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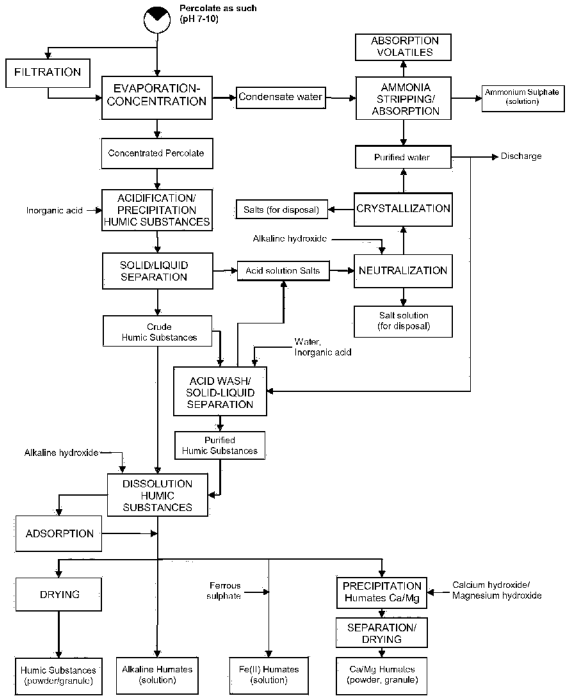
(54) **Title**: PROCESS FOR RECOVERING HUMIC SUBSTANCES FROM PERCOLATE ORIGINATING FROM URBAN SOLID REFUSE DUMPS OR THE LIKE, AND HUMIC SUBSTANCE OBTAINED BY THE PROCESS



(57) **Abstract**: A process for recovering humic substances from percolate originating from urban solid refuse dumps or the like during the maturation stage with pH between 7.0 and 10.0, characterised by: - subjecting the percolate to an evaporation-concentration stage at a temperature between 50 and 130°C and a pressure between 5 and 200 kPa, - subjecting the concentrated percolate containing the substances in solution to an acidification stage with inorganic acid to a pH between 1 and 3 to obtain precipitation of humic substances in the form of flocky solid, - separating the flocky humic substance solid from the liquid phase to obtain crude humic substances.

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PROCESS FOR RECOVERING HUMIC SUBSTANCES FROM PERCOLATE ORIGINATING FROM URBAN SOLID REFUSE DUMPS OR THE LIKE, AND HUMIC SUBSTANCE OBTAINED BY THE PROCESS

The present invention relates to a process for recovering humic substances from percolate originating from urban solid refuse dumps or the like, and a humic substance obtained by the process.

Humic substances are complex organic substances of variable and still not completely defined structure (supramolecular, macromolecular structure), consisting of branched chains of mainly but not exclusively mono and polycyclic, including heterocyclic, aromatics with mainly carboxyl, phenol and hydroxyl functional groups, but also ethers, esters, amino, etc.

These substances are classified by their "solubility" (more precisely their capacity to form colloidal "sols") in water at various pHs (acid pH 0-7, neutral pH 7, basic pH 7-14) as indicated below:

- humic acids (HA)	insoluble at acid pH and soluble at basic pH
- fulvic acids (FA)	soluble at acid pH and at basic pH
- humines	insoluble at acid pH and at basic pH

These solubility characteristics enable humic substances to be extracted from carbonaceous minerals such as leonardite, lignite, peat and also, recently proposed, from compounds produced by transformation and stabilization of organic refuse such as the organic fraction of solid urban refuse (S.U.R) in controlled plants.

Leonardite, which forms in the slow decomposition of organic substances (in particular lignin) is the most recent surface oxidized phase of the geochemical transformation of vegetable organic substances in peat and lignite. It is particularly rich in humic substances, which are extracted in basic aqueous solution with potassium hydroxide (pH 9-12). These solutions, which can contain inorganic salts soluble in basic water in variable quantities, according to the zones of origin, are normally marketed, with various humic substance concentrations, in particular as soil improvers in agriculture. In this respect, humic substances modify the characteristics of soils and improve growth and health of the most varied agricultural crops both by soil treatment and by leaf application.

In particular, humic substances improve:

- soil water retention capacity;
- soil structure and fertility; by virtue of the chelating effect of the functional groups present in humic substances, the nutrients and microelements (iron, calcium, phosphorous, etc.) are prevented from being washed away and their availability is increased over time to the advantage of plant growth and health.

Humic substances are virtually non-biodegradable; they consist of macromolecules of medium (FA) and high molecular weight (HA) with hydrophobic parts and hydrophilic functional groups which are partly acid, and in their salified forms with alkaline metals exhibit surfactant properties which enable them to be also used as surfactants in the washing of earth and soils for their decontamination from hydrocarbons and/or heavy metals by also using their chelating properties on various heavy metals.

Substances similar to humic substances, but not of natural origin, have been obtained by controlled oxidation of coal and proposed as soil improvers or for inerting industrial ash rich in heavy metals.

It is known that, depending on the refuse quality and the degree of maturation of the dump and the rain level, the percolate from S.U.R. dumps can contain humic substance quantities (0.05-5 % by weight) considered interesting for industrial and commercial purposes; however their direct recovery from percolate by known methods does not enable a product to be obtained at competitive cost which is free from the various contaminants present in the percolate, with particular regard to nitrogenated and ammoniacal compounds, and consequently unsuitable for use similar to the humic substances obtained by previously described methods.

The object of the present invention is to provide a process enabling humic substances of marketable quality to be obtained from the percolate of S.U.R. dumps and similar refuse, while achieving lesser consumption of reagents (acids, additives) and using simple technologies, which can be integrated and used with existing technologies, to achieve low investment and running costs.

In attaining this object the following has to be considered.

The humic substance concentration in the percolate changes with the time (age) of activity of the S.U.R. dump; the succession of biological degradation stages which take place on the organic component of refuse once dumped are known to be the following:

- an initial short stage of aerobic biodegradation, principally due to interstitial oxygen, during which there is little production of percolate, or of humic substances;
- a second prolonged stage of anaerobic degradation, itself divided into the following successive stages:
  a) acidogenic stage, in which volatile fatty acids and carbon dioxide form by fermentation, with consequent pH decrease. A large quantity of percolate forms with acid pH (5-6) having high BOD_5, high salt

concentration, heavy metal mobilization but low humic substance presence;

b) acetogenic stage, in which volatile short chain acids form by fermentation, these being further degraded by acetogenic bacteria to acetic acid, a substrate of methanogenic bacteria. Methane is produced, hydrogen and carbon dioxide decrease and the pH increases. The percolate presents a lesser metal and BOD_5 concentration than in the previous stage and an increase in humic substance and ammonia concentration;

c) methanogenic stage, in which methane is formed in large quantity by the prevalence of methanogenic, hydrogenophilic and above all acetophilic bacteria (responsible for the production of 70% of methane). This stage characterises the dump "maturity": the percolate presents neutral-alkaline pH (7-10); low volatile acid and dissolved solids concentrations (low BOD_5), low mobility of heavy metals (for example Fe, Zn), high ammonia concentration, maximum humic substance concentration'

The percolate from a "mature" dump is in fact visually recognizable by its dark brown colour typical of humic substances (HA brown-black colour; FA yellow-brown colour). Studies conducted on the chemical and structural nature of humic substances obtained from the percolate of various S.U.R. dumps by chemico-physical analyses (spectroscopic, UV, FTIR, NMR, etc.) have shown that these are similar, but not equal, to those obtained by extraction from leonardite, peat, lignite, compost.

In purifying dump percolates, the humic substances are mainly removed together with the hydroxides and the basic carbonates of heavy metals by precipitation/clariflocculation with aluminium and iron salts, calcium hydroxide, organic flocculants, etc. implemented by technologies with membranes (ultrafiltration, reverse osmosis) which are however easily clogged by the humic substances. The sludges produced by the percolate purification are usually recycled to the dump or otherwise disposed of, it not being economically convenient to recover humic substances of sufficient commercial quality.

The "mature" percolate is already a basic humic substance solution and is normally classified, in accordance with Italian and European regulations, as "percolate refuse, special non-dangerous" (CER code 190703). A possible initial filtration is also provided to ensure that any "suspended solids" are at low level, less than 500 mg/litre, it being well known that certain dangerous organic microcontaminants, such as polychlorodibenzodioxins and polychlorodibenzofurans, if present, are practically absorbed into the insoluble particulate (suspended solids).

The object of the invention is to recover humic substances from this solution and to purify them of any contaminants present which render them unsuitable for each specific use.

In the present invention it has been found that if instead of treating the mature percolate at pH 7-10 with inorganic acid, for example sulphuric acid, until complete precipitation of the humic substances at pH 2-2.5, the same operation is carried out on the percolate after concentrating it from ten to twenty times by evaporation, for example under vacuum, it is sufficient to use an inorganic acid quantity equal to one quarter of that which would be used if the same quantity of non-concentrated percolate were treated. This reduction of about four times in the specific acid consumption is achieved by the significant decrease in the percolate alkalinity during the concentration procedure, because of the thermal decomposition of the bicarbonates and in particular of ammonium bicarbonate, typically present in high concentration in mature percolate, into ammonia and carbon dioxide, which are then removed from the percolate by evaporation.

Another advantage of operating the humic substance acid precipitation on the percolate concentrated by evaporation, for example under vacuum, is the virtually total absence in the concentrated percolate, and consequently in the humic substances precipitated from it, of possible volatile contaminants, either organic (carboxylic acids, hydrocarbons, other aliphatic/aromatic organic substances, including halogenated and nitrogenated) or inorganic (primarily ammonia); this facilitates the subsequent humic substance purification stage to obtain humic substances of commercial quality.

