

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 January 2008 (31.01.2008)

PCT

(10) International Publication Number
WO 2008/014526 A2

(51) International Patent Classification:
B01J 20/24 (2006.01) **B01J 20/30** (2006.01)

(21) International Application Number:
PCT/ZA2007/000043

(22) International Filing Date: 19 July 2007 (19.07.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2006/06169 26 July 2006 (26.07.2006) ZA

(71) Applicant (for all designated States except US): **NAN-OTECH INVESTMENT 2 (PTY) LTD** [ZA/ZA]; Suite 8, Panorama Office Estate, 917 Kudu Street, Allen's Nek X 27, 1709 Roodepoort (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **VAN DER MERWE, Pieter, Gideo** [ZA/ZA]; Plot 63,, Swavelpoort, 0001 Pretoria (ZA). **HANNACHE, Hassan** [MA/MA]; 20 Rue Attabari, Maarif, 20 100 Casablanca (MA). **BEKRI, Omar** [MA/MA]; 2 Rue Aguelmane Sidi Ali, Agdal, 10 000 Rabat (MA).

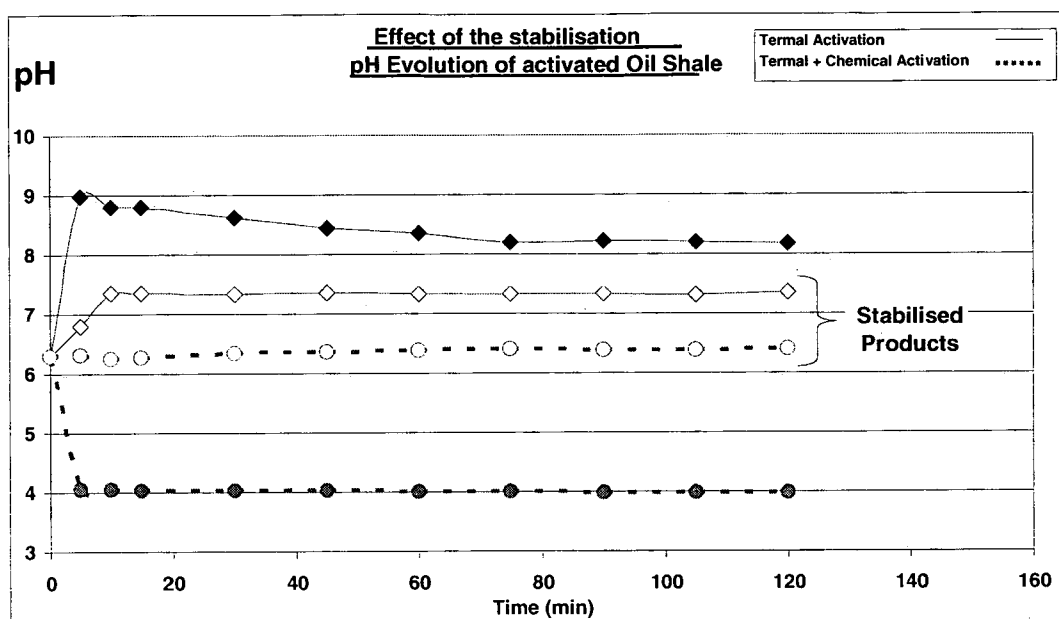
(74) Agent: **HAHN & HAHN INC. WHEELER, CJ, DUNLOP, AJS; WILLIAMS, VW; LUTEREK, JF; MICHAEL, C; VENTER, PCR; BERNDT, C.**; 222 Richard Street, Hatfield, 0083 Pretoria (ZA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: ACTIVATION, REFINING, AND USE OF OIL SHALE



(57) Abstract: The invention provides the activation, refining and stabilization of oil shale. The stabilization may be performed by recirculative extraction, the activation by electromagnetic irradiation, steam, or by an inorganic base, and the refining by ion beam irradiation. The thus processed oil shale may be used to adsorb organic and inorganic contaminants from a variety of materials including materials of vegetable origin.



Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ACTIVATION, REFINING, AND USE OF OIL SHALE

The disclosure in South African Patent Application 2006/6169 is hereby incorporated by reference and forms an integral part of the disclosure in the present application.

5

Field of the Invention

The invention relates to the fields of the production and use of adsorbent materials. More particularly, it relates to the activation, refining, stabilisation, and use of oil shale as an adsorbent.

10

Background to the Invention

By far, the most widely used type of adsorbent materials are “activated” carbon products (the use of the terms “adsorbent” and “adsorption” herein include respectively any type of sorbent or sorption). Activated carbon is made from a substance having high carbon content -- such as coal, wood and nut shells -- by treating it to create many tiny pores between the carbon atoms. Due to this porosity, the activated carbon has a very large surface area per unit volume (i.e., specific surface) allowing it to be used to adsorb a variety of substances from gases or liquids. For instance, activated carbon is used in gas purification, metal extraction, water purification, medicine, sewage treatment, air filters and many other applications. The activation process typically involves some type of thermal and/or chemical treatment. For example, carbon-based material may be converted to activated carbon by thermal decomposition in a furnace using a controlled atmosphere and heat.

25

Unfortunately, despite its effectiveness, activated carbon’s adsorption properties for some materials are not sufficiently strong. Furthermore, the raw materials needed to

produce activated carbon may be costly and/or time consuming to obtain. For these reasons, attention has relatively recently been turned to the use of activated oil shale as an adsorbent material.

- 5 Oil shale is a general term applied to a fine-grained sedimentary rock containing significant amounts of kerogen (a solid mixture of organic chemical compounds). When oil shale is heated to a sufficiently high temperature (i.e., pyrolysis), a vapor is driven off which can be distilled or retorted to yield a petroleum-like shale oil and a combustible hydrocarbon shale gas. The thermal decomposition of oil shale in the
10 absence of oxygen typically occurs between 250 and 550°C. Oil shale can also be burnt directly as a low-grade fuel for power generation.

- Oil shale has been proposed for use as an adsorbent in various different states. For example, US1676151 describes that residue from oil shale distillation may be used
15 to remove impurities from waste waters produced during distillation. This residue, typically referred to as "spent" or retorted shale, is the solid material remaining after the retorting of the oil shale. Spent shale still contains organic carbon (residual carbon) and is often burned to produce energy used for the retorting of raw shale. Oil shale ash is produced by burning oil shale or spent shale.

20

In addition, the use of "raw" (i.e., generally untreated) oil shale as an adsorbent has also been proposed. For example, US4308146 discloses how crushed raw oil shale is used as an oil spill adsorbent. Oil floating on the surface of another liquid is contacted with crushed raw oil shale to adsorb the oil onto the shale.

