



(51) International Patent Classification:

B01J 20/18 (2006.01) *B01J 29/08* (2006.01)
B01D 53/00 (2006.01)

(21) International Application Number:

PCT/IN2009/000399

(22) International Filing Date:

13 July 2009 (13.07.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2539/DEL/2008 7 November 2008 (07.11.2008) IN

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, 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, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, 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, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

(54) Title: A PROCESS FOR THE PREPARATION OF MOLECULAR SIEVE ADSORBENT USEFUL FOR THE SELECTIVE ADSORPTION OF OXYGEN FROM ITS GASEOUS MIXTURE WITH ARGON

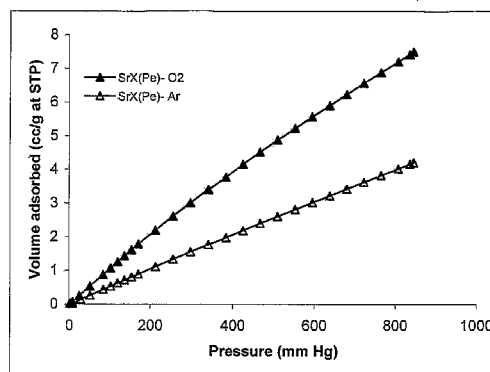


FIG. 2

(57) Abstract: The invention provides a process for the preparation of a zeolite molecular sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon. More particularly, the present invention provides a process for the preparation of an adsorbent, which is more selective towards oxygen from a gaseous mixture of oxygen with argon, and also relates to the processes which utilize this adsorbent as an oxygen selective adsorbent.

“A process for the preparation of molecular sieve adsorbent useful for the selective adsorption of oxygen from its gaseous mixture with argon”

Field of the Invention

5 The present invention relates to a process for the preparation of a molecular sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon. The present invention also relates to the use of a cation exchanged zeolite of faujasite type as a selective adsorbent for the separation of gases having closely related physical properties. More particularly, the present invention relates to process for the preparation
10 of an adsorbent, which is more selective towards oxygen from a gaseous mixture of oxygen with argon, and also relates to the processes which utilize this adsorbent as an oxygen selective adsorbent.

Background of the Invention

15 Adsorption process is established commercially as pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) for the separation of gases. Since the advent of synthetic zeolites in 1959, innovations in adsorbent development and adsorption process cycle have made adsorption a key separation process in the chemical, petrochemical and pharmaceutical industries. The selection of a proper adsorbent for a given separation is
20 the most important step in any adsorption processes. Oxygen production from air using zeolite adsorbent is one of the main commercial PSA processes. However, the maximum attainable oxygen purity by adsorption processes is around 95% and the rest consists of mostly argon present in the feed air. Separation of 0.934 mole percent argon present in the air is difficult from the oxygen product due to the closeness in their physical

properties. However, there are many situations where high purity oxygen (>99%) is required. Furthermore, oxygen-argon separation is also required for the purification of argon produced as a by product during the cryogenic separation of oxygen and nitrogen from air. The boiling points of argon, oxygen and nitrogen are -185.9, -182.96 and -195.8 °C respectively. Since the relative volatility of argon to oxygen is very low, the argon stream from cryogenic distillation unit contains significant amount of oxygen in it, which is known as crude argon. Typical concentration of crude argon is around 3% oxygen and 1% nitrogen. Presently this crude argon is purified by a combination of distillation and “de-oxo” process. In de-oxo process, the crude argon is heated and the oxygen in the stream is reacted with controlled amount of hydrogen to form water. This hot gas stream is cooled and the resulting water vapour from oxygen-hydrogen reaction is removed, usually in a dual bed adsorber drier system. Finally pure argon is produced by removing the nitrogen and unreacted hydrogen in a “pure argon tower” by cryogenic distillation. However this process is very energy intensive due to the heating and cooling of the crude argon stream and also the capital cost is high for additional installation on the cryogenic distillation unit. Thus, it is desired to develop a commercially attractive separation process for oxygen-argon separation. Adsorption based process can compete with the energy intensive cryogenic separation of oxygen-argon mixture if a suitable adsorbent, which is selective towards one of the components and is having requisite adsorption capacity, is available.