Another advantage is that the stage of humic substance precipitation with acid can be carried out hot, at 50-100ºC, at the temperature of the concentrated percolate discharge from the evaporator, without additional energy costs, so improving the precipitate morphology and the efficiency of the subsequent stages of solid-liquid separation and purification by washing with water, possibly acidified with inorganic acid to pH <7 to reduce impurities such as inorganic salts and water-soluble organic compounds.

Another advantage of operating on the concentrated percolate is that during evaporation it undergoes thermal treatment with temperatures of 50-130°C for a high average residence time (2-7 hours) with consequent reduction of the initial bacterial load, which is also further reduced in the next stage of acidification to pH 2, obtaining a product virtually free of dangerous bacteria, such as Escherichia coli and salmonella.

Finally the present invention, in addition to the advantageous economical implications (humic substances are a valuable product which, in addition to the current aforesaid uses, could find further profitable applications in the future) also has considerable environmental validity because it recovers from refuse a highly eco-compatible substance particularly useful for the recovery and improvement of arid and/or washed-out soils, favouring the conversion of carbon dioxide into vegetable biomass intended for food purposes or for the formation of renewable energy sources, with consequent reduction of emission of this greenhouse gas into the atmosphere.

This object is attained according to the invention by a process for recovering humic substances from percolate originating from urban solid refuse dumps or the like as described in claim 1.

A preferred embodiment of the present invention is further clarified hereinafter with reference to the accompanying block diagram and to some examples given by way of non-limiting example.

As can be seen from the block diagram, in the process according to the invention if the percolate originating from a S.U.R. dump or the like in its "maturation" phase contains suspended solids, it is initially filtered with suitable filters such as sand filters, microfilters, decanters, centrifuges to obtain a "suspended solids" concentration of less than 500 mg/litre (determined by the IRSA-CNR 2090 method) to remove any contaminant organic substances such as polychlorodibenzodioxins and polychlorodibenzofurans which, if present, are known to be adsorbed in the suspended solid particulate.

The particular percolate presents neutral or basic pH (pH 7-10), is brown in colour, contains more than 0.1% of organic substances by weight determined as the difference between the dry residue at 105ºC (R105) and the dry residue at 600ºC (R600), determined by the IRSA Q64(2) 84 met.02 method, and in particular more than 0.05% of humic carbon by weight, determined by the DM 23-01-91 S.O.G.U No. 29/91 method.

The percolate is then subjected to a continuous evaporation stage under vacuum at a pressure of 5-200 KPa, temperature of 50-130ºC, preferably by a continuous multiple effect process, for an average residence time of 2-7 hours, until a liquid residue is obtained with a reduced volume equal to 1/5 - 1/29 of the initial percolate volume, at basic pH 8-11.

The concentrated percolate contains all the humic substances in solution, in particular humic acids soluble in a basic environment, fulvic acids and inorganic salts, in particular chlorides, sulphates, phosphates, alkaline silicates (Na, K salts) and alkaline-earth silicates (Ca, Mg salts).

The condensate water of the evaporation-concentration stage contains all the volatile contaminants present in the starting percolate, such as ammonia, volatile organic substances, hydrocarbons, halogenated organic substances. These substances are eliminated from the condensate water in a subsequent stripping/absorption stage which also enables an ammonium sulphate solution to be recovered, usable in industry. The condensate water purified in this manner can be used in the crude humic substance acid wash stage or discharged into the public sewer, surface waters or soil, after possible further purification by known processes, for example oxidation, adsorption on active carbon, ultrafiltration, reverse osmosis, etc., to attain the contamination limits allowable for discharge.

The concentrated percolate is subjected to an acidification stage with the addition of an aqueous solution of organic acid, for example 37.5 wt%

concentrated sulphuric acid, 37.5 wt% hydrochloric acid, 75 wt% phosphoric acid, at a temperature between ambient and the boiling point of the concentrated percolate, under agitation, in a discontinuous or continuous precipitator, for example three-stage, with continuous line dispensing of acid, under pH control and under agitation, for example by recycling with static mixers, until complete precipitation of a flocky humic substance solid at pH 1-3, preferably 2.0 stable (constant); the acid quantity required varies with the type of percolate and the type of acid: for example for a mature percolate, for 37.5 wt% sulphuric acid it can be about 10 vol% of the concentrated percolate volume.

Humic substance precipitation commences at pH 4.5-4.0 with possible formation of foam which can be reduced and controlled by adding small quantities of anti-foaming agent, for example of silicone type; the acidification and precipitation system is provided with agitation means, means for bleeding and treatment of vapours and uncondensables such as carbon dioxide, hydrogen sulphide and weak inorganic and organic acid substances volatile under said pH and temperature conditions; consequently this stage also contributes to purification of humic substances from substances which would reduce their quality, for example dangerous sulphides of unpleasant odour.

The humic substances are then subjected to a solid/liquid separation stage achieved by one or more known methods such as filtration, including vacuum filtration, centrifugation, decantation, floatation, etc. To improve the efficiency of these operations, it can be opportune to add small quantities, generally less than 1.0 vol%, of polymer flocculation agents such as polyacrylates, polyacrylamide based cationic polyelectrolytes, additives which in any event do not influence final product quality.

On termination of these stages the following are obtained:

- an acid solution of inorganic salts at pH 1-3, preferably 2.0, in a quantity of 20-90 vol% of the suspension previously obtained by acidification, containing a part of the fulvic acids (yellow coloration) and other water soluble non volatile organic substances present in the starting percolate; this solution is fed to a neutalization section at pH greater than 4 and then to disposal or to a concentration and crystallization stage for separation by precipitation in particular of the alkaline and heavy metal salts, mainly chlorides and sulphates, while the condensate waters are recovered and recycled to the next wash section or fed to discharge after possible treatment.
- a concentrated acid suspension of crude humic substances of pH 1-3, preferably 2.0, in a quantity of 80-10 vol% of the crude humic substance suspension previously obtained by acidification of the concentrated percolate, with dry residue at 105°C of 10-80 wt% of crude humic substances, consisting mostly of humic acid and to a lesser extent of fulvic acid. The crude humic substances are then dissolved as soluble alkaline humates by adding an aqueous solution of alkaline hydroxide, preferably potassium, to pH 5.0-10.0, preferably pH 7.0; an aqueous solution of crude humic substances results which, possibly diluted, can be used as a soil improver in agriculture after qualitatively and quantitatively verifying compliance with the analytical limits provided by current regulations for products of similar origin such as sludge from municipal effluent water purifiers and composts from the S.U.R. organic fraction.

If considered necessary, before being dissolved with the aqueous solution of alkaline hydroxide, the crude humic substances are purified by washes with water, possibly deriving from purification of the condensates produced in the evaporation stages of the present process (Fig. 1), acidified to pH <7 with inorganic acid, for example sulphuric acid and/or hydrochloric acid and/or phosphoric acid, all by known methods with cyclic or continuous washes.

A suspension of purified humic substances is obtained with dry residue at 105ºC of 10-80 wt%, preferably 40%, at pH 5-7, and with low salinity expressed as dry residue at 600ºC of less than 15 wt%, preferably 5 wt%.

If considered necessary, the aqueous solution of crude or purified humic substances solubilized as alkaline humates can be further purified by known treatment with solid adsorbent products such as active carbons, kaolins, clay etc. to remove any organic microcontaminants such as alkylphthalates, in particular 2-ethyl-hexylphthalate, nonyl- and octyl-phenols, bisphenol A.

The aqueous solution of crude or purified humic substances described above, besides being used after possible dilution as a soil improver for crops in agriculture in compliance with qualitative and quantitative limits provided by regulations, can be variously transformed into the following forms similar to those existing on the humic substance market:

- powder or granulate product, moisture content 10-30 wt%, obtained by drying for example in lagoon pools and exposure to air, electrically heated or microwave ovens, infrared rays, etc.,
- product as iron (II) humate solution obtained by adding ferrous sulphate to the basic solution,

- suspended or dried product of calcium or magnesium humate obtained by adding CaO, $Ca(OH)_2$, or MgO or $Mg(OH)_2$, to pH >7, with precipitation of insoluble calcium or magnesium humates at basic pH.

The following examples illustrate the present invention but without limiting its scope.

Example 1)

Successive incremental quantities (ml) of an aqueous 37.45 wt% sulphuric acid solution, density 1.28 g/ml were added at ambient temperature under continuous agitation, to 100 ml of filtered percolate as such (sample 1p) originating from a "mature" S.U.R. dump (A) with less than 500 mg/l of suspended solids, of dark brown colour, having the characteristics stated in Table 1, while measuring the pH with a pH meter provided with a calibrated glass electrode, and recording the values at constant pH for each acid addition.

Effervescence is initially observed with foam production which is reduced and controlled by adding silicone antifoaming agent (0.2 ml of 10% Dinapan 16WD solution). At about pH 4 a flocky brown precipitate begins to form, with the solution colour clearing towards yellow, effervescence and foaming cease, and sulphuric acid addition is continued.

At pH 2 sulphuric acid addition is interrupted and a portion of the suspension was placed in a test tube and centrifuged at 3200 rpm for 10 minutes and the supernatant separated as clear solution. Sulphuric acid was added to this; no further precipitate formation was observed, thus precipitation was considered virtually complete. The entire product obtained is centrifuged in a suitable laboratory apparatus at 3200 rpm for 10 minutes and the clear supernatant separated from the precipitate, the bottom suspension consisting of moist crude humic substances of 10 g (sample HS1) with the chemical characteristics given in Tab.2.

Tab.3. shows for the said sample (1p) the quantities, expressed in volume and weight, of 37.45 wt sulphuric acid added and the pH values obtained after each addition; at pH 2.2 1.97 g of pure sulphuric acid (20.1 mgmoles) were used per 100 ml of percolate as such.