25

More recently, there have been several proposals to activate oil shale, in a manner similar to the activation of carbon, in order to obtain highly adsorbent materials for a variety of industrial and environmental applications. Unlike raw or spent oil shale,

activated oil shale has been treated in order to carbonize the carbon matter and to decompose a portion of the mineral matter thereby to create a porous body having an active surface area.

- 5 For instance, Moroccan patent document MA24030 describes processes for activating the oil shale as well as use of the activated oil shale as an adsorbent. This activation is carried out by a thermal and/or chemical (acid) treatment process. More detailed processes for activation of oil shale are further described in the following articles:

10

- "New adsorbents from oil shales: Preparation, characterization and U, Th isotope adsorption tests", Khouya E; Fakhi S; Hannache H; Abbe J C; Andres Y; Naslain R; Pailler R; Nourredine A, Journal of Radioanalytical and Nuclear Chemistry, Kluwer Academic Publishers, Do, VOL - 260, NR - 1, PG - 159-166 (2004-04-01);

15

- "Influence of the experimental conditions on porosity and structure of adsorbents elaborated from Moroccan oil shale of Timahdit by chemical activation", Ichcho S; Khouya E; Fakhi S; Ezzine M; Hannache H; Pallier R; Naslain R, Journal of Hazardous Materials, Elsevier, VOL - 118, NR - 1-3, PG - 45-51, (2005-02-14);

20

- "Elaboration et caractérisation d'un nouveau matériau adsorbant à partir des schistes bitumineux du Maroc", Oumam M; Abourriche A; Adil A; Hannache H; Pailler R; Naslain R; Birot M; Puillot J-P, Annales de Chimie, Masson, Paris, FR, VOL - 28, NR - 4, PG - 59-74 (2003-07-00);

25

- "Synthesis and characterization of activated carbo-aluminosilicate material from oil shale", Shawabkeh R A, Microporous and Mesoporous Materials, Elsevier Science Publishing, New York, US, VOL - 75, NR - 1-2, PG - 107-114 (2004-10-12);

- 5 - “ New adsorbents prepared by phosphoric acid activation of Moroccan oil shales: Influence of the experimental conditions on the properties of the adsorbents”, Khouya El Hassane ; Ichcho Salah ; Legrouri Khadija ; Hannache Hassan ; Fakhi Said ; Nourredine Abdelmjid ; Pailler Rene ; Naslain Roger, Ann. Chim. Sci. Mater.; Annales de Chimie: Science des Matériaux September/October 2006, VOL - 31, NR - 5, PG - 583 - 596 (2006-09-00) ;
- 10 - “Adsorption of chromium ions from aqueous solution by using activated carbo-aluminosilicate material from oil shale”, Shawabkeh Reyad Awwad, Journal of Colloid and Interface Science Jul 15 2006, VOL - 299, NR - 2, PG - 530 - 536 (2006-07-15);
- 15 - “Production of a new adsorbent from Moroccan oil shale by chemical activation and its adsorption characteristics for U and Th bearing species”, Khouya E ; Fakhi S ; Hannache H ; Ichcho S ; Pailler R ; Naslain R ; Abbe J C., Journal De Physique. IV : JP; Proceedings - 9th International Seminar on the Physical Chemistry of Solid State Materials, REMCES IX 2004 (CONF- REMCES IX: 9th International Seminar on the Physical Chemistry of Solid State Materials; Agadir, Morocco Oct 30-Nov 1 2002), VOL - 123, PG - 87 - 93 (2002-10-30); and
- 20 - “Phosphoric acid activation of Moroccan oil shale of Timahdit: Influence of the experimental conditions on yield and surface area of adsorbents”, Ichcho S ; Khouya E ; Abourriche A ; Ezzine M ; Hannache H ; Naslain R ; Pailler R, Journal De Physique. IV : JP; Proceedings - 9th International Seminar on the Physical Chemistry of Solid State Materials, REMCES IX 2004 (CONF- REMCES IX: 9th International Seminar on the Physical Chemistry of Solid State Materials; Agadir, Morocco Oct 30-Nov 1 2002), VOL - 123, PG - 81 - 85 (2002-10-30).
- 25

The contents of the above documents are incorporated herein by reference.

To illustrate the benefits of activation, Table 1 below shows a specific example of differences between raw, spent and activated oil shale:

5 **Table 1:** Organic Carbon Content and Specific Surface of Spent shale and Activated Oil shale From Tarfaya (Morocco) Oil Shale.

	Raw Oil Shale	Spent Shale	Activated Oil Shale		
			Thermal	Hydrochloric Acid (HCl)	HCl+Phosphoric Acid + Thermal Activation
		A	B	C	D
C org %	15	3-5	13	40	60
Spec. Surf. m2/g	15-20	25-30	40-50	50-100	500-600

From the organic carbon content and the specific surface of the spent shale and the activated shale, one can easily deduct the difference between the adsorption capacities of these two materials. In terms of the organic carbon content, it is noted in particular that:

A: The spent shale is the solid residue remained after the retorting of oil shale. In this example, 20 to 30 % of the initial organic carbon is left in the spent shale (residual carbon). Some processes like "Hytort" use pressurized Hydrogen (tens of

bars) to transform the maximum amount of carbon into oil vapor further reducing the quantity of residual carbon.

B: 85% of the Organic Carbon is left in this thermally activated oil shale. The 15 %
5 reduction is due to release during the thermal treatment and would typically be recovered as hydrocarbon gases and light oil and used as fuel for the heating of the raw oil shale.

C & D: The amount of organic carbon actually increases due to the loss of the
10 mineral matter during the activation process(es).

In view of the above, and as set out in the above references, activated oil shale boasts considerable potential as a new adsorbent material, in many cases with adsorption properties that are significantly superior to activated carbon. Furthermore,
15 because oil shale resources in many parts of the world are vast and largely unexploited, the necessary raw material for these adsorbents is in many cases widely and inexpensively available.

However, the processes for activating oil shale described in the above-mentioned
20 references remain largely academic and research-based in nature. In particular, these processes may not result in an adsorbent that is sufficiently refined and stable for use in commercial applications so that, for example, leaching does not occur during use of the adsorbent. Furthermore, the prior art processes may also not result in an adsorbent material that is sufficiently homogeneous in its porosity and/or in an
25 adsorbent material in which the pores are not sufficiently "open" to optimize their adsorption capacity. As a result, there remains a need for oil shale activation processes capable of producing improved adsorbents on a reproducible and commercial scale.

Summary of the Invention

According to a first aspect of the invention, there is provided an oil shale activation process including one or more process steps selected from:

- 5 - exposing oil shale to electromagnetic radiation resulting in carbonization of a portion of organic matter and transformation of a portion of mineral matter in the oil shale resulting in generation of gases within the oil shale thereby creating pores inside the oil shale;
- heating oil shale by contacting with steam at elevated temperature; and
- 10 - chemically treating oil shale by contacting oil shale with an inorganic base compound .