In the prior art, U. S. Pat. No. 6,087, 289 (2000) to Choudary et al. disclosed the manufacturing of a molecular sieve adsorbent which is selective towards oxygen from its gaseous mixture with argon and/or nitrogen. They exchanged cerium cations into faujasite zeolites, particularly zeolite X which contains alkali metal and/or alkaline earth metal cations as extra framework cations, for the preparation of oxygen selective adsorbent. Chromatographic technique was used to study the adsorption of oxygen, argon and nitrogen in this cerium exchanged zeolite X. However, the adsorption capacity for

oxygen was low in this adsorbent.

U. S. Pat. No. 4,713,362 (1987) to Maroulis et al. disclosed the preparation and activation of a selective zeolite adsorbent for the chromatographic separation of argon-oxygen from their gaseous mixture. The adsorbent of their choice was mainly divalent cation containing chabazite zeolite, particularly calcium exchanged chabazite and the
5 thoroughly dehydrated adsorbent was activated in an oxidising atmosphere for the argon-oxygen separation. But the separation mechanism was mainly based on kinetic selectivity towards oxygen in its mixture with argon.

U. S. Pat. No. 5,601,634 (1997) disclosed a cryogenic temperature swing adsorption
10 process for the production of high purity argon from a two-phase vapour-liquid mixture. According to their invention, the two phase mixture of argon, oxygen and nitrogen is passed through two adsorbent beds; each of them contains a nitrogen selective adsorbent layer and an oxygen adsorbent layer preceding to the nitrogen selective adsorbent layer, at a temperature between the bubble point and the dew point of the two phase mixture. In
15 addition, according to their invention, the nitrogen selective adsorbent was zeolite X or mordenite, and the oxygen selective adsorbent layer was carbon molecular sieve or zeolite 4A. This process has drawbacks in terms of being at cryogenic temperatures and also employing different adsorbents.

U. S. Pat. No. 5,159,816 (1992) to Kovak et al. disclosed the production of high purity
20 argon by cryogenic adsorption wherein a crude argon stream flows through a bed of adsorbent that preferentially adsorbs nitrogen, and then through another adsorbent bed that preferentially adsorbs oxygen. U. S. Pat. No. 4,477,265 (1984) to Kumar et al. also discloses the adsorption of oxygen and nitrogen from an argon-rich feed taken from the rectification column of a cryogenic air separation plant. According to this patent, high
25 purity argon is separated and recovered from the crude argon stream containing minor amounts of oxygen and nitrogen, by passing through two separate adsorbent columns in

series wherein the first column contains a nitrogen equilibrium selective adsorbent used for nitrogen removal and the second bed contains an oxygen kinetic selective adsorbent used for oxygen removal. Further purification of the recovered argon is carried out by catalytic hydrogenation of residual oxygen therein. The process needs additional catalytic hydrogenation step to obtain high purity argon, which is a drawback of this invention.

U. S. Pat. No. 6,527, 831 (2003) to Baksh et al. disclosed a vacuum pressure swing process (VPSA) for the purification of argon in crude argon stream from cryogenic air separation plant. In their invention they utilized two adsorption beds and continuously promoted the crude feed gas to the bed during the process and simultaneous equalization of pressure in the two beds in top-to-top end and bottom-to-bottom end equalizations in each bed following purging of each bed. The adsorbent used for this VPSA process was oxygen rate selective adsorbent such as carbon molecular sieve (CMS) to separate the argon-oxygen mixture. The process makes use of expensive carbon molecular sieve type adsorbent for the selective adsorption of oxygen.

U. S. Pat. No. 5,081,097 (1992) to Sharma et al. disclosed finely divided elemental copper modified carbon molecular sieves for the selective adsorption of oxygen at elevated temperatures. The copper modified carbon molecular sieves were prepared by pyrolysis of a mixture of a copper-containing material and polyfunctional alcohol to form an adsorbent precursor. The adsorbent precursors were then heated and reduced to produce copper modified carbon molecular sieves. The process suffers from a drawback of being as a high temperature process.