2000 ml of the said percolate (sample 1p) were concentrated by evaporation in a Rotavapor laboratory apparatus at a temperature of 70°C under vacuum at a pressure of 46 KPa for about three hours until a volume reduction of 11 times is reached, to obtain 182 ml of concentrated percolate (sample 1pc, characteristics in Tab.1) of dark brown colour and 1818 ml of aqueous condensate. After cooling to ambient temperature, quantities of sulphuric acid are added to 100 ml of concentrated percolate, sample 1pc (corresponding to 1100 ml of percolate as such), and the pH is measured until complete humic substance precipitation, in the same manner and with the same observations as for the previously described sample 1p; after centrifugation 41.8 g of moist crude humic substances (sample HS1c) were obtained with the characteristics given in Tab.2.

Tab. 3 shows the volumes (ml) and weight (g) of sulphuric acid used against pH for:

1) Sample 1p per 100 ml of percolate as such;
2) Sample 1pc per 100 ml of percolate concentrated 11 times (corresponding to 1100 ml of percolate as such);
3) Sample 1pc normalized to 100 ml of percolate as such (corresponding to 9.09 ml of concentrated percolate).

The comparison shows that 5.71 g (5.82 mgmoles) of sulphuric acid were used per 100 ml of concentrated percolate (1pc) which by calculation correspond to 0.519 g (5.29 mgmoles) of sulphuric acid per 100 ml of percolate as such prior to concentration; while for the non-concentrated sample (sample 1p) a much higher quantity, 1.97 g (20.1 mgmoles), of sulphuric acid per 100 ml of percolate as such (sample 1p) were required, with an increase of about 3.7 times on this consumption.

Tab. 2 shows the differences between the chemical characteristics of the two samples, in particular the concentrated product (sample HS1c) shows a higher dry residue at 105ºC, 23.50%, a good humic and fulvic carbon level, low levels of heavy metals, and a high level of soluble alkaline salts (sodium, potassium) possibly reducible by subsequent washes.

This example highlights the novelty of the invention which consists in implementing the innovative acid precipitation on the concentrated percolate obtained by thermal evaporation, hence achieving an important reduction in the required acid quantity with consequent economic advantage.

With regard to the possible contamination of the percolate as such (sample 1p) and of the relative concentrate (sample 1pc) by dangerous organic compounds, the following were also sought in these samples by normal analytical methods of adequate sensitivity and specificity:

- polychlorobiphenyls (PCB);
- aromatic polycyclic hydrocarbons (APH) (naphthalene, benzo(e)pyrene, acenaphthylene, acenaphthene, fluorine, phenanthrene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene,

dibenzo(ah)anthracene, benzo(ghi)perylene, dibenzo(al)pyrene, dibenzo(ae)pyrene, dibenzo(ai)pyrene, dibenzo(ae)pyrene);

- carcinogenic halogenated aliphatic compounds (bromoformio, 1,2-dibromomethane, chlorodibromomethane, bromodichloromethane);
- non-carcinogenic chlorinated aliphatic compounds (1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, 1,1,2-trichloroethane, 1,2,2-trichloropropane, 1,1,2,2-tetrachloroethane)
- carcinogenic chlorinated aliphatic compounds (chloromethane, dichloromethane, chloroform, vinyl chloride, 1,2-dichloroethane, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene);
- chlorinated aromatic compounds (chlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene);
- aromatic organic solvents (benzene, toluene, ethyl benzene, styrene, xylenes, isopropylbenzene).

The relative results for all the aforesaid organic compounds were of a content less than the limits of measurability of the analytic methods of 1 mg/kg. The following were also less than the respective analytical measurement limits:

- total hydrocarbons (< 10 mg/kg);
- C<12 hydrocarbons (< 5 mg/kg);
- C>12 hydrocarbons (< 5 mg/kg).

Consequently even after concentration by 11 times the "mature" dump percolate (A) did not show contamination by said dangerous organic compounds with the specified analytical measurement limits.

Example 2)

2000 ml of "mature" dump percolate (A) as in Example 1) were concentrated in the laboratory with the same method, temperature and pressure as in Example 1) to obtain 166 ml of 12 times concentrated percolate (sample 2pc).

Successive quantities of 75 wt% phosphoric acid (d:1.5) were added under agitation at ambient temperature to a 100 ml portion of said concentrated percolate while measuring the pH continuously, as in the previous example; the quantities by volume and weight (ml and g) against pH are shown in Tab.4 per 100 ml of concentrated percolate and for the quantity of 8 ml of concentrate corresponding to 100 ml of non-concentrated percolate as such.

It can be seen that the humic substance precipitation commences, as in Example 1), at pH 4.4 and finishes at pH 2.3; the phosphoric acid used is 143 mgmoles per 100 ml of concentrated percolate and 11.48 mgmoles per 100 ml of percolate as such.

To improve the filterability of the precipitate, a solution of flocculant, Hydrapol C180 (80 mg/100ml), was added thereto, then after agitation the mixture was filtered through filter paper (black band) under vacuum (0.8 KPa of residual pressure); moist humic substances were obtained for 31.7% w/w of the concentrated percolate, with dry residue of 26 wt% at 105° (R105).

The use of phosphoric acid enables humic substances containing phosphates to be obtained, usually used as fertilisers in agriculture, hence enabling the raw materials used in the present invention to be upvalued.

Example 3)

An industrial concentrated percolate was used obtained by thermal evaporation under vacuum at a plant operating in a "mature" dump (B) having the following characteristics:

pH: 9.6
dry residue 105ºC (R105): 14.1 wt%
dry residue 600ºC (R600): 10.0 wt%
organic substances (R105- R600): 4.37 wt%
chlorides (Cl): 3.9 wt%
sulphates (SO4): 0.4 wt%

200 ml of said percolate (sample 3pc) were heated to 65ºC, to simulate possible precipitation by acidification at the concentrator exit temperature, then while maintaining the sample heated, progressive quantities of 37.45 wt% sulphuric acid were added in the same manner as in Example 1), while continuously measuring pH, which at the end of precipitation was pH: 2.2; 22 ml of sulphuric acid were required (equal to 11 vol% of the concentrated percolate).

Tab 5 shows the quantities, expressed in volume and weight, of 37.45 wt% sulphuric acid added to 100 ml of concentrated percolate (sample 3pc) and the pH values obtained after each addition; 53.8 mgmoles/100ml of concentrated percolate were required in total, a value very similar to that found in Example 1) of 58.2 mgmoles/100ml of a different concentrated percolate.

Crude moist humic substances (7.1 wt% of sample 3pc) were separated from the obtained suspension by centrifugation, as in Example 1), with dry residue 105ºC: 28.9 wt%; dry residue 600ºC: 17.1 wt%; (R105-R600): 10.8 wt%.

The supernatant, a clear yellow-brown solution, is 92.9 wt% with R105: 14.67 wt% and R600: 12.5 wt%; (R105- R600): 2.17 wt%.

To verify the efficiency of purification from the soluble salts by water wash, an equal quantity (ratio 1/1 by weight) of water acidified to pH 1 with sulphuric acid was added; after normal mixing by agitation, centrifugation was used to separate the supernatant consisting of a clear yellow solution, from the washed humic substance precipitate; R105; R600; chlorides; sulphates were determined on both fractions; four washes were carried out in successive sequence.

Tab. 6 shows the analytical results, from which it can be observed that:

- in the supernatant the quantities extracted reduce by about 50 wt% for each wash on a 1/1 wt ratio wash basis; after the 4th wash, the values of the determinations made are reduced to about 10% of the initial value, indicating a satisfactory capacity for extracting the soluble salts;
- in the precipitated humic substances it can be seen that at the 4th wash R105 is reduced by 10.7 wt%; R600 is reduced by 10.4 wt%, while the organic substances (R105-R600) are 11.5 wt%, virtually unvaried. These results demonstrate the facility for purifying the humic substances from soluble salts by washes with water, better if acidified. In an integrated technology system, water originating from the condensates of the thermal concentration stage can be used, including that under vacuum, as indicated in the process diagram of Fig. 1.

Example 4)

20 ml of the silicone antifoaming solution used in Example 1) were added under agitation to 25 kg of industrial concentrated percolate (sample

4pc) originating from the plant operating at the same dump (B) as Example 3) but of a different period, with the following characteristics:

pH:	9.6
density	1.1 g/ml
dry residue 105ºC (R105):	13.8 wt%
dry residue 600ºC (R600):	10.5 wt%
organic substances (R105- R600):	3.3 wt%
calcium (Ca):	0.22 wt%
sodium (Na):	3.0 wt%
magnesium (Mg):	0.1 wt%

and, while slowly checking the effervescence and the relative foams, 2.7 litres of 37.45 wt% sulphuric acid were added at 20ºC to pH 2.1; a dark brown flocky precipitate as obtained to which 25 g of Idrapol C180 flocculant are added; the product is maintained under agitation for 1 hour and then filtered by gravity through non-woven polypropylene cloth, type Polyfelt TS20(4.01), separating the precipitate and obtaining 2.5 kg of crude moist humic substances.

A 10 g fraction of crude moist humic substances is withdrawn and washed with water acidified to pH 1 with sulphuric acid in a 1/1 v/v ration of crude humic substances/water followed by centrifugation and separation of the precipitate; a total of four washes were carried out in successive steps for purification from the water-soluble salts. A sample of purified humic substances is obtained (sample HS4). The results of the analysis of sample HS4 expressed in wt% on the dry residue at 105ºC, and the methods used are given in Tab. 7. In particular the high dry residue at 600ºC can be observed together with high calcium (Ca) content (9.5 wt%) and high sulphate (SO4) content (30.5 wt%), in a molar ratio (0.7:1) such as to assume the presence of most of the sulphate ion (SO4) as calcium sulphate (CaSO4).