The transformation of the mineral matter may include carbonate decomposition.

- 15 The oil shale activation process may include a refining step in which undesired species such as unconverted organic material, N, S, H, and O are reacted in the activated oil shale by means of ion beam irradiation of activated oil shale thereby to increase the specific surface area active for adsorption.
- 20 The oil shale activation process may include a stabilization process which includes contacting the oil shale with distilled de-ionized water by recirculative extraction.

Further and/or alternative stabilization processes may include:

- electrically charging the active surface of the oil shale; and/or
- 25 - electrically neutralizing the active surface oil shale.

According to a second aspect of the invention, there is provided an oil shale activation process, said process including exposing oil shale to be activated to electromagnetic radiation to carbonize a portion of organic matter and transform a portion of mineral matter in the oil shale resulting in generation of gases within the oil shale thereby creating pores inside the oil shale.

The oil shale may be in the form of particles having a particle size of from 0.1 mm to 200 mm, typically from 1 mm to 10 mm.

10

The electromagnetic radiation may be so called microwave radiation, typically at a frequency of 2450 MHz.

The oil shale may be exposed to the electromagnetic radiation for a period of from 1 s/g to 60 s/g, or more depending on the specific oil shale, particle size, and frequency.

The intensity, or power, of the electromagnetic radiation may be from 1 W/g to 20 W/g, depending on the chemical and physical properties of the oil shale, and the period for which the oil shale is to be exposed to the radiation.

20

Typically, for oil shale particles of a size from 1 mm to 10 mm, at an intensity of 6 W/g, the exposure time is from 2 to 4 s/g, more typically 3 s/g.

It is believed that the carbonization of the organic matter creates adsorptive sites thereon.

25

The pores may be created homogeneously throughout an oil shale particle.

The electromagnetic activation process may be a step in a multi-step activation
5 process.

The electromagnetic radiation may be ultraviolet radiation, RF plasma radiation, or any other suitable type of electromagnetic radiation.

10 According to a third aspect of the invention, there is provided a thermal oil shale activation process, said process including contacting oil shale with steam at a temperature of from 150°C to 1000°C, typically from 250° to 900°C.

In one embodiment the thermal activation process may be carried out with steam at
15 a temperature of from 500°C to 1000°.

In another embodiment the thermal activation may be carried out with steam at 900°C.

20 The oil shale may be in the form of particles having a particle size of from 0.1 to 5 mm, typically from 0.5 mm to 2 mm.

The contact time for the oil shale and steam may be from 120 s to 3600 s, typically from 240 s to 1800 s. Usually the contact time will be 600 s.

It is expected that the contact time is a function of the steam temperature and the oil shale particle size.

- 5 It is believed that the use of steam in the activation results in oxidation of the organic matter and the opening of the pores.

The thermal activation process may be a step in a multi-step activation process.

- 10 The thermal activation process may be carried out in combination with another activation process.

- According to a fourth aspect of the invention, there is provided a chemical oil shale activation process, said process including contacting oil shale with inorganic base
15 compounds thereby to transform at least a portion of organic matter and/or carbonates in the oil shale creating and/or opening pores inside the oil shale.

The inorganic base compounds may be selected from the group including, but not limited to, sodium hydroxide and potassium hydroxide.

20

The particle size of oil shale to be activated chemically ranges from 0.1 to 10 mm typically from 0.5 to 2 mm.

- The contact time for the oil shale may be from 7200 s to 43 200 s, typically from 10
25 800 s to 18 000 s.

After the base compound and shale contact time, the mixture may be followed by a thermal treatment at a temperature ranging from 200 to 500°C for a period of from 1800 s to 10 800 s, typically at 250 °C for 3600 s to 7200 s.

5

It is expected that the contact time is a function of the inorganic compound used, the temperature, and the oil shale particle size.

10 The effectiveness of the activation of the oil shale is a function of the particle size of the oil shale, the type of inorganic compound used, the concentration of said inorganic compound, the temperature at which the process is performed, and the residence or treatment time of the oil shale by the process.

The chemical activation process may be a step in a multi-step activation process.

15

The chemical activation process may be carried out in combination with another activation process, typically one or more of thermal and electromagnetic activation.

20 According to a fifth aspect of the invention, there is provided an activated shale refining process, said process including irradiating activated oil shale with an ion beam to reduce uncarbonized organic material, N, S, H, and O thereby to increase the specific surface area active for absorption and/or adsorption.

The ion beam irradiation may be oxygen ion beam irradiation.

25

The ion beam irradiation may be carried out at from eV 50 to eV 1000 and from 20 to 500 $\mu\text{A}/\text{cm}^2$. Typically, an oxygen ion beam at eV 200 and 200 $\mu\text{A}/\text{cm}^2$ is used.

5 The thus treated activated oil shale has in excess of 90 mass % Carbon, typically in excess of 95 mass% and an increased specific absorption rate. This means that the oil, shale is enriched in active carbon sites in comparison to unrefined activated oil shale.

10 The specific adsorption rate per gram of adsorbent may be increased over unrefined activated oil shale by at least 5%, typically in excess of 8%.

15 According to a further aspect of the invention, there is provided a stabilization process for activated and/or refined oil shale, said stabilization process including contacting the oil shale with a solvent by recirculative extraction.

The stabilization process may include the dissolving of mineral compounds from the activate oil shale with heated extraction solvent.

20 The dissolving may be carried out by recirculative extraction with hot water and steam, such as that performed in a Soxhlet extractor.

The heater extraction solvent may be demineralised water, typically de-ionised distilled water.

The stabilization process may include dissolving the mineral compounds destabilized during the activation of oil shale from the activated oil shale with heated extraction solvent.

- 5 It is believed that the stabilized activated oil shale doesn't has a reduced leaching phenomenon when used as an adsorbent in contact with polluted water.

10 In this context, it is important to note that distilled water is water which has been evaporated and recondensed and which includes minerals and other ions. De-ionised water is water, whether distilled or not, which has been passed through an ion exchanger and has a lower ionic content than distilled water. The use of de-ionised water is believed to be important as this permits a greater amount of ions to be flushed from the activated oil shale thereby leaving more active sites available for adsorption within the oil shale.

15

The extraction solvent may be heated to a temperature of from 40°C to 130°C, typically below 100°C.

20 The process may be carried out at a pressure of from 20 mBar(Abs) vacuum to several Bar (Abs) pressure.

Further and/or alternative stabilization processes may include:

- electrically charging the active surface of the oil shale; and/or
- electrically neutralizing the active surface oil shale.

25

The electrical charging may be performed by a corona discharge device or by electrostatic charging.

Electrostatic charging may be performed by agitating dry oil shale particles in a drum
5 or the like thereby to impart an electrostatic charge to the oil shale.