U. S. Pat. No. 6,878,657 (2005) to Jasra et al. disclosed a process for the manufacturing of a pore mouth controlled zeolite molecular sieve adsorbent for the size/shape selective adsorption of gas molecules from their gaseous mixture. More specifically, their invention related to the preparation and use of a molecular sieve adsorbent, which is selective towards oxygen from its gaseous mixture with nitrogen and argon by pore mouth control

of zeolite NaA with liquid phase alkoxide deposition on the external surface at ambient conditions of temperature and pressure. The process has limitation as the adsorbent has a very small adsorption capacity.

U. S. Pat. No. 7,319,082 (2008) to Jasra et al. disclosed another process for the preparation of oxygen selective adsorbent for the separation of oxygen from its gaseous mixture with nitrogen and/or argon. More specifically, the invention related to the manufacture and use of molecular sieve adsorbent by cation exchange in zeolite X especially using rare earth cations like cerium to obtain oxygen selective adsorbent for the adsorption of oxygen from its gaseous mixture with nitrogen and oxygen at ambient temperature and pressure.

U. S. Pat. No. 5,226,933 (1993) to Knaebel et al. disclosed a pressure swing adsorption (PSA) process for splitting oxygen from a feed gas comprising 95% oxygen and 5% argon to achieve an oxygen purity of at least about 99.7%. A column used in the PSA process includes therein a bed of silver mordenite, as an argon selective adsorbent.

U. S. Pat. No. 5,470,378 (1995) to Kandybin et al. disclosed a process for removing argon from a feed gas stream comprising oxygen and argon to yield a high purity oxygen stream and the system for carrying out the process. The process included the steps of: (a) providing a feed gas of oxygen and argon at a temperature between -30° C. and 100° C. and a pressure between 5 psia and 160 psia; and (b) passing the feed gas over an adsorbent bed comprising a Ag ion exchanged type X zeolite wherein at least 80% of the available ion sites are occupied by Ag such that at least a portion of the argon in the feed gas is adsorbed by the adsorbent bed thereby leaving an oxygen-enriched gas stream.

U. S. Pat. No. 6,423,70 (2002) to Chiang et al. also disclosed a process for making an AgX-type zeolite having a silver exchange level of 20-70% and a Ar/O₂ Henry's law selectivity ratio at 23° C. of 1.05 or greater has an optimum combination of selectivity

for argon over oxygen at lower cost than higher silver exchange levels. According to their claim, this material can be used in oxygen VSA/PSA processes to produce oxygen at purities above 97%.

5 There are other prior art for the removal of oxygen from the gaseous using adsorbent other than zeolite molecular sieve and carbon molecular sieve as oxygen selective adsorbent. For example, Ramprasad et al. (J. Am. Chem. Soc., 1995, 117, 10694-10701) reported reversible oxygen binding lithium pentacyanocobaltate coordination polymers as an oxygen selective adsorbent. Kuznicki et al. (Letters to Nature, 2001, Vol. 412, 720-724) reported a titanosilicate molecular sieve with adjustable pores for size-selective
10 adsorption of molecules. This adsorbent was demonstrated for the selective adsorption of oxygen based kinetic selectivity.

Objects of the Invention

The main object of the present invention is to provide a process for the preparation of a
15 molecular sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon at ambient temperatures.

Another object of the present invention is to provide an oxygen selective zeolite based adsorbent prepared by a simple post-synthesis modification.

Yet another object of the present invention is to provide an adsorbent with high
20 adsorption selectivity and capacity for oxygen from its gaseous mixture with argon.

Yet another object of the present invention is to provide an oxygen selective adsorbent, which can be prepared by the exchange of inexpensive alkaline earth cations in the place of sodium cations present in zeolite X.

Yet another object of the present invention is to provide an adsorbent and the activation technique of that adsorbent, which can be used as a gas chromatography column packing material for the analysis of air samples, more particularly argon-oxygen gaseous mixtures.

Yet another object of the present invention is to provide a process for the preparation of
5 a commercially inexpensive oxygen selective adsorbent which can be used in a pressure swing adsorption (PSA) process, vacuum swing adsorption (VSA) process or vacuum pressure swing adsorption (VPSA) process for the production of pure argon gas product either in conjunction with cryogenic air separation process where crude argon can be purified, or in combination with oxygen PSA process where the product oxygen gas
10 contains around 5% argon and this argon gas can be separated to get pure argon gas product.