The composition of sample HS4, partially reproduced below, highlights a reduced chloride (Cl), sodium (Na) and potassium (K) content:

sulphates (SO4): 30.5 %s/s
chlorides (Cl): 0.37 %s/s
calcium (Ca): 9.5 %s/s
silica (SiO2): 5.9 %s/s
sodium (Na): 0.22 %s/s
potassium)K): 0.08 %s/s

It can hence be sent that by acidification with sulphuric acid, together with the humic substances there also precipitate alkaline earth metal sulphates, in particular calcium sulphate, and colloidal silica. These compounds are insoluble in water acidified to pH 1 with sulphuric acid used for the washes, whereas the alkaline metal salts, in particular chlorides (Cl) of sodium (Na) and potassium (K) are present in a total concentration of less than 1%.

It can be seen that calcium sulphate (CaSO4) and colloidal silica (SiO2) are also used as soil improvers and soil pH correctors in agriculture (calcium sulphate); consequently from calcium-rich percolates, by using the same technology, product mixtures can be obtained which can perform several useful functions in agriculture.

A small portion of the sample HS4 was dried in an oven in air at 105ºC to constant weight, for two hours; about 0.6 g were used mixed with about 200 mg of potassium bromide (KBr) and a tablet produced by compression; on this latter an FT-IR spectrum was obtained compared with the spectra of KBr tablets produced by the same method from a commercial humic substance sample extracted from leonardite (COM2) and of standard calcium sulphate. The spectra comparison shows the simultaneous presence of absorption bands characteristic of commercial humic substances (COM2) and of calcium sulphate, confirming the presence of this latter in Samp/HS4.

With regard to possible contamination by dangerous non-volatile organic compounds, it can be seen in Tab. 7 that even in the dump percolate (B) and in the purified humic substances, most of those sought are not present at concentrations greater than the limiting quantities of analytical methods, those found being present at concentrations less than the regulation limits current in Italy and the European Union relative to use of purification sludges as agricultural soil improvers, with particular reference to micro-contaminants such as polychlorodibenzodioxins/furans (PCDD/PCDF), 2-ethyl-hexylphthalate, aromatic polycyclic hydrocarbons (APH), polychlorobiphenyls (PCB).

Finally with regard to biological contamination in the dump percolate (B), in concentrated percolate obtained therefrom by evaporation and in purified humic substances HS4, the total coliform concentrations found pass from 18000 UFC/100ml in the percolate to <1 UFC/100ml both in the concentrated percolate and in purified humic substances HS4. This demonstrates how the percolate concentration process by thermal evaporation under vacuum conducted at high temperature is effective in sterilizing the concentrated percolate. A further guarantee of precipitated humic substance sterilization is the acid treatment of the concentrated percolate to pH 2.

Salmonella was instead not found, either in the dump percolate (B) or in the concentrated percolate or in the purified humic substance sample HS4.

Example 5)

1ml of antifoaming agent (0 wt% Dinapan 16WD) and progressive quantities of 37.45 wt% hydrochloric acid (density: 1.186 g/ml) are added under agitation to 200 ml of industrial concentrated percolate originating from the same dump (B) as Example 3-4) but of a different period, with the following characteristics:

pH:	10
dry residue 105°C (R105):	15.4 wt%
dry residue 600°C (R600):	11.1 wt%
organic substances (R105- R600):	4.3 wt%
chlorides (Cl):	3.2 wt%
sulphates (SO4):	0.6 wt%

Tab. 8 shows the hydrochloric acid volumes and weights (ml and g) against pH.

Precipitation commences at pH: 4.3, as in the previous examples, of a dark brown flocky solid, and is completed at pH: 2.0. A total of 15.6 ml of 37.45 wt% hydrochloric acid (density: 1.186 g/ml), 6.85 g of pure acid, corresponding to 3.42 g of acid per 100 ml of concentrated percolate (sample 5pc) equivalent to 95 mgmoles of acid (HCl).

After adding the flocculant followed by centrifugation, as in the previous examples, a crude moist humic substance solid was separated (sample HS5g) of 20.0 g, equal to 10% of (5pc) with dry residue at 105°C of 25 wt%.

After drying at 105°C to constant weight, a portion of HS5g was subjected to four successive washes with water acidified to pH approximately 1 with hydrochloric acid in the manner described in Example 4. A purified moist humic substance solid was recovered (sample HS5) with dry residue at 105°C of 36 wt%. When dried at 105°C the sample HS5 has a weight equal to 26% of the weight of HS5g dried at 105°C from which it was obtained.

Tab. 9 shows the characteristics of the samples HS5g and HS5.

From Tab. 9 it can be seen that by using hydrochloric acid for humic substance precipitation, the presence of calcium sulphate and other possible inorganic compounds insoluble in the purified humic substances is drastically reduced. In this respect, the sample HS5 presents a dry residue at 600°C of 3.7% (equal to 10% of the dry residue at 105°C) while the sample HS4, rich in calcium sulphate, presents a dry residue at 600°C of 17.3% (equal to 48% of the dry residue at 105°C).

Moreover, as shown in Examples 1), 2), 3) it is also demonstrated in this example that precipitation commences at pH less than 5 and is completed at pH less than 2.5 for different percolate types and different inorganic acids.

Small portions of samples HS5g and HS5, oven dried in air at 105°C to constant weight for two hours, were mixed with potassium bromide and formed into tablets, on which FT-IR spectra were obtained in the same manner as for HS4 in Example 4. The HS5g and HS5 spectra are very similar to each other, indicating the absence of significant variations following the wash process. Both are well superimposable on that of the commercial product.

The spectra of samples HS5g and HS5 also show good superimposability with the spectrum of said reference material.

Example 6)

20.0 kg of percolate as such of a mature Italian dump (C) (sample 6p) was concentrated 18 times in the laboratory, to obtain 1.10 kg of concentrated percolate (sample 6pc) by the method stated in the previous examples and with the characteristics given in Tab. 10 in which for the concentrate (6pc) a net reduction of ammoniacal nitrogen and sulphides is particularly noted.

37.45 wt% sulphuric acid was added to the concentrated percolate (6pc) to pH 2.0 in the same manner as in Example 4) to obtain a dark brown flocky precipitate which when separated from the supernatant (clear solution of mother liquors) by centrifugation forms the crude moist humic substance sample not purified by water washes; potassium hydroxide (KOH) was added to this humic substance suspension sample until neutrality (pH 7.0) was reached to obtain an aqueous solution of soluble potassium humates (sample HS6). The characteristics of said sample compared with a commercial product (COM1) of potassium humate solution and of a further commercial humic substance powder product (COM2) extracted from leonardite are shown in Tab. 11.

It can be seen in particular that the sample (HS6) in solution contains a humic carbon quantity similar to the commercial sample in solution (COM1), the soluble inorganic salt quantities (residue at 600°C) are similar and consist of alkaline salts (potassium, sodium) of chlorides, sulphates, in particular the powder sample (COM2) shows high phosphate quantities, the heavy metals are low and virtually similar between the three samples and within the regulation limits for agricultural applications; the two commercial samples obtained by extraction from leonardite show high quantities of iron, which however is used as a soil improver in agriculture.

Consequently it has been demonstrated that products of composition similar to that of the various different commercial products used in agriculture can be prepared from humic substances obtained by acid precipitation from concentrated percolate.

Example 7)

The samples of the previous Example 6) (HS6) and (COM1) in the form of humic substance solutions were analyzed by th Chemical-Agrarian Analysis Laboratory of the Agrarian Biotechnology Department of the University of Padua (Italy) to determine their biostimulant activity in accordance with the methods indicated in:

- Fertilias Agrorum 1(1): 47-53 –Serenella Nardi, Andrea Ertani, Giuseppe Concheri, Diego Pizzeghiello – “Metodi di determinazione dell’attività biostimolante” (Methods for determining biostimulant activity)

Tab. 12 shows the humic substance characteristics, namely: density, total organic carbon (TOC), total extractable carbon (TEC), humic acids (HA), fulvic acids (HF); humification degree HD=(HA+HF)/TEC; humification rate HR=(HA+HF)/TOC; humification index HI=[TEC-(HA+HF)]/ (HA+HF).

The two samples show similar values, both with satisfactory humification (HD, HR, HI), typical of "mature" products.

The molecular weight distribution, Tab. 13, determined by gel permeation (LPLC), is similar for the two samples, with Sample HS6 showing a greater quantity of 1st and 3rd fraction, generally correlated with the degree of humic substance maturation and biological activity. The biostimulant activity determined by the biotest "AUDUS", Tab. 14, in which the two samples were treated with increasing quantities of 3-indoleacetic acid and gibberellic acid (GA3) to determine the inhibition of radical development on watercress and stimulation of hypocotyl elongation on white Trieste chicory, obtained maximum auxinic activity for Sample HS6, while neither sample showed any gibberellinic activity.

Finally Tab. 15 shows evaluations of biostimulant activity on 14 day maize seedlings;

the test, which consists of a hydroponic cultivation of maize seedlings for 12 days with daily replacement of the nutrient solution, followed by a period of 48 hours in which the seedlings are brought into contact with two concentrations (1.0 ml and 0.5 ml per litre) of the two humic extract samples, showed that Sample HS6 gives a better and good growth of the seedling fresh weight.

Consequently the example shows that even crude humic substances, as obtained by the process of the present invention, even without washing to reduce soluble salts (purification), show good characteristics for application as soil improvers in agriculture.