Where the oil shale requires to be neutralized the corona discharge device or the electrostatic charging method may be used to achieve same.

10 Yet further, the invention extends to activated, refined, and/or stabilized oil shale prepared by a process as described above.

The invention also extends to the use of an activated, refined, and or stabilized oil shale in the removal of organic toxins or contaminants, inorganic toxins or
15 contaminants, micro-organisms, and other undesired substances from a gaseous or a liquid phase containing said toxins and/or undesired substances by contacting said liquid or gaseous phase with said oil shale.

The inorganic toxins or contaminants may include one or more of cadmium, lead,
20 and arsenic.

The inorganic toxins or contaminants may include one or more of nickel, cobalt, mercury, lead, and chromium.

The organic toxins or contaminants may include pesticides and/or non-biodegradable compounds

5 The gaseous phase may be selected from the group including, but not limited to, factory chimney gasses, air circulating through air conditioning systems, vehicle emissions, and smoke.

10 The liquid phase may be selected from liquids selected from the group including, but not limited to, aqueous solutions, organic solvent solutions, aqueous suspensions, radioactive effluents, factory effluents, mining effluents, and aqueous extracts.

The liquid phase may be water being treated in a potable water facility.

15 It can be appreciated that the lists of gaseous and liquid phases are by no means exhaustive and the principles disclosed here may be applicable across many industries.

20 The invention extends yet further to a method for the reduction of undesired organic and inorganic substances from a vegetable origin material, said method including the steps of:

- extracting soluble substances from the material into a solvent;
- contacting the solvent including the extracted soluble substances with an activated oil shale, whether refined and/or stabilized or not;
- maintaining the contact for a desired period at a desired temperature; and

- separating the solvent including the extracted soluble substances in which the undesired organic and inorganic substances have been reduced from said oil shale.

- 5 The method may include recovery of valuable components from the oil shale in which the organic and/or inorganic substances have been retained.

The method may include evaporating or otherwise removing at least a portion of the solvent from the extracted soluble substances.

10

The method may include drying the extracted soluble substances, for example by spray drying or freeze drying.

- 15 The method may include the recombining of the extracted soluble substances in which the undesirable organic and inorganic substances have been reduced with its source material from which it was extracted.

The material may include tea, coffee, cocoa, or other vegetable material for human consumption.

20

The material may include one or more of the roots, stem, and leaves of a plant, and/or products thereof.

- 25 The invention extends yet further to the use of activated oil shale in cigarette filters in order to reduce the amount of cadmium, lead and/or arsenic inhaled by a smoker.

The cigarette filters may include refined, activated oil shale as the volume thereof is less than that of unrefined activated oil shale and the specific absorption and/or adsorption rates are higher thereby permitting a smaller volume of the activated oil shale to achieve the same degree of removal of cadmium, lead and/or arsenic from the cigarette smoke.

The inventors believe that the invention has numerous advantages over known shale based absorption and adsorption preparation processes and used, including but not limited to:

- increased active surface area;
- removal of toxins or contaminants from materials by simple processes; and
- high adsorption activity for heavy metals, radioactive substances, and the like.

The specific description which follows forms an integral part of the disclosure of the invention and where the context allows, should be interpreted generally and not be limited to the specifics of any example.

Summary of the Drawings

20

The specific description references the appended drawings, in which:

Fig. 1 is a chart illustrating how, for a single oil shale deposit, samples collected at different levels and treated by the same activation mode(s) yield to products having different adsorption capacities;

Fig.2. is a diagram of a Soxhlet extractor apparatus suitable for use in stabilizing activated oil shale in accordance with an embodiment of the invention;

Fig. 3 is a chart illustrating the evolution of the pH of the solutions containing activated products before and after a stabilization step using the apparatus of Fig. 2;
5 and

Fig 4 is a UV adsorption spectrum chart of olive oil extraction effluent both before and after treatment with the activated oil shale of the invention.

Specific Description of Examples of the Invention

10

The invention will now be described, by way of non-limiting example only, with reference to the accompanying examples.

15

The activation of oil shale, in accordance with one aspect of the present invention, is carried out by one or more activation processes selected from chemical activation by a base, thermal activation by steam, and electromagnetic radiation activation. Optionally, one (or more) of the above activation processes may also be combined with a known process for activating oil shale, such as chemical activation by an acid or thermal activation in an atmosphere of air or nitrogen.

20

Table 1a below sets out the various parameters affecting each of the three novel activation modes indicated above, as well as certain known thermal and chemical activation modes.

Table 1a. Activation Modes and Operating Parameters

ACTIVATION MODE	Chemical	Thermal	Electromagnetic Radiation
OPERATING PARAMETERS	▪ Particle Size of OS or AOS	▪ Particle Size of OS or AOS	▪ Particle Size of OS or AOS
	▪ Chemical Agent (CA) ▪ Chlorhydric Acid ▪ Phosphoric Acid ▪ Sulfuric Acid ▪ Potassium Permanganate	▪ Temperature	▪ Frequency
		▪ Atmosphere ▪ Air ▪ Nitrogen ▪ Steam	▪ Energy
			▪ Exposure Time
	▪ Concentration of CA	▪ Residence time	
	▪ Ratio (CA/(OS or AOS))		
	▪ Residence Time		

5

Each mode in the table may be used as a primary activation mode or as a complementary activation mode. However, in accordance with this aspect of the invention, at least one of these modes is: chemical activation by a base, thermal activation by steam, or electromagnetic radiation activation. A series of 2, 3 or 4 application modes could be applied to the same oil shale sample to achieve the desired properties. The activation modes may be applied in different order to the sample so that they yield to products having different properties.

10

The combination of the activation modes added to the variation of the operating parameters yield to a large range of oil shale based adsorption products and consequently to a wide field of industrial applications.

5 **Example 1: Electromagnetic Radiation Activation of Oil Shale**

During thermal activation, heat is transmitted from outside to the centre of oil shale particles by thermal conduction transforming an organic matter portion of the oil shale by carbonization and partial or total decomposition of carbonates of a mineral portion thereof. The expansion of gases generated by these reactions creates pores
10 inside the grains.

In the case of chemical activation with hydrochloric acid for example, the penetration of the acid is also achieved from outside the particle towards the interior of the particle. The acid attacks the carbonates and dissolves certain alkaline elements like
15 calcium, magnesium, sodium or potassium. The evolution of CO₂ creates pores inside the grains.

Contrary to the above two activation modes, the activation mode by electromagnetic radiation reaches the entire particle at the same time allowing a more homogeneous
20 activation.

Experimentation

The experiments were performed using a microwave digestion oven (Mars 5, CEM
25 Corporation, Matthews, USA).