Summary of the Invention

Accordingly, the present invention provides a process for the preparation of a molecular
15 sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon, the process comprising the steps of:

- (i) subjecting the zeolite X or zeolite Y taken in the form of powder, binderless pellets and/or granular beads to cation exchange by treating it with 0.01-1.0M aqueous solution of a divalent alkaline earth metal cation salts, at a temperature of
20 303 - 373 K for a period of 2 - 24 hrs;
- (ii) filtering the above said solution and washing the powder or pellets with copious amount of distilled water till the adsorbent is free from the anions;
- (iii) repeating the above said cation exchange process described in steps (i) & (ii) until the complete or above 90 percentage exchange of extra framework sodium cation

present in zeolite X with divalent alkaline earth metal cations;

(iv) drying the above said resultant exchanged zeolite at a temperature of 350–360 K in a hot air oven for a period of 10–13 hrs and

5 (v) activating the resultant cation exchanged zeolite by heating gradually from ambient temperature to 673 K and keeping it at this temperature for 4 – 8hrs, under an inert atmosphere of either helium, nitrogen, argon, oxygen or vacuum to obtain the desired molecular sieve adsorbent.

In an embodiment of the present invention the divalent alkaline earth metal cation used in step (i) is selected from the group consisting of calcium, strontium and barium.

10 In an embodiment of present invention commercially available zeolite X in powder form or in granular form can be used for the preparation of the oxygen selective molecular sieve adsorbent.

In another embodiment of the present invention zeolite X is exchanged with alkaline earth metal cations at a temperature range of 303 to 363 K for 4– 24 hrs using 0.01 – 1 molar
15 solution of the specific salt.

In yet another embodiment of the present invention at least 30% of any exchangeable ion capacity of zeolite is exchanged with an alkaline earth metal cation or the mixture of alkaline earth metal cations thereof.

In another embodiment of the present invention the molecular sieve adsorbent is useful
20 for the selective adsorption of oxygen from its mixture with argon, for the production of highly pure argon from a feed gas consists of argon at varying concentration with other gases like oxygen.

In another embodiment of the present invention the molecular sieve adsorbent obtained is

useful for the preparation of chromatographic column for the analysis air samples, particularly for argon-oxygen mixtures.

In another embodiment of the present invention the molecular sieve adsorbent obtained is useful for the preparation of chromatographic column, which is selective towards oxygen
5 and argon as in the order of oxygen > argon.

In still another embodiment of present invention the alkaline earth metal exchanged zeolite X in binderless pellet form can be used as the adsorbent for the preparation of the chromatographic column having a dimension of 2 meter length and 3 mm outside diameter for the chromatographic separation of argon-oxygen gaseous mixture.

10 In still another embodiment of the present invention the alkaline earth metal exchanged zeolite X in binderless pellet form especially strontium cation exchanged zeolite X pellets are activated at high temperature in the range of 473K - 773K, specifically 523K - 673K under an inert atmosphere like helium, nitrogen, argon, oxygen or under vacuum.

In still another embodiment of the present invention strontium exchanged zeolite X
15 spherical beads were used for the dynamic adsorption studies of argon and oxygen gas mixture in an adsorbent column at different feed concentration of 5 -95% of oxygen in argon.

In still another embodiment of the present invention the alkaline earth metal exchanged zeolite X spherical beads were activated under argon gas flow at a heating rate of 2
20 K/min upto 623 K and kept at this temperature for 8 hrs, prior to the dynamic adsorption studies of argon-oxygen gas mixtures.

In still another embodiment of the present invention the saturated cation exchanged zeolite X adsorbent after dynamic adsorption studies of argon-oxygen gas mixture, can be reused after activation under argon gas purge or by applying vacuum inside the adsorbent
25 column at ambient temperature.

In still another embodiment of present invention the alkaline earth metal cation exchanged zeolite X adsorbent; especially strontium exchanged zeolite X adsorbent can be used in pressure swing adsorption or vacuum swing adsorption process for the separation of argon from its gaseous mixture with oxygen.

- 5 In still another embodiment of the present invention, the cation exchanged zeolite adsorbent has an oxygen equilibrium adsorption capacity in the range of 5.0 – 8.0 cc/g and an equilibrium selectivity for oxygen over argon in the range of 1.4 – 2.0, at 303 K and 760 mmHg.”