TAB. 1 - Percolate characteristics (Bellolampo, Sicily) as such (sample 1p) and concentrate (sample 1pc) - Example 1 -

		Samples	
	m.u.	**1p**	**1pc**
Volume	mL	2000	180
specific gravity (20°C/20°C)	kg/L	1	1,07
pH	pH	8,26	9,6
Residue at 105°C	% mass	1,9	19,5
Residue at 600°C	% mass	1,28	14,2
Residue at 105°C - Residue at 600°C	% mass	0,62	5,3
BOD5	mg/kg	640	5025
COD	mg/kg	7350	95550
ACID ALKALINE RESERVE	mg/Kg CaCO3	15700	39500
Alkalinity (NaOH equivalents)	meq/Kg	314	789
TOC (Total Organic Carbon)	mg/Kg	1667	25250
Total Kjeldahl Nitrogen(TKN)	mg/kg	4615	3470
Ammoniacal Nitrogen (N)	mg/kg	3500	122
Carbon/Nitrogen ratio	-	2,8	7,3
BOD5/COD ratio	-	0,09	0,05
Total Phosphorus (P)	mg/kg	32	402
TOTAL METALS			
Total Arsenic (As)	mg/kg	0,68	5,2
Barium (Ba)	mg/kg	0,59	3,8
Cadmium (Cd)	mg/kg	< 0,1	< 0,1
Total Chromium (Cr)	mg/kg	3,29	37
Hexavalent Cromium (Cr (VI)	mg/kg	<1	<1
Total Copper (Cu)	mg/kg	0,26	30,5
Iron (Fe)	mg/kg	19,6	202
Potassium (K)	mg/kg	4404	35630
Mercury (Hg)	mg/kg	< 0,1	<0,1
Sodium (Na)	mg/kg	6305	41600
Nickel (Ni)	mg/kg	0,88	9,2
Lead (Pb)	mg/kg	< 0,1	< 0,1
Total Antimony (Sb)	mg/kg	< 0,1	< 0,1
Selenium (Se)	mg/kg	< 0,1	< 0,1
Zinc (Zn)	mg/kg	< 0,1	< 0,1
ANIONS			
Chlorides (Cl)	mg/kg	5790	38280
Sulphates (SO4)	mg/kg	105	1170
Nitric Nitrogen (N)	mg/kg	< 10	130
Nitrous nitrogen (N)	mg/kg	< 0,02	<0.02
ORGANICS			
Polychlorobiphenyls (PCB)			
Aroclor 1242, 1254, 1260	mg/kg	<1	<1
IPA	-		
Naphthalene	mg/kg	<1	<1
Benzo(j)fluoranthene	mg/kg	<1	<1
Benzo(e)pyrene	mg/kg	<1	<1
Acenaphthylene	mg/kg	<1	<1
Acenaphthene	mg/kg	<1	<1
Fluorene	mg/kg	<1	<1
Phenanthrene	mg/kg	<1	<1
Anthracene	mg/kg	<1	<1
Fluoranthene	mg/kg	<1	<1

TAB. 1 - (continued)

		Samples	
	u.m.	**1p**	**1pc**
Pyrene	mg/kg	<1	<1
Benzo(a)anthracene	mg/kg	<1	<1
Chrysene	mg/kg	<1	<1
Benzo(b)fluoranthene	mg/kg	<1	<1
Benzo(k)fluorantene	mg/kg	<1	<1
Benzo(a)pyrene	mg/kg	<1	<1
Indeno(123cd)pyrene	mg/kg	<1	<1
Dibenzo(ah)anthracene	mg/kg	<1	<1
Benzo(ghi)perylene	mg/kg	<1	<1
Dibenzo(al)pyrene	mg/kg	<1	<1
Dibenzo(ae)pyrene	mg/kg	<1	<1
Dibenzo(a,i)pyrene	mg/kg	<1	<1
Dibenzo(ah)pyrene	mg/kg	<1	<1
Total Hydrocarbons	mg/kg	< 10	<10
C<12 Hydrocarbons	mg/kg	<5	<5
C>12 Hydrocarbons	mg/kg	<5	<5
CARCINOGENIC HALOGENATED ALIPHATICS			
Bromoform	mg/kg	<1	<1
1,2-Dibromoethane	mg/kg	<1	<1
Clorodibromometano	mg/kg	<1	<1
Bromodichlorometane	mg/kg	<1	<1
NON-CARCINOGENIC CHLORINATED ALIPHATICS			
1,1-Dichloroethane	mg/kg	<1	<1
1,2-Dichloroethylene	mg/kg	<1	<1
1,1,1-Trichloroethane	mg/kg	<1	<1
1,2-Dichloropropane	mg/kg	<1	<1
1,1,2-Trichloroethane	mg/kg	<1	<1
1,2,3-Trichloropropane	mg/kg	<1	<1
1,1,2,2-Tetrachloroetane	mg/kg	<1	<1
CARCINOGENIC CHLORINATED ALIPHATICS			
Chlorometane	mg/kg	<1	<1
Dichlorometane	mg/kg	<1	<1
Chloroform	mg/kg	<1	<1
Vinyl Chloride	mg/kg	<1	<1
1,2-Dichloroetane	mg/kg	<1	<1
1,1-Dichloroethylene	mg/kg	<1	<1
Trichloroethylene	mg/kg	<1	<1
Tetrachloroethylene	mg/kg	<1	<1
CHLOROBENZENE			
Chlorobenzene	mg/kg	<1	<1
1,2-Dichlorobenzene	mg/kg	<1	<1
1,4-Dichlorobenzene	mg/kg	<1	<1
1,2,4-Trichlorobenzene	mg/kg	<1	<1
AROMATIC ORGANIC SOLVENTS	-		
Benzene	mg/kg	<1	<1
Toluene	mg/kg	<1	<1
Ethylbenzene	mg/kg	<1	<1
Styrene	mg/kg	<1	<1
Xylene (mixed isomers)	mg/kg	<1	<1
Isopropylbenzene (Cumene)	mg/kg	<1	<1

TAB. 2 - Characteristics of Humic Substances from percolate (A) as such (sample HS1) e concentrate (sample HS1c) - Example 1-

		Campioni	
	m.u.	**HS1**	**HS1c**
Specific gravity (20 °C/20 °C)	kg/L	1,02	1,4
pH	pH	2,26	2,38
Residue at 105°C	% mass	8	23,5
Residue at 600°C	% mass	1,22	13,7
Residue at 105°C - Residue at 600°C	% mass	6,78	9,8
TOC (Total Organic Carbon)	% s.s.	46,0	24,26
Humic Carbon (HA)	% C	15,1	6,8
Fulvic Carbonio (FA)	% C	15,7	7
Total Kjeldahl Nitrogen (TKN)	mg/kg s.s.	3680	4850
Carbon/Nitrogen ratio	-	125	50
Total Phosphorus (P)	mg/kg ss	467	916
TOTAL METALS			
Total Arsenic (As)	mg/kg ss	< 0,1	< 0,1
Barium (Ba)	mg/kg ss	3,16	14
Cadmium (Cd)	mg/kg ss	< 0,1	< 0,1
Total Chromium (Cr)	mg/kg ss	25,3	88,2
Hexavalent Cromium (Cr)	mg/kg	<1	<1
Total Copper (Cu)	mg/kg ss	4,19	7,04
Iron (Fe)	mg/kg ss	104	406
Potassium (K)	% s.s.	1,98	8,0
Manganese (Mn)	mg/kg ss	0,63	2,13
Molybdenum (Mo)	mg/kg ss	0,8	2
Sodium (Na)	% s.s.	3,22	13,8
Nickel (Ni)	mg/kg ss	6	21,4
Lead (Pb)	mg/kg ss	0,48	2,45
Total Antimony (Sb)	mg/kg ss	< 0,1	4,4
Selenium (Se)	mg/kg ss	< 0,1	< 0,1
Zinc (Zn)	mg/kg ss	29,2	42,6
ANIONS			
Chlorides (Cl)	% s.s.	0,52	32,3
Sulphates (SO4)	% s.s.	1,78	5,77

TAB. 3 - Humic Substance precipitation from percolate (A) - 37.45 wt% sulphuric acid quantity (d: 1.28 Kg/dm^3) referred to 100mL of percolate as such. - mL H_2SO_4 vs pH)
- sample 1p: percolate as such (100 mL)
- sample 1pc: percolate concentrated 11 times (100 mL)

- Example 1-

Sample 1p (100mL)				**Sample 1pc** (100mL)			
37.45 wt% H_2SO_4 solution (mL)	H_2SO_4 (g)	pH	Notes	37.45 wt% H2SO4 solution (mL)	H_2SO_4 (g)	pH	Notes
0,0	0,00	7,95		0,0	0,00	9,5	
1,0	0,48	6,77		5,0	2,40	6,80	
2,0	0,96	6,48		10,0	4,80	4,47	Commencement precipitation
2,5	1,20	6,20		11,0	5,28	3,68	
3,0	1,44	5,80		11,5	5,52	3,00	
3,3	1,58	5,10		11,7	5,62	2,70	
3,4	1,63	4,75		11,9	5,71	2,38	precipitation complete
3,5	1,68	4,43	Commencement precipitation				
3,6	1,73	4,30					
3,7	1,78	4,00					
3,8	1,82	3,70					
3,9	1,87	2,70					
4,0	1,92	2,40					
4,1	1,97	2,20	precipitation complete				

TAB. 4 - Humid Substance precipitation from percolate concentrated (A) - 75 wt% phosphoric acid quantity (d: 1.57 Kg/dm^3) referred to 100mL of percolate as such - (mL H_3PO_4 vs pH)
- sample 2pc: percolate concentrated 12.1 times, 100mL

- Example 2 -

Sample 2pc				**Sample 2pc** calculation standardized to 100mL of percolate as such (8.0mL of sample 2pc)		
75 wt% H_3PO_4 solution (mL)	H_3PO_4 (g)	pH	Notes	75 wt% H3PO4 solution (mL)	H_3PO_4 (g)	pH
0,0	0,00	9,5		0,0	0,00	9,5
1,0	1,18	8,90		0,1	0,09	8,90
2,0	2,36	7,20		0,2	0,19	7,20
3,0	3,53	6,60		0,2	0,28	6,60
4,0	4,71	6,30		0,3	0,38	6,30
5,0	5,89	5,80		0,4	0,47	5,80
6,0	7,07	5,50		0,5	0,57	5,50
7,0	8,24	5,00		0,6	0,66	5,00
8,0	9,42	4,70		0,6	0,75	4,70
9,0	10,60	4,40	commencement precipitazione	0,7	0,85	4,40
9,5	11,19	4,00		0,8	0,89	4,00
10,0	11,78	3,80		0,8	0,94	3,80
10,5	12,36	3,20		0,8	0,99	3,20
11,0	12,95	3,00		0,9	1,04	3,00
11,5	13,54	2,80		0,9	1,08	2,80
12,5	14,72	2,30	precipitation complete	1,0	1,18	2,30

TAB. 5 - Humid Substances precipitation from industrial concentrated percolate (B) - 37.45 wt% sulphuric acid quantity (d: 1.28 Kg/dm^3) referred to 100mL of concentrated percolate - (mL H_2SO_4 vs pH) - sample 3pc.