The microwave oven is equipped with 14 reactors type XP 1500 PLUS and controlled by the EST Plus Device both for pressure and temperature control. The microwave oven operates at 2450 MHz and three levels of power may be used: 300 W, 600W and 1200 W.

5

The operating conditions as well as the results of the adsorption tests are shown in tables 2a and 2b.

Timahdit (Morocco) oil shale samples were introduced into the microwave oven and submitted to a 1200 W microwave radiation for 10 min (600 s). The gray color of the oil shale becoming dark black after the treatment indicates that a high carbonization yield has been achieved.

Table 2a. Activation By Microwave Radiation – Operating Conditions

Microwave Oven	☐ Energy ☐ Oil Shale ☐ Particle size ☐ Exposure Time	1200 W 200 g 0.1 – 1 cm 10 min
Adsorption Tests	Methylene Blue (MB)	Introduction of 100 mg of Activated oil shale in a 100 ml MB solution at a concentration of 40 mg/l. Stirring time : 2 hr
	Nickel (Ni)	Introduction of 200 mg of Activated oil shale in a 100 ml Ni solution at a concentration of 100 mg/l. Stirring time : 2 hr

15

Table 2b. Activation By Microwave Radiation – Adsorption Tests

Adsorption Test	Microwave Activation	Thermal Activation
	mg adsorbed per g of TSN Product	
Nickel	44.4	43.4
Methylene Blue	10.3	11.3

5 The adsorption tests consisted of introducing 100 mg of the activated oil shale successively in two 100 ml solutions:

- The first one containing methylene blue at a concentration of 40 mg/l
- The second one containing Nickel at a concentration of 25 mg/l.

10 After 2 hours of stirring, the analysis of the two solutions showed that 100 % of the nickel and 100 % of the methylene Blue were adsorbed by the microwave activated oil shale.

15 The results of the adsorption tests show clearly that oil shale activated by microwave radiation acquires at least equivalent adsorption capacity for Methylene blue and Nickel as oil shale activated thermally.

Example 2: Effect of the Origin of Oil Shale on Activated Oil Shale Performance

20 The activation of the oil shales creates adsorption sites in the carbonized organic matter and in the decomposed mineral matter. The adsorption of the organic

compounds is attributed to the organic matter sites and the adsorption of metals is attributed to the mineral matter sites.

This represents an advantage of the activated oil shale in comparison with activated carbon since they could adsorb a larger range of contaminants. It is most probable that a transition phase composed with carbo–alunino-silicates occurs during the thermal activation of the oil shale thereby enhancing the adsorption phenomenon. As a result, the specific characteristics of the oil shale may significantly influence the properties of the activated products.

10

First, the composition varies from one oil shale deposit to another. Table 3 shows the composition of two Moroccan oil shale deposits: Timahdit in the Middle Atlas mountains and Tarfaya near the southern Atlantic coast.

15 **Table 3. Chemical Composition of Oil Shales**

Chemical Composition (wt%)	Timahdit	Tarfaya
Calcite	21.9	63.7
<u>Dolomite</u>	15.9	3.5
Quartz	19.1	6.5
Pyrite	1	<1
Clays and other minerals	24.0	10.0
Kerogen	17.7	15.9

The Timahdit oil shales contain more quartz and are more argillaceous than those of Tarfaya where the carbonates dominate the mineral matrix.

Furthermore, Table 4 shows the difference between the compositions of the Timahdit oil shale layers. The oil shales are more argillaceous and siliceous (aluminosilicates) in the T zone and became more and more carbonated in depth (Y, X and M zones). The Tarfaya oil shale layers are more homogenous with carbonate predominance. They vary practically only by their organic matter content.

10 **Table 4. Oil Shales Layers Composition**

Oil Shale Deposit	Layers	Organic Matter (%)	Ash Composition (wt %)					
			CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
Timahdit	T4	18.45	15.68	5.15	44.58	16.07	7.15	3.50
	Y	20.83	20.44	5.64	43.20	12.76	5.72	3.10
	X	25.23	27.02	5.64	39.02	10.87	3.75	2.95
	M1	17.72	33.74	5.48	31.16	6.62	2.68	3.25
Tarfaya	R0	9.2	54.04	1.59	14.57	4.10	1.82	4.71
	R1	13.1	59.08	1.24	17.14	4.23	2.08	6.53
	R2	9.0	66.92	1.20	9.43	3.08	1.46	4.61
	R3	18.0	57.96	1.33	11.65	3.11	1.66	5.60
	R4	12.3	58.24	0.93	7.75	2.49	1.32	5.60

Figure 1 illustrates that, in a single oil shale deposit (Timahdit for example), samples, collected at different levels and treated by the same activation mode(s) yield to products having different adsorption capacities.

- 5 As a result, in addition to the combination of the activation modes and their operating conditions, the selection of the oil shale deposit or the oil shale layer may also be considered as an important criterion for the production of an adsorbent developed and dedicated specifically for the solution of a particular environmental issue.

10 **Example 3: Stabilisation of Activated Oil Shale by Soxhlet Extraction**

Once activated, it is clearly important for the adsorption properties of the oil shale to remain as stable as possible.

- 15 The Soxhlet extractor is a laboratory apparatus shown in Figure 2, normally used to extract a desired compound from a solid material. In the present invention, the extractor is used to eliminate the mineral elements which may undesirably cause leaching during the utilisation of the activated oil shale products.

- 20 In Figure 2, the reference numerals identify the following components : 1: stirrer bar; 2: still pot; 3: distillation path; 4: thimble; 5: solid; 6: siphon top; 7: siphon exit; 8: expansion adapter; 9: condenser; 10: cooling water in valve; and 11: cooling water out valve.

- 25 An activated oil shale sample (50 g) is placed inside the thimble 4 made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor.

The condenser 9 ensures that any steam cools and drips back down into the chamber housing the solid material.

5 The Soxhlet extractor is placed onto a still pot 2 containing 500 ml of distilled de-ionised water which is used as the extraction solvent. The water is heated to reflux. The steam travels up the distillation path 3, and floods into the chamber housing the thimble 4 of activated oil shale.

10 The chamber containing the solid material slowly fills with warm solvent (60- 80°C). Some of the undesired compound will then dissolve in the warm water/solvent.

When the Soxhlet chamber is almost full, the chamber is automatically emptied by the siphon top 6, with the water running back down to the distillation flask. This cycle is repeated several times for approximately 2 hours.

15

During each cycle, a portion of the destabilised mineral elements in the oil shale dissolves into the water. After many cycles the dissolved mineral elements are concentrated in the distillation flask.

20 An advantage of this system is that instead of many portions of hot water being passed through the sample, just one batch of water is recycled. The stabilised oil shale product is then removed from the thimble and dried in a drying oven at 110°C.