10 Brief Description of the Drawings

FIG. 1 is a diagram of equilibrium adsorption isotherms of oxygen and argon in NaX(Pe) at 303 K.

FIG. 2 is a diagram of equilibrium adsorption isotherms of oxygen and argon in SrX(Pe) at 303 K.

- 15 FIG. 3 is a chromatogram for the separation of argon and oxygen utilizing the adsorbent material produced in Example 2, at 308 K. The concentration of argon was 5.5% and that of oxygen was 94.5% on volume basis.

- FIG. 4 is a chromatogram for the separation of argon and oxygen utilizing the adsorbent material produced in Example 2, at 308 K. The concentration of argon was 10% and that
20 of oxygen was 90% on volume basis.

FIG. 5 is a chromatogram for the separation of argon and oxygen utilizing the adsorbent material produced in Example 2, at 308 K. The concentration of argon was 54% and that of oxygen was 46% on volume basis.

FIG. 6 is a diagram of breakthrough curves of oxygen in SrX(G) adsorbent at 303 K as described in Example 4.

FIG. 7 is a diagram of breakthrough curves of oxygen in SrX(G) adsorbent at 303 K as described in Example 5.

5 FIG. 8 is a diagram of breakthrough curves of oxygen in SrX(G) adsorbent at 303 K as described in Example 6.

FIG. 9 is a diagram of breakthrough curves of oxygen in SrX(G) adsorbent at 303 K as described in Example 7.

10 Detailed Description of the Invention

The present invention provides mainly a process for the preparation of a molecular sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon, such an adsorbent is prepared by cation exchange of faujasite type zeolite taken in the form of powder, binderless pellets and granular beads, with an aqueous solution of alkaline
15 earth metal salts at an elevated temperature for 2 – 24 hrs using 0.01 – 1 molar solution of the specific salt followed by activation of the molecular sieve at an increased temperature under an inert atmosphere or vacuum. The dry zeolite X, containing 50 to 100% strontium cations of the total exchangeable sodium cations, after activation at high temperature and vacuum was subjected to adsorption studies of oxygen and argon using a
20 static volumetric adsorption system supplied by Micromeritics Corp. USA (Model ASAP 2010). The pure component adsorption isotherms, capacity and selectivity of cation exchanged zeolite X for oxygen and argon were measured at 288 K and 303 K, in the pressure range of 0.5 mm Hg – 850 mm Hg.

The present invention provides a process for the preparation of a zeolite molecular sieve

adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon. Zeolites, which are microporous crystalline aluminosilicates, are finding increased applications for the separation of mixtures of compounds having closely related molecular properties. In a zeolite framework, SiO_2 and AlO_2 tetrahedra are connected by sharing oxygen atoms. Al^{3+} and Si^{4+} ions are buried in the tetrahedra of oxygen atoms and are not directly exposed to adsorbate molecules. Thus, the main interactions of the adsorbate molecules in a zeolite structure are through lattice oxygen atoms and extra framework cations. The zeolite of interest in the present invention was of faujasite type zeolite, specifically zeolite X. Zeolite NaX powder (procured from Zeolites and Allied Products, Mumbai, India) having a chemical composition $\text{Na}_{88}\text{Al}_{88}\text{Si}_{104}\text{O}_{384} \cdot w\text{H}_2\text{O}$ (w changes from 220 to 280) was used as the starting material and zeolite X spherical beads were procured from Zeochem AG, Switzerland which was used for the dynamic adsorption measurements. The zeolite X, with exchangeable cations mainly consists of sodium ions, was first pressed up to 5 tonnes force to make pellets using a hydraulic pelletizer. These pellets are then crushed and sieved to collect adsorbent particles in the range of 30 – 100 mesh size. The adsorbent particles are exchanged repeatedly with alkaline earth metal cations in an aqueous solution of their salts, especially chloride, nitrate and acetate, and more particularly chloride salt, until the complete exchange of sodium cations with alkaline earth metal cations. The concentration of the aqueous solution of alkaline earth metal salt was in the range of 0.01 M – 1 M, particularly between 0.05 M – 0.25 M and the adsorbent particles were treated with this solution for two times repeatedly and then filtered, washed with distilled water until the washings are free from chloride ions and dried in a hot air oven for overnight at 353 K. The percentage exchange of alkaline earth metal cations into the zeolite X samples were measured using energy dispersive x-ray analyzer (Oxford INCA, Energy 200 Suite) attached to the scanning electron microscope (LEO 1430 VP).

