wherein the coagulant is obtained by reacting an organic polymer capable of forming a complex with a divalent or trivalent metal, and a source of a bivalent or trivalent metal in an aqueous solution at a temperature of between 0°C and 45°C, preferably between 10°C and 30°C.

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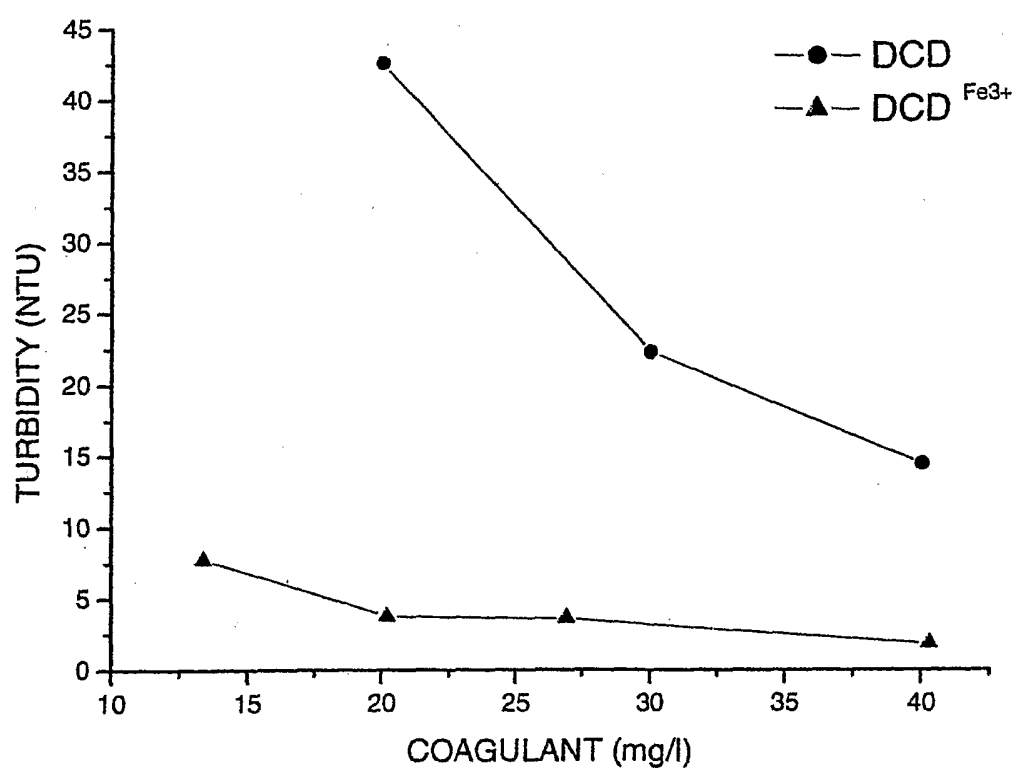


Fig. 1

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/FI2004/000566

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/12 C02F1/52 C02F1/56 C02F3/12 C02F9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	FR 2 194 655 A (TATABANYAI SZENBANYAK) 1 March 1974 (1974-03-01) figure 3	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 December 2004

Date of mailing of the international search report

21/12/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FI2004/000566

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