Stabilisation Control – pH Evolution

25

When activated oil shale is put in contact with water, the evolution of the pH of the solution is a simple and a significant indicator to show the leaching phenomenon.

Leaching tests have been conducted on two activated oil shales before and after
5 stabilisation by Soxhlet Extractor:

The first oil shale product (PTM) was activated thermally at 880 °C and the second one (PTC) activated thermally and then chemically by hydrochloric acid attack.

10 For each test, one gram of product is introduced in a 100 ml distilled solution. The solution is stirred for two hours and the pH is noted.

Figure 3 shows the diagrams of the evolution of the pH of the solutions containing activated products PTM and PTC before and after their stabilisation by Soxhlet
15 extractor:

□ The pH of the solutions containing PTM and PTC products before stabilisation became respectively basic (due to the dissolution of alkaline elements like Ca and Magnesium) and acidic (due to the solubilisation of the chlorine remained in the
20 product).

□ The pH of the solutions containing PTM and PTC products washed by the Soxhlet extractor are stabilized around pH 7, thus showing the efficiency of this treatment allowing the stabilization of the products.

25

Example 4: Refining of Activated Oil Shale by Oxygen Ion Beam Radiation

Oil Shale activated by one of the activation processes was further refined to increase adsorption capacity and to increase the specific surface and to optimize the carbonization of all the residual organic matter in the activated oil shale.

5

Ion beam irradiation (also referred to as ion beam radiation or ion beam treatment) of the activated shale modifies the chemical composition, chemical state and surface nanomorphology of the activated oil shale.

- 10 The ion beam irradiation affects structures via a molecular and not a radiative vehicle, thus confining their effect within a certain atomic penetration and diffusion boundaries. Some common methods are RF plasma treatment, corona discharges and ion beam bombardments. Of these methods ion beam sources offer the most promising capabilities for adhesion improvements. On the other hand, broad beam
- 15 ion sources having the ability to operate in reactive gas atmospheres offer the possibility of chemical as well as physical modification.

In an experiment, 50 grams of activated oil shale was bombarded with an oxygen ion beam at eV 200 and 200 uA/cm² for 5 minutes with the following result:

20

- A decrease in mass of 6,8% and an absorption increase of 9,2% was observed. An absorption test was performed using a column method and MB (Methylene Blue) which showed the 9.2% increase. This may be attributed to the oxidization of N, H, S into NO₂, H₂O, SO₂, as well as further carbonization of organic matter in the
- 25 activated oil shale.

Example 5: Olive Oil Extraction Effluent Treatment

Physicochemical characteristics of the Effluent

The effluents produced by the extraction of the olive oil have a dark brown or brown-
5 reddish colour with a turbid aspect. These effluents have a high load of salts and are
very acid, rich in organic matter and non-biodegradable poly-phenols. This waste
water is characterized by a pH from 4,5 to 5 and a conductivity of about 10
msec./cm, mainly due to the potassium, chloride, calcium and magnesium ions. The
DCO (chemical demand for oxygen) can vary from 50 to 220 g/l.

10

Adsorption Tests

The sample used for the tests comes from a deposit of olive oil extraction waste in
the area of Fez, Morocco. The very concentrated sample of this effluent has a black
15 colour and releases a putrefied olive oil odour.

Two adsorption tests, respectively on a thermally activated oil shale product column
and a thermally and chemically activated oil shale product column, were carried out
on the sample diluted twice. The solutions treated by the two products were
20 colourless and odourless. The first colouring (chestnut-clearly) starts to appear after
having poured 30 ml in the thermally activated oil shale column and 60 ml in the
chemically and thermally activated column.

Measurements of concentrations and the corresponding adsorption yields obtained
25 for the sample treated by the two oil shale products were collected and show the
capacity of the activated oil shale and in particular the thermally and chemically

treated product to adsorb almost totally the organic matter of this effluent including the poly-phenols.

The Chemical Oxygen Demand (COD), which drops from 57.7 g/l for the effluent to
5 6,72 mg/l after chemically and thermally activated oil shale adsorption treatment confirms the fixation of the organic matter in the oil shale bed.

A UV adsorption spectrum of olive oil extraction effluent both before and after treatment with the activated oil shale of the invention is shown in Figure 4.

10

Example 6: Treatment Of An Effluent Of Used Vegetable Oil Processing

Origin and Characteristics of the Effluent Sample

. An effluent sample of used vegetable oil was obtained and processed with the
15 following steps:

- heating of the collected oil;
- decantation;
- separation of the organic and mineral phases:
- The final product is sent to a chemical processing plant for fatty acids and
20 biodiesel production.
- The waste water is sent to a water treatment plant.

The water treatment is made difficult by the presence of non-biodegradable compound in the waste water. Table 5 shows the characteristics of the effluent.

Table 5 Characteristics of the Effluent

COD (g/l)	40
BOD (g/l)	10
Dry matter	40
Organic matter	25
Mineral matter	15
pH	5
C/N	5

Adsorption Test

5

The adsorption test of the effluent was performed according to the following procedure:

40 ml of the effluent sample was poured progressively in a 3,5 cm diameter glass
10 column containing 50 g of thermally and chemically activated oil shale product prepared with a particle size lower than 0,63 mm and higher than 0,2 mm. Glass wool was placed at the bottom of the column to trap the fine solid particles.

The brown orange coloured sample became colourless after the filtering through the
15 column. The UV adsorption peaks at 235 and 300 nm of the effluent UV spectrum disappear almost totally after treatment, which shows that all the organic matter of the sample has been retained in the oil shale bed.

Example 7: Use as a Tobacco Filter**The Tobacco Industry**

- 5 Although a lot has been done to improve cigarette filters and to make tobacco safer to use, it is common knowledge that tobacco imposes great health and risk factors to humans and the environment.

- 10 Every time a cigarette is smoked, up to 4000 different chemicals, some highly toxic, which are the cause of cancer and other heart and lung diseases, are inhaled by the smoker as well as the passive smoker.

- 15 According to the relevant literature, widespread research has focused on the determination mainly of organic components of tobacco. Metal analysis of tobacco is comparatively under explored, because of the carcinogenic nature of many organic substances. However, with smoking certain metals could accumulate to toxic levels in the body and this is equally deleterious.

- 20 Some of the elements which could be present in concentrations in many tobaccos are Boron, Calcium, Magnesium, Nitrogen, Lead, Arsenic, Cadmium, Phosphorous and Potassium.

Health awareness, legislation and public pressure are demanding a solution for this life threatening scenario.

This example carries out an analysis of normal tobacco smoke trapped onto embedded cotton plug for heavy metals vs. tobacco smoke through cotton plug treated with the product of the invention.

5 Method and Equipment

Although elementary, an effective and inexpensive method was used to simulate a “big smoker’s pipe” by using a ceramic container 500ml shaped as a funnel connected to a vacuum hose, sucked by an extractor. A cotton plug (10 grams)
10 served as a “filter” on the control. 75 gm of Boxer™ tobacco was used during the extraction period of 10 minutes.