Oxygen and argon adsorption at 288 K and 303 K were studies in a static volumetric

adsorption system (Micromeritics, USA, Model ASAP 2010), after activating the sample at 623 K under vacuum for about 4 – 8 hrs as described in the examples herein. During analysis, the samples were evacuated completely and requisite amount of the adsorbate gas was injected into the volumetric set up at volumes required to achieve a targeted set of pressures ranging from 0.1 to 850mmHg. A minimum equilibrium interval of 5 seconds with a relative target tolerance of 5.0% of the targeted pressure and an absolute target tolerance of 5.000 mmHg were used to determine equilibrium for each measurement point. Adsorption temperature was maintained (± 0.1 K) by circulating water from a constant temperature bath (Julabo F25, Germany).

- 10 The pure component selectivity of two gases A and B was calculated by using the equation,

$$\alpha_{A/B} = \left[\frac{V_A}{V_B} \right]_{P,T}$$

where V_A and V_B are the volumes of gas A and B respectively adsorbed at any given pressure P and temperature T.

- 15 Isosteric heats of adsorption were calculated from the adsorption data collected at 288 K and 303 K using Clausius–Clapeyron equation.

$$-\Delta_{ad}H^\circ = R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_\theta$$

where R is the universal gas constant, θ is the fraction of the adsorbed sites at a pressure P and temperature T.

- 20 The important inventive step of the process includes in developing a material with very high oxygen adsorption capacity of 6.86 cc/g and oxygen/argon selectivity of 1.8 at 303 K and 760 mm Hg.

Another important inventive step involved in the present invention is the preparation of a chromatographic column which can be used for the chromatographic analysis of air, especially argon-oxygen mixtures, at ambient temperatures or even at higher temperatures. Presently, very long fused silica PLOT Molecular Sieve 5A columns (capillary columns) are used for the separation of permanent gases especially for argon-oxygen separation. However, this column can handle only very low sample volume and also needed cryogenic temperatures for the separation of argon and oxygen. In the present invention, 2 meter long 3mm OD stainless steel column was used as the chromatographic packed column and strontium exchanged zeolite X adsorbent was used as the packing material for the chromatographic column for the analysis of argon-oxygen mixture. Strontium exchanged zeolite X particles having a size in the range of 30 - 100 mesh size were activated externally at a temperature in the range of 473 K - 673 K under an inert atmosphere or vacuum for 12 - 48 hrs. The activated adsorbent is cooled to room temperature and then transferred suddenly to the column under moisture free conditions and this column is coiled into spiral form and then connected to the GC instrument (GC-7610, Chemito Technologies Pvt. Ltd., Nasik, India) equipped with a TCD detector (TCD 866). Helium gas was used as the carrier gas and this column was again heated to 523 K under helium flow at flow rate of 100 ml/min inside the GC oven for 24 hrs to remove the adsorbed atmospheric gases during the packing of the GC column and then it is cooled to 308 K and the carrier gas flow rate is set to 60 ml/min. A 0.5 ml pulse of argon-oxygen mixture is injected into the packed column at 308 K using a gas-tight gas sampling syringe and the retention times of argon and oxygen are measured. Argon eluted first and there was clear separation of the peaks of argon and oxygen in the chromatogram.