- Example 3 -

Sample 3pc			
37.45 wt% sulphuric acid solution (mL)	H_2SO_4 (g)	pH	Notes
0,0	0	9,50	
7,5	3,60	6,70	
8,0	3,84	5,50	
8,5	4,08	4,70	precipitation commences
9,0	4,32	3,90	
9,5	4,56	3,70	
10,0	4,80	2,90	
11,0	5,28	2,20	precipitation complete

TAB. 6 - Humid Substances purification (sample HS3) - by washed with water acidified to pH 1 with sulphuric acid -

- Example 3 -

	Wash No.	R 105°C (%)	R 600°C (%)	R 105°C - R 600°C (%)	Chlorides (mg/L)	Sulphates (mg/L)
supenatant solution	0	14,67	12,50	2,17	36200	52700
	1°	7,60	5,20	2,40	13000	22000
	2°	3,98	2,90	1,00	6900	14000
	3°	2,33	1,70	0,63	3100	7800
	4°	1,48	0,84	0,21	2600	5000
precipitated moist Humic Substances	0	28,9	17,1	11,8		
	1°	23,2	13,2	10,0		
	4°	18,2	6,7	11,5		

TAB. 7 - Chemical characteristics purified Humic Substances dry matter from concentrated percolate (B) (Samp.HS4) and of percolate (B) as such - Example 4 -

		Sample		Sample
	u.m.	**HS4**	u.m.	**percolate (B)**
Specific gravity (20°C/20°C)	kg/L	1,4	kg/L	nd
pH	pH	2,1	pH	7,6
Residue at 105°C	% mass	36	% mass	0,3
Residue at 600°C	% mass	17,3	% mass	<1
Residue a 105°C - Residue a 600°C	% mass	18,7	% mass	<1
TOC (Total Organic Carbon)	% dry matter	36,3	% dry matter	0,017
Humic Carbon (HA)	% C	11,4	% C	nd
Fulvic Carbon (FA)	% C	9,0	% C	nd
Total Kjeldahl Nitrogen (TKN)	%N	2,6	%N	0,031
Carbon/Nitrogen ratio		14,0		0,6
Total Phosphorus (P)	mg/kg dry matter	404	mg/kg	41,2
TOTAL METALS	-		-	nd
Total Arsenic (As)	mg/kg dry matter	7	mg/kg	<0,1
Barium(Ba)	mg/kg dry matter	151	mg/kg	nd
Cadmium (Cd)	mg/kg dry matter	<0,5	mg/kg	<0,1
Total Chromium (Cr)	mg/kg dry matter	191	mg/kg	0,13
Hexavalent Chromium (Cr)	mg/kg dry matter	<0,5	mg/kg	<0,1
Total Copper (Cu)	mg/kg dry matter	38	mg/kg	<5
Iron (Fe)	mg/kg dry matter	1618	mg/kg	1,99
Potadry matterium (K)	mg/kg dry matter	765	mg/kg	268
Manganese (Mn)	mg/kg dry matter	1,3	mg/kg	0,226
Molybdenum (Mo)	mg/kg dry matter	7,2	mg/kg	nd
Sodium (Na)	mg/kg dry matter	2172	mg/kg	345
Nickel (Ni)	mg/kg dry matter	99	mg/kg	0,0716
Lead (Pb)	mg/kg dry matter	13	mg/kg	<5
Total Antimony (Sb)	mg/kg dry matter	<0,1	mg/kg	nd
Selenium (Se)	mg/kg dry matter	22	mg/kg	nd
Zinc (Zn)	mg/kg dry matter	71	mg/kg	0,074
Aluminium (Al)	mg/Kg dry matter	413	mg/kg	nd
Boron (B)	mg/Kg dry matter	55	mg/kg	nd
Cobalt (Co)	mg/Kg dry matter	25	mg/kg	nd
Mercury (Hg)	mg/Kg dry matter	<0.1	mg/kg	<0,1
Tin (Sn)	mg/Kg dry matter	85	mg/kg	nd
Strontium (Sr)	mg/Kg dry matter	343	mg/kg	nd
Magnesium (Mg)	mg/Kg dry matter	320	mg/kg	70,3
Calcium (Ca)	% dry matter	9,5	%	0,018
Silicon (as SiO2)	% dry matter	5,9	%	nd
ANIONS				
Chlorides (Cl)	% dry matter	0,37	%	0,077
Sulphates (SO4)	% dry matter	30,5	%	0,0082
ORGANICS				
Polychlorobiphenyls (PCB)				
Aroclor 1242, 1254, 1260	µg/Kg dry matter	<1000	µg/Kg	nd
Total Polychlorobiphenylsi	µg/Kg dry matter	270	µg/Kg	0,006
indicator PCBs	µg/Kg dry matter	90,0	µg/Kg dry matter	<0,0025
dioxin-like PCBs	ng I-TE/Kg dry matter	0,91	ng I-TE/Kg	0,000031

TAB. 7 - (continued)

		Sample		Sample
	m.u..	**HS4**	m.u.	**percolate (B)**
IPA				
Naphthalene	mg/Kg dry matter	<1	mg/Kg	<5
Benzo(j)fluoranthene	mg/Kg dry matter	<1	mg/Kg	nd
Benzo(e)pyrene	mg/Kg dry matter	<1	mg/Kg	nd
Acenaphthylene	mg/Kg dry matter	<1	mg/Kg	<0,5
Acenaphthene	mg/Kg dry matter	<1	mg/Kg	<0,5
Fluorene	mg/Kg dry matter	<1	mg/Kg	<0,5
Phenanthrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Anthracene	mg/Kg dry matter	<1	mg/Kg	<5
Fluoranthene	mg/Kg dry matter	<1	mg/Kg	<0,5
Pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Benzo(a)anthracene	mg/Kg dry matter	<1	mg/Kg	<0,5
Chrysene	mg/Kg dry matter	<1	mg/Kg	<0,5
Benzo(b)fluoranthene	mg/Kg dry matter	<1	mg/Kg	<0,5
Benzo(k)fluoranthene	mg/Kg dry matter	<1	mg/Kg	<0,5
Benzo(a)pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Indeno(123cd)pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Dibenzo(ah)anthracene	mg/Kg dry matter	<1	mg/Kg	<0,5
Benzo(ghi)perylene	mg/Kg dry matter	<1	mg/Kg	<0,5
Dibenzo(al)pyrene	mg/Kg dry matter	<1	mg/Kg	<5
Dibenzo(ae)pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Dibenzo(a,i)pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Dibenzo(ah)pyrene	mg/Kg dry matter	<1	mg/Kg	<0,5
Total Hydrocarbons	mg/Kg dry matter	<10	mg/Kg	nd
2-ethysil phthalate	mg/Kg dry matter	32,6	mg/Kg	nd
other phthalates	mg/Kg dry matter	<5	mg/Kg	nd
2,3,7,8-PCDD/F	ng I-TE/Kg dry matter	15,0	ng I-TE/Kg	0,017
Biocides and phytopharmaceutical substances (99 compounds sought)	μg/Kg	ND	μg/Kg	<0,01 - <50
Total Coliforms	UFC/100g	absent	UFC/100mL	18000
Salmonellas	-	absent	-	absent

TAB. 7/1 - Organic and inorganic contaminants present in purified humic substances from concentrated percolate (B) (Samp.HS4) e maini regulatory references - Example 4 -

PARAMETERS	**U.M.**	**Campione HS4**	D.Lgs 75 26/04/2010 (discipline fertilizersi - Limits for soil improvers)	European Directive 86/278/CEE 27/04/2000 - under revision - ("Third draft" values proposed for use of purified sludges in agriculture)	Veneto Region - DGRV 235 10/02/2009 (non toxic-harmful sludges of proven usefulness for agronomic purposes)	Emilia Romagna Region - DGR n. 2773 30/12/04 (use of purified sludges in agriculture)
METALS						
As	mg/Kg (dry matter)	7		10	10	10
Cd	mg/Kg (dry matter)	<0,5	1,5	20	20	20
Total Cr	mg/Kg (dry matter)	191		1000	750	1000
Cromium VI	mg/Kg (dry matter)	<0,5	0,5			
Cu	mg/Kg (dry matter)	38	230	1000	1000	1000
Hg	mg/Kg (dry matter)	<0,1	1,5	16	10	10
Ni	mg/Kg (dry matter)	99	100	300	300	300
Pb	mg/Kg (dry matter)	13	140	750	750	750
Zn	mg/Kg (dry matter)	71	500	2500	2500	2500
ORGANICS						
IPA (1)	mg/Kg (dry matter)	<1		6	6	6
PCB (2)	mg/Kg (dry matter)	0,1		0,8	0,8	0,8
PCDD/F	ng I-TE/Kg (dry matter)	15		100	50	100
DEHP (diethylhexylphthalate)	mg/Kg (dry matter)	32,6		100		100
BIOLOGICAL						
Salmonellas	MPN/g dry matter	absent		1000	1000	1000