A similar apparatus was used to repeat the exercise but 2,5 grams of activated oil shale of the invention was wrapped in filter paper was placed in front of the cotton
15 plug.

On completion of the extracting process, the vacuum hose, containing the water plug (for the control) and the cotton plug with activated oil shale product in the filter was cut. This was repeated 4 times and all samples were submitted for analysis.

20

Since the levels of heavy metals are expected to be extremely low, it was decided that a composite sample be analysed in both cases. One without the oil shale product and one with said powder.

25 The experiment was repeated using Camel™ cigarettes. A random selection of 5 volunteers also participated in a “taste and effect” test. Forty cigarettes were

prepared, 20 with normal filters and 20 with activated oil shale product powder inserted in front of the filter. None of the 5 volunteers could detect any deviation or any difference in tastes.

- 5 The laboratory which was used to conduct the testing is an external ISO 3001/2000 laboratory.

The application which was used was the Inductively Coupled Plasma.

10 **Table 6: Comparison of activated oil shale and non-oil shale filters**

	Sample ID	Cadmium µg Cd	Lead µg Pb	Arsenic µg As
1.	Condensate after filter	9	5	<2
	Condensate after filter with oil shale	15	505	16
2.	75 g Boxer	64	9	<2
	75 g Boxer with 2,5 g oil shale	70	622	27

The above results clearly indicate that a large amount of lead (Pb) and arsenic (As) were collected in the filter bed treated with oil shale product.

Claims:

1. A stabilization process for activated and/or refined oil shale, said stabilization process including contacting the oil shale with a solvent by recirculative extraction.
5
2. A process as claimed in claim 1, which includes dissolving of mineral compounds from the activated oil shale with heated extraction solvent.
- 10 3. A process as claimed in claim 1 or claim 2, which is performed with hot water and steam.
4. A process as claimed in any one of the preceding claims, wherein the solvent is demineralised water, typically de-ionised distilled water.
15
5. A process as claimed in any one of the preceding claims, wherein the extraction solvent is heated to a temperature of from 40°C to 130°C, typically below 100°C.
- 20 6. An oil shale activation process, said process including exposing oil shale to be activated to electromagnetic radiation to carbonize a portion of organic matter therein and transform a portion of mineral matter in the oil shale resulting in generation of gases within the oil shale thereby creating pores inside the oil shale.

25

7. A process as claimed in claim 6, wherein the oil shale is in the form of particles having a particle size of from 0.1 mm to 200 mm, typically from 1 mm to 10 mm.
- 5 8. A process as claimed in claim 6 or claim 7, wherein the electromagnetic radiation is so called microwave radiation, typically at a frequency of 2450 MHz.
- 10 9. A process as claimed in any one of claims 6 to 8, wherein the oil shale is exposed to the electromagnetic radiation for a period of from 1 s/g to 60 s/g
- 10.A process as claimed in claim 9, wherein the intensity, or power, of the electromagnetic radiation is from 1 W/g to 20 W/g.
- 15 11.A process as claimed in any one of claims 6 to 10, wherein for oil shale particles of a size from 1 mm to 10 mm, at an intensity of 6 W/g, the exposure time is from 2 to 4 s/g, more typically 3 s/g.
- 20 12.A thermal oil shale activation process, said process including contacting oil shale with steam at a temperature of from 150°C to 1000°C, typically from 250°C to 900°C.
- 13.A process as claimed in claim 12, which is carried out with steam at a temperature of from 500°C to 1000°C.
- 25 14.A process as claimed in claim 13, which is carried out with steam at 900°C.

15. A process as claimed in any one of claims 12 to 14, wherein the oil shale is in the form of particles having a particle size of from 0.1 to 5 mm, typically from 0.5 mm to 2 mm.
- 5
16. A process as claimed in any one of claims 12 to 15, wherein the contact time for the oil shale and steam may be from 120s to 3600s, typically from 240s to 1800s.
- 10
17. A process as claimed in claim 16, wherein the contact time is 600s.
18. An activated shale refining process, said process including irradiating activated oil shale with an ion beam to reduce uncarbonized organic material, and one or more of N, S, H, and O thereby to increase the specific surface area active for absorption and/or adsorption.
- 15
19. A process as claimed in claim 18, wherein the ion beam irradiation is oxygen ion beam irradiation.
- 20
20. A process as claimed in claim 18 or claim 19, wherein the ion beam irradiation is carried out at from eV 50 to eV 1000 and from 20 to 500 $\mu\text{A}/\text{cm}^2$.
21. A process as claimed in claim 19, in which the oxygen ion beam at eV 200 and 200 $\mu\text{A}/\text{cm}^2$ is used.

22. A process as claimed in any one of claims 18 to 21, wherein the specific adsorption rate per gram of adsorbent is increased over unrefined activated oil shale by at least 5%, typically in excess of 8%.
- 5 23. A chemical oil shale activation process, said process including contacting oil shale with inorganic base compounds thereby to transform at least a portion of organic matter and/or carbonates in the oil shale creating and/or opening pores inside the oil shale.
- 10 24. A process as claimed in claim 23, wherein the inorganic base compounds are selected from the group including sodium hydroxide and potassium hydroxide.
- 15 25. A process as claimed in claim 23 or claim 24, wherein the particle size of oil shale to be activated chemically ranges from 0.1 to 10 mm typically from 0.5 to 2 mm.
- 20 26. A process as claimed in any one of claims 23 to 25, wherein the contact time for the oil shale is from 7200 s to 43 200 s, typically from 10 800 s to 18 000 s.
- 25 27. A process as claimed in any one of claims 23 to 26, wherein after the base compound and shale contact time, the mixture is subjected to a thermal treatment at a temperature ranging from 200 to 500°C for a period of from 1800 s to 10 800 s, typically at 250 °C for 3600 s to 7200 s.

28. An oil shale activation process including two or more process steps as claimed in any one of the preceding claims.

5 29. Activated, refined, and/or stabilized oil shale prepared by a process as claimed in any one of the preceding claims.

10 30. Use of an activated, refined, and or stabilized oil shale as claimed in claim 29, in the removal of organic contaminants, inorganic contaminants, micro-organisms, and other undesired substances from a gaseous or a liquid phase containing said contaminants and/or undesired substances by contacting said liquid or gaseous phase with said oil shale.

15 31. Use as claimed in claim 30, wherein the inorganic contaminants include one or more of cadmium, lead, and arsenic.

32. Use as claimed in claim 30, wherein the inorganic contaminants include one or more of nickel, cobalt, mercury, lead, and chromium.

20 33. Use as claimed in claim 30, wherein the organic contaminants include pesticides and/or non-biodegradable compounds.