Another important embodiment of present invention is the dynamic adsorption data of oxygen from its gaseous mixture with argon in the oxygen selective adsorbent. For the dynamic adsorption studies, zeolite X spherical beads were exchanged with an aqueous

solution of strontium salts as described above for zeolite X binderless pellets. The completely strontium exchanged zeolite X beads were dried in a hot air oven for overnight and the dried oxygen selective adsorbent was filled in an adsorbent column having a dimension of 35 cm length and 1.9 cm diameter. The adsorbent inside the column was activated at heating rate of 2 K/min to 623 K and the temperature was maintained for 12- 24 hrs. The activated adsorbent is then cooled to the adsorption temperature, 303 K and feed containing oxygen and argon at particular concentration and feed flow rate passed through the adsorbent column to get the dynamic adsorption data of oxygen in strontium exchanged zeolite X. The feed concentration and product concentration at the other end of adsorbent column is measured in a GC instrument (GC-7610, Chemito Technologies Pvt. Ltd., Nasik, India) equipped with a TCD detector (TCD 866) using the packed column mentioned above in the present invention. The concentration profile of oxygen at the outlet of the adsorbent column is plotted against time and it is defined hereafter as the breakthrough curve of oxygen in the particular adsorbent.

The invention will now be illustrated with help of typical examples. It may be understood that the following examples do not limit the scope of the invention and it is possible to work the invention outside the parameters specified in the following examples.

EXAMPLE 1

Zeolite NaX powder was first pressed up to 5 tonnes force to make pellets using a hydraulic pelletizer. These pellets are then crushed and sieved to collect adsorbent particles in the range of 30 -100 mesh size and is named as NaX(Pe). Around 0.5 g of this NaX(Pe) particles were activated at 623 K under vacuum (5×10^{-3} mm Hg) for 6 - 12 hrs. Equilibrium adsorption measurements of ultra high pure oxygen and argon gases in this adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 288 K and 303 K. The equilibrium adsorption isotherms of oxygen

and argon in NaX(Pe) particles at 303 K are give in FIG. 1. The equilibrium adsorption capacities of oxygen and argon were 2.96 cc/g and 2.75 cc/g respectively at 303 K and 760 mm Hg. The equilibrium selectivities for oxygen over argon were 1.09, 1.03 and 1.08 respectively at 25 mm Hg, 100 mm Hg, 760 mm Hg pressure and 303 K.

5

EXAMPLE 2

25 g of NaX(Pe) prepared by the method described in Example 1 was treated with 0.1M aqueous solution of strontium chloride at a solid to liquid ratio of 1:80 and the solids were filtered, washed with copious amount of distilled water until the filtrate is free from chloride ions, and dried at 353 K in a hot air oven for overnight. The cation exchange was
10 conducted at each time at a temperature of 353 K for 4 hrs until the total exchangeable sodium cations are replaced with strontium cations. The adsorbent sample thus prepared was named as SrX(Pe). Around 0.5 g of this SrX(Pe) particles were activated at 623 K under vacuum (5×10^{-3} mm Hg) for 6 hrs. Equilibrium adsorption measurements of ultra
15 high pure oxygen and argon gases in this adsorbent were carried out in a static volumetric adsorption system at 288 K and 303 K. The equilibrium adsorption isotherms of oxygen and argon in SrX(Pe) particles at 303 K are give in FIG. 2. The equilibrium adsorption capacities of oxygen and argon were 6.86 cc/g and 3.8 cc/g respectively at 303 K and 760 mm Hg. The equilibrium selectivities for oxygen over argon were 2.23, 1.96 and 1.81 respectively at 25 mm Hg, 100 mm Hg, 760 mm Hg pressure and 303 K.

20

Example 3

15 g of SrX(Pe) sample, prepared by the method described in Example 2, sufficient to fill the packed column was transferred into the column the column is coiled into spiral form and then connected to the GC instrument. The dimensions of column used for this purpose was 2 meter in length and 3 mm in OD and was made up of stainless steel. The
25 chromatographic separation of argon-oxygen mixture is conducted in this column as per the procedure described above. FIG. 3 – FIG. 5 shows the chromatogram of argon and

oxygen at different concentrations in the gaseous mixture. There was a clear peak separation for argon and oxygen at different concentrations of argon-oxygen gaseous mixture with argon and oxygen retention times observed at 1.46 -1.5 and 1.95 - 2.20 minutes respectively.