(1) acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene

(2) PCB markers: # 28, #52, #101, #118, #138, #153, #180

(3) Sum of at least: Lindane, endosulfan, trichloroethylene, tetrachloroethylene, chlorobenzene

TAB. 8 - Precipitation HS from concentrated industrial percolate (B) - amount of hydrochloric acid to 37.45% w / w (d: 1,186 Kg/dm3) referred to 100mL of concentrated percolate - (mL HCl vs pH)
- 5pc sample - example 5 -

Campione 5pc			
Solution HCl 37,45 %p. (mL)	HCl (g)	pH	Note
0,0	0,00	10	
0,5	0,22	9,80	
0,8	0,33	9,80	
1,0	0,44	9,70	
1,3	0,56	9,50	
1,5	0,67	9,40	
2,0	0,89	9,20	
2,5	1,11	8,50	
3,0	1,33	8,00	
3,5	1,55	6,90	
4,0	1,78	6,80	
4,5	2,00	6,60	
5,0	2,22	6,30	
5,5	2,44	6,20	
5,8	2,55	5,60	
6,0	2,66	5,50	
6,3	2,78	5,30	
6,5	2,89	4,70	
6,8	3,00	4,30	commencecment precipitation
7,0	3,11	3,80	
7,3	3,22	3,30	
7,5	3,33	2,70	
7,6	3,38	2,40	
7,7	3,42	2,20	
7,8	3,46	2,00	precipitation complete

TAB. 9 - Physical and Chemical characteristics of HS precipitated with HCl percolate (B) concentrated before and after purification with acid wash - sample HS5g and HS5
- Example 5 -

		Sample	
	u.m.	**HS5 g**	**HS5**
Residue a 105°C	% mass	25	36
Residue a 600°C	% mass	14,6	3,7
Residue a 105°C - Residue a 600°C	% mass	10,4	32,3
Total Phosphorus (P)	mg/kg dry matter	842	597
TOTAL METALS	-		
Total Arsenic (As)	mg/kg dry matter	12,7	17,4
Barium (Ba)	mg/kg dry matter	9,02	3,44
Cadmium (Cd)	mg/kg dry matter	<1	<1
Total Chromium (Cr)	mg/kg dry matter	193	550
Hexavalent Cromium (Cr)	mg/kg dry matter	<0,5	<0,5
Total Copper (Cu)	mg/kg dry matter	15,2	37,2
Iron (Fe)	mg/kg dry matter	1264	1250
Potassium (K)	% dry matter	6,48	0,18
Manganese (Mn)	mg/kg dry matter	21,9	<1
Molibdeno (Mo)	mg/kg dry matter	6,46	16,6
Sodium (Na)	% dry matter	12,7	0,25
Nickel (Ni)	mg/kg dry matter	84,5	187
Lead (Pb)	mg/kg dry matter	<3	<3
Total Antimony (Sb)	mg/kg dry matter	<2	<2
Zinc (Zn)	mg/kg dry matter	44	20,8
Aluminium (Al)	mg/Kg dry matter	4835	2357
Boron (B)	mg/Kg dry matter	512	537
Cobalt (Co)	mg/Kg dry matter	20,4	50,3
Mercury (Hg)	mg/Kg dry matter	<1	<1
Tin (Sn)	mg/Kg dry matter	75,6	233
Strontium (Sr)	mg/Kg dry matter	7,73	<1
Magnesium (Mg)	% dry matter	0,26	0,019
Calcium(Ca)	% dry matter	0,31	0,059
Silicon (as SiO2)	% dry matter	2,0	8,0
ANIONS			
Sulphates (SO4)	% dry matter	2,6	2,7

TAB. 10 - Chemical characteristics of percolate (C) as such (sample 6p) and concentrated (sample 6pc).
- Example 6 -

		Sample	
	m.u.	**6p**	**6pc**
Density	Kg/L	1,01	1,13
Residue at 105°C	% mass	1,03	18,9
Residue at 600°C	% mass	0,73	14
Residue at 105°C - Residue at 600°C	% mass	0,3	4,9
pH	-	8,1	10,1
TOC (Total Organic Carbon)	mg/Kg	1500	24500
BOD5	mg/Kg	1575	9900
COD	mg/Kg	4780	96900
BOD5/COD ratio	-	0,33	0,10
Total Kjeldahl Nitrogen (TKN)	mg/kg	2580	2720
Ammoniacal Nitrogen	mg/kg	2430	111
Carbon/Nitrogen ratio	-	0,58	9,01
Total Phosphorus (P)	mg/kg	25	359
TOTAL METALS			
Total Chromium (Cr)	mg/kg	1,2	19
Iron (Fe)	mg/kg	6	77
Potassium (K)	mg/kg	975	14870
Sodium (Na)	mg/kg	1710	31500
Magnesium (Mg)	mg/kg	76	882
Calcium (Ca)	mg/kg	34	558
ANIONS			
Chlorides (Cl)	% dry matter	2060	32800
Sulphates (SO4)	% dry matter	200	2200

TAB. 11 - Chemical characteristics of (HS6) compared with commercial products (COM1) e (COM2).
- Example 6 -

		Sample		
	m.u.	**HS6**	**COM1**	**COM2**
Residue at 105°C	% mass	28,4	25,8	87,3
Residue at 600°C	% mass	17,4	20,1	34,1
Residue at 105°C - Residue at 600°C	% mass	11	5,7	53,2
pH	-	7,2	12,8	7,9
TOC (Total Organic Carbon)	%	8,5	9,2	25,5
Humic Carbon (HA)	% C	4,8	5,17	23,8
Fulvic Carbon (FA)	% C	1,1	0,26	0,58
Totale Kjeldahl Nitrogen (TKN)	% N	0,7	0,13	0,89
Carbon/Nitrogen ratio	%C/%N	12,1	70,8	28,7
Total Phosphorus (P)	mg/kg	78,2	36,2	44370
TOTAL METALS	-			
Total Arsenic (As)	mg/kg	1,4	3,8	4,9
Cadmium (Cd)	mg/kg	<1	<1	<1
Total Chromium (Cr)	mg/kg	48,2	8,5	4
Total Copper (Cu)	mg/kg	1,5	7	2,3
Iron (Fe)	mg/kg	188	3900	3431
Potassium (K)	%	3,6	3,8	12,5
Manganese (Mn)	mg/kg	1,1	7,6	152
Sodium (Na)	%	2,3	0,5	0,23
Nickel (Ni)	mg/kg	14	7,2	4,7
Lead (Pb)	mg/kg	0,2	3,1	2,5
Selenium (Se)	mg/kg	0,8	1,8	<4
Zinc (Zn)	mg/kg	4,4	8,8	3,6
Mercury (Hg)	mg/kg	<0,2	<1	<1
ANIONI				
Cloruri (Cl)	%	3,8	0,05	2
Solfati (SO4)	%			1,3

TAB. 12 - Agrinomic characterists of (HS6) compared with commercial products (COM1).
- Esempio 7 -

		Campione	
	m.u.	**HS6**	**COM1**
Density	Kg/L	1,122	1,124
TOC (Total Organic Carbon)	% (wt)	8,96	9,31
TEC (Extractable Organic Carbon)	% (wt)	7,78	8,15
Humic Carbon (HA)	% (wt)	5,96	6,32
Fulvic Carbon (FA)	% (wt)	0,25	0,67
HA + HF	% (wt)	6,2	7
Humification degree (HD)	%	79,0	85,0
Humification rate (HR)	%	69	75
Humification index (HI)	%	0,25	0,17

HD= HUMIFICATION DEGREE = (HA+HF)/TEC
This is a quasi-quantitative parameter: in soils and peats it assumes intermediate values (70-80) even if generally very high; in humified materials (leonardite and humic extracts) it has values close to 100; in only slightly mature materials (non-mature composts and organic fertilizers) it assumes values close to zero;

HR= HUMIFICATION RATE = (HA+HF)/TOC
This is a quantitative parameter: the same considerations are valid as for HD;

HI= HUMIFICATION INDEX = NH/ (HA+HF) where NH = TEC-(HA+HF)
This is lower the greater the quantity di humic substances in the soil: in humified peats and mature fertilizers it assumes values <0,5; in leonardites and derived humic extracts iti has values close to 1; in non-humified materials (non-mature composts and sludges, organic fertilizers) it assumes values >1.

TAB. 13 - Analyses of apparent molecular weights of (HS6) compared with commercial product (COM1).
- Example 7 -

		Sample	
	m.u.	**HS6**	**COM1**
1st fraction (>100 KDs)	%	5,2	3,6
2nd fraction (100-25 KDs)	%	84,8	87
3rd fraction (<25 KDs)	%	10	9,4

Interpretation of results

The literature on the subject considers the percentage abundance of 1st fraction (molecular weights >100KD) and of 3rd frazione (molecular weights >250KDa) directly correlated with the degree of maturation of the humic substances and with the biological activity which they can exert.

From this viewpoint the humic extract HS6 presents una better division of the three fractions than the humic extract COM1 in that it shows a greater presence of 1st and 3rd fraction and a smaller presence of 2nd fraction.

TAB. 14 - Determination of biostimulant activity by "AUDUS" bioassay of (HS6) compared with commercial product (COM1).
- Example 7 -

		Campione	
	m.u.	**HS6**	**COM1**
Auxin activity - similar	%	35,2	32
Gibberellin activity - similar	%	absent	absent

Interpretation of results

The humic extract samples were compared, by bioassay, with increasing quantities of 3 indoleacetic acid and gibberellic acid (GA3) to determine, respectively, inhibition of radical development on watercress and stimulation of hypocotyl elongation on white Trieste chicory.