25 34. Use as claimed in any one of claims 30 to 33, wherein the gaseous phase is selected from the group including factory chimney gasses, air circulating through air conditioning systems, vehicle emissions, and smoke.

35. Use as claimed in any one of claims 30 to 34, wherein the liquid phase is selected from liquids selected from the group including aqueous solutions, organic solvent solutions, aqueous suspensions, radioactive effluents, factory effluents, mining effluents, and aqueous extracts.

36. Use as claimed in any one of claims 30 to 34, wherein the liquid phase is water being treated in a potable water facility.

37. A method for the reduction of undesired organic and inorganic substances from a vegetable origin material, said method including the steps of:

- extracting soluble substances from the material into a solvent;
- contacting the solvent including the extracted soluble substances with an activated oil shale, whether refined and/or stabilized or not;
- maintaining the contact for a desired period at a desired temperature; and
- separating the solvent including the extracted soluble substances in which the undesired organic and inorganic substances have been reduced from said oil shale.

38. A method as claimed in claim 37, including recovery of valuable components from the oil shale in which the organic and/or inorganic substances have been retained.

39. A method as claimed in claim 37 or claim 38, including evaporating or otherwise removing at least a portion of the solvent from the extracted soluble substances.

- 40.A method as claimed in claim 39, including drying the extracted soluble substances.
- 5 41.A method as claimed in any one of claims 37 to 40, including recombining of the extracted soluble substances in which the undesirable organic and inorganic substances have been reduced with its source material from which it was extracted.
- 10 42.A method as claimed in any one of claims 37 to 41, wherein the material is selected from the group including one or more of tea, coffee, cocoa, or other vegetable material for human consumption.
- 15 43.A method as claimed in claim 42, wherein the material includes one or more of the roots, stem, and leaves of a plant.
- 44.Use of activated oil shale in cigarette filters in order to reduce the amount of cadmium, lead and/or arsenic inhaled by a smoker.
- 20 45.Use as claimed in claim 44, wherein the cigarette filters include refined, activated oil shale as the volume thereof is less than that of unrefined activated oil shale and the specific absorption and/or adsorption rates are higher thereby permitting a smaller volume of the activated oil shale to achieve the same degree of removal of cadmium, lead and/or arsenic from
- 25 the cigarette smoke.

Figure 1

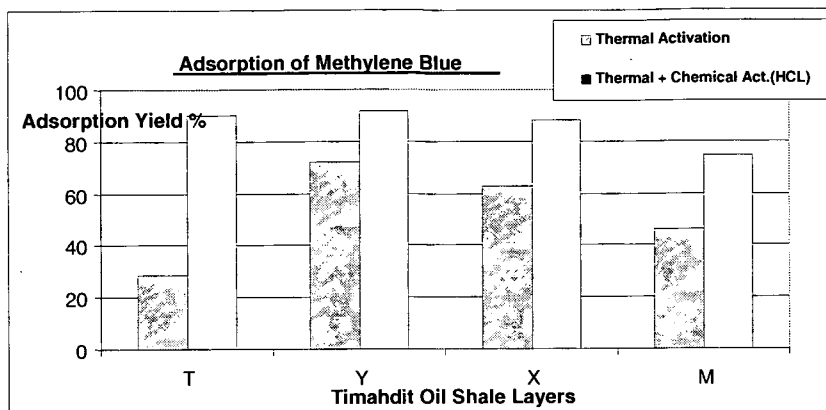


Figure 2

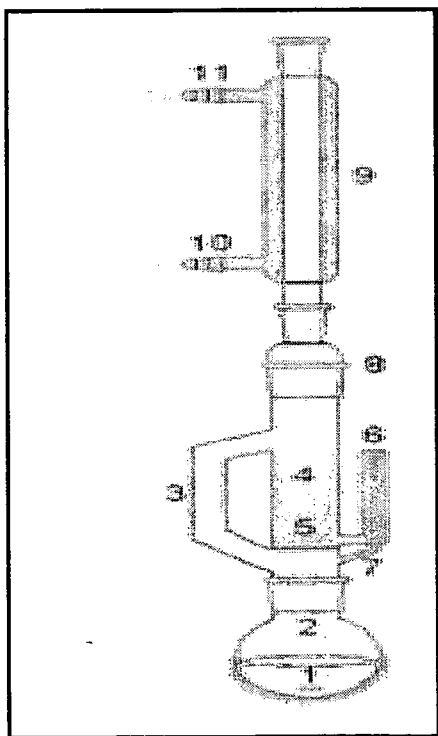


Figure 3

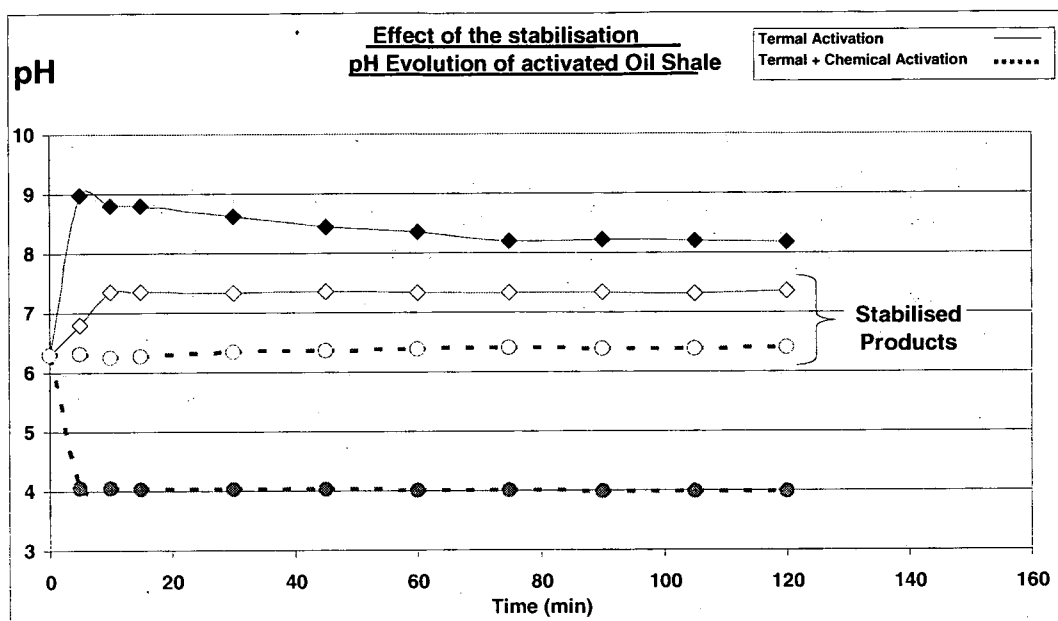


Figure 4