Maximum auxin activity was found in the sample known as HS6. The tested samples did not show gibberellinic activity.

TAB. 15 - Determination of biostimulant activity of (HS6) on maize plants compared with commercial product (COM1).
- Example 7 -

		Sample	
	m.u.	**HS6**	**COM1**
Epigeous system stimulation (extract dose 1.0 mL/L)	%	113	98
Hypogeous system stimulation (extract dose 1.0 mL/L)	%	120	63
Whole plant stimulation (extract dose 1.0 mL/L)	%	115	87
Epigeous system stimulation (extract dose 0.5 mL/L)	%	115	74
Hypogeous system stimulation (estract dose 0,5 mL/L	%	118	78
Whole plant stimulation (extract dose 1.0 mL/L)	%	116	75

Interpretation of results

The test consists of a hydroponic cultivation of maize seedlings for 12 days with daily replacement of the nutrient solution, followed by a period of 48 hours in which the seedlings are brought into contact with two concentrations (1.0 ml and 0.5 ml per litre) of the different humic extracts. The determination showed that the humic extract sample HS6 gives an increase in the whole seedling fresh weight (about +15%) for both tested concentrations, with the most significant increases (+19%) in the hypogeous portion. In contrast, the sample COM1 showed an averagely negative trend.

CLAIMS

1. A process for recovering humic substances from percolate originating from urban solid refuse dumps or the like during the maturation stage with pH between 7.0 and 10.0, characterised by:

- subjecting the percolate to an evaporation-concentration stage at a temperature between 50 and 130°C and a pressure between 5 and 200 kPa,
- subjecting the concentrated percolate containing the substances in solution to an acidification stage with inorganic acid to a pH between 1 and 3 to obtain precipitation of humic substances in the form of flocky solid,
- separating the flocky humic substance solid from the liquid phase to obtain crude humic substances.

2. A process as claimed in claim 1, characterised in that before implementing the evaporation-concentration stage, a percolate filtration stage is implemented to achieve a suspended solids concentration of less than 500 mg/l.

3. A process as claimed in claim 1, characterised in that the acidification stage is achieved by adding sulphuric acid.

4. A process as claimed in claim 1, characterised in that the acidification stage is achieved by adding phosphoric acid.

5. A process as claimed in claim 1, characterised by implementing purification treatment of the crude humic substances by washing with water possibly adicified to pH <7, such as to reduce the concentration of inorganic salts and of any water soluble organic substances, to obtain purified humic substances.

6. A process as claimed in one or more of claims from 1 to 5, characterised in that an alkaline hydroxide is added to the crude or purified humic substances until the humic substances are obtained in solution in the form of soluble alkaline salts.

7. A process as claimed in one or more of claims from 1 to 6, characterised in that the humic substances in solution are further purified by adsorbing organic substances such as alkylphthalates, alkylphenols, bisphenolA, alkylbenzenesulphates which may be present, by treatment with adsorbent solids such as active carbons, clays, kaolins.

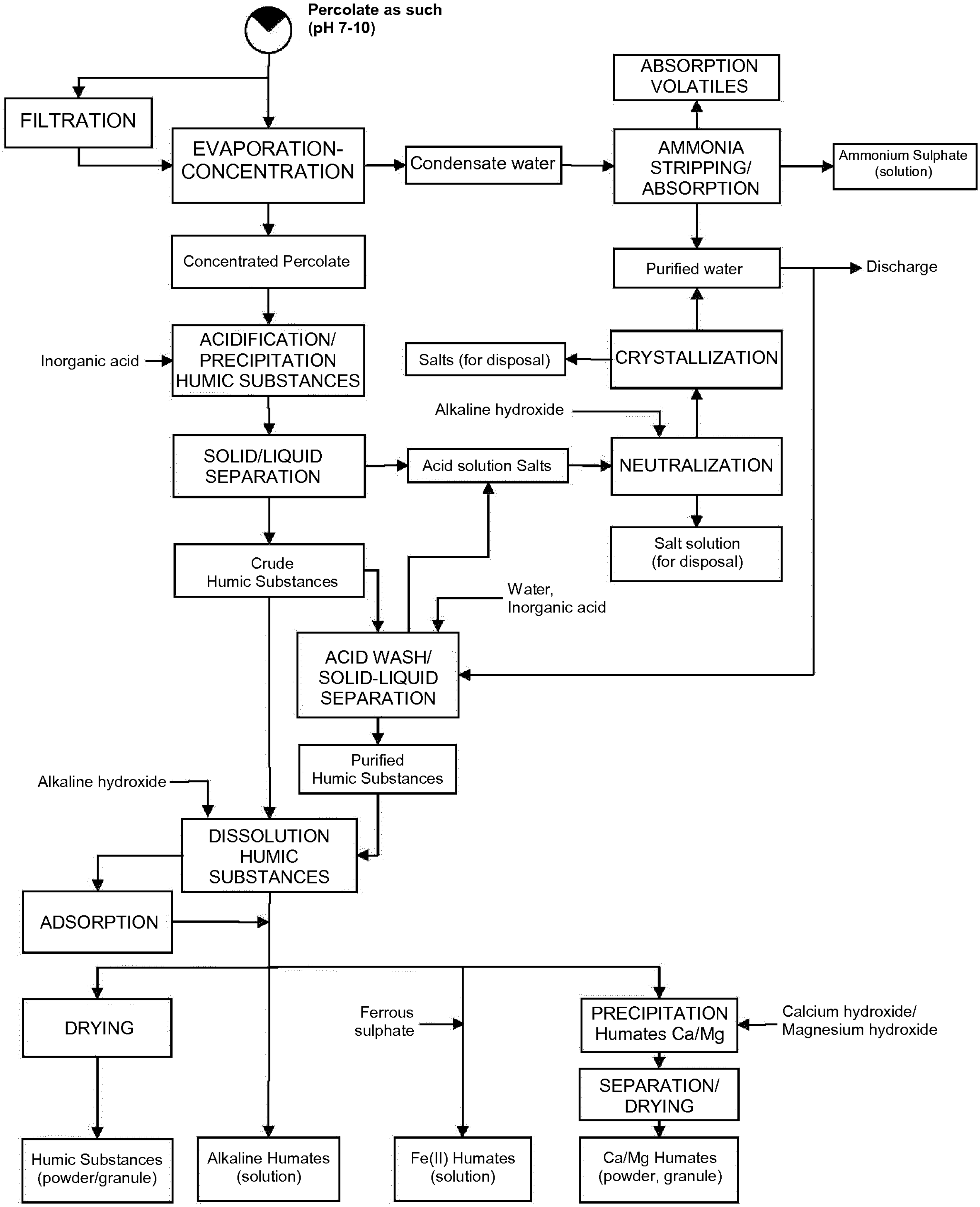
8. A process as claimed in one or more of claims from 1 to 7, characterised by subjecting the humic substances in solution to drying treatment to obtain a product in powder form.

9. A process as claimed in one or more of claims from 1 to 7, characterised by adding ferrous sulphate to the humic substances in solution at neutral pH to obtain iron humates in solution.

10. A process as claimed in one or more of claims from 1 to 7, characterised by adding calcium hydroxide and/or magnesium hydroxide to the humic substances in solution to obtain a precipitate of calcium and/or magnesium humates which is fed to subsequent drying.

11. A process as claimed in one or more of claims from 1 to 5, characterised in that after stripping the ammonia and volatile compounds, the condensate water obtained in the evaporation-concentration stage is used in the wash stage during the acid wash purification treatment of the crude humic substances.

12. Humic substances obtained by the process claimed in one or more of claims from 1 to 11 and substantially as illustrated and described.


Percolate as such
(pH 7-10)
FILTRATION
EVAPORATION-CONCENTRATION
Condensate water
AMMONIA STRIPPING/ ABSORPTION
ABSORPTION VOLATILES
Ammonium Sulphate (solution)
Concentrated Percolate
Purified water
Discharge
Inorganic acid
ACIDIFICATION/ PRECIPITATION HUMIC SUBSTANCES
Salts (for disposal)
CRYSTALLIZATION
Alkaline hydroxide
SOLID/LIQUID SEPARATION
Acid solution Salts
NEUTRALIZATION
Salt solution (for disposal)
Crude Humic Substances
Water, Inorganic acid
ACID WASH/ SOLID-LIQUID SEPARATION
Purified Humic Substances
Alkaline hydroxide
DISSOLUTION HUMIC SUBSTANCES
ADSORPTION
DRYING
Ferrous sulphate
PRECIPITATION Humates Ca/Mg
Calcium hydroxide/ Magnesium hydroxide
SEPARATION/ DRYING
Humic Substances (powder/granule)
Alkaline Humates (solution)
Fe(II) Humates (solution)
Ca/Mg Humates (powder, granule)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/056081

A. CLASSIFICATION OF SUBJECT MATTER
INV. B09B1/00 B01D43/00 C02F1/00 C02F11/00 C05F17/00
ADD.

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)
B09B B01D C02F C05F

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 practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58 112086 A (HITACHI PLANT ENG & CONSTR CO) 4 July 1983 (1983-07-04) abstract -----	1-12
A	US 4 459 149 A (MORAN EDWARD F [US] ET AL) 10 July 1984 (1984-07-10) claim 1; figure 1 -----	1-12

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

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 24 September 2013	Date of mailing of the international search report 02/10/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Devilers, Erick

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/056081

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 58112086 A	04-07-1983	--	
US 4459149 A	10-07-1984	CA 1207751 A1	15-07-1986
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