5

Example 4

20 g of zeolite NaX powder was treated with 0.1M aqueous solution of barium chloride at a solid to liquid ratio of 1:80 and the solids were filtered, washed with copious amount of distilled water until the filtrate is free from chloride ions, and dried at 353 K in a hot air oven for overnight. The cation exchange was conducted at each time at a temperature of 353 K for 8 hrs until the total exchangeable sodium cations are replaced with barium cations. The adsorbent sample thus prepared was named as BaX. Around 0.5 g of this BaX powder was activated at 623 K under vacuum (5×10^{-3} mm Hg) for 12 hrs. Equilibrium adsorption measurements of ultra high pure oxygen and argon gases in this adsorbent were carried out in a static volumetric adsorption system at 288 K and 303 K. The equilibrium adsorption capacities of oxygen and argon were 5.2 cc/g and 3.35 cc/g respectively at 303 K and 760 mm Hg. The equilibrium selectivities for oxygen over argon were 2.13, 1.59 and 1.55 respectively at 25 mm Hg, 100 mm Hg, 760 mm Hg pressure and 303 K.

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Example 5

20 g of zeolite NaX powder was treated with 0.1M aqueous solution of calcium chloride at a solid to liquid ratio of 1:80 and the solids were filtered, washed with copious amount of distilled water until the filtrate is free from chloride ions, and dried at 353 K in a hot air oven for overnight. The cation exchange was conducted at each time at a temperature of 353 K for 8 hrs until the total exchangeable sodium cations are replaced with calcium cations. The adsorbent sample thus prepared was named as CaX. Around 0.5 g of this CaX powder was activated at 623 K under vacuum (5×10^{-3} mm Hg) for 12 hrs. Equilibrium

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adsorption measurements of ultra high pure oxygen and argon gases in this adsorbent were carried out in a static volumetric adsorption system at 288 K and 303 K. The equilibrium adsorption capacities of oxygen and argon were 7.61 cc/g and 4.96 cc/g respectively at 303 K and 760 mm Hg. The equilibrium selectivities for oxygen over argon were 1.48, 1.53 and 1.53 respectively at 25 mm Hg, 100 mm Hg, 760 mm Hg pressure and 303 K.

Example 6

0.5 g of zeolite NaY was activated at 623 K under vacuum (5×10^{-3} mm Hg) for 6 hrs. Equilibrium adsorption measurements of ultra high pure oxygen and argon gases in this adsorbent were carried out in a static volumetric adsorption system at 288 K and 303 K. The equilibrium adsorption capacities of oxygen and argon were 2.23 cc/g and 2.0 cc/g respectively at 303 K and 760 mm Hg.

Example 7

100 g of zeolite NaX spherical beads (procured from Zeochem AG, Switzerland) were treated with 0.1M aqueous solution of strontium chloride at a solid to liquid ratio of 1:40 and the solids were filtered, washed with copious amount of distilled water until the filtrate is free from chloride ions, and dried at 353 K in a hot air oven for overnight. The cation exchange was conducted at each time at a temperature of 353 K for 4 8 hrs until the total exchangeable sodium cations are replaced with strontium cations. The adsorbent sample thus prepared was named as SrX(G). Around 70 g of this sample is used for the breakthrough measurements of oxygen in SrX(G) adsorbent column. The adsorbent column was 35 cm long with 1.9 cm internal diameter. The adsorbent was activated at 623 K under argon atmosphere for 12 hrs and then cooled to the adsorption measurement temperature, 303 K. An oxygen- argon mixture at a composition of 90% oxygen and 10% argon on volume basis was fed into the SrX(G) adsorbent column at a flow rate of 70 ml/min. The column pressure and temperature were 1 atm (absolute) and 303 K for the

breakthrough measurement of oxygen in SrX(G) adsorbent. The concentration profile of oxygen at the outlet of the adsorbent column is plotted against time and shown in FIG. 6. The SrX(G) adsorbent column is regenerated by applying vacuum after the adsorbent got saturated with oxygen. Again the breakthrough measurement is conducted in this
5 adsorbent column and concentration profile of oxygen at the outlet of the adsorbent column is shown in FIG. 6 as second run data. From the FIG. 6, it is clear that the adsorbent can be easily regenerate by simple application of vacuum. The breakthrough capacity of oxygen in the above adsorbent was 2.66 cc/g at 303 K.

Example 8

10 Breakthrough measurement of oxygen in the adsorbent system described in Example 7 was conducted with a feed concentration of 90% oxygen and 10% argon on volume basis at a flow rate of 60 ml/min and the desorption of was carried out by passing pure argon at a flow rate of 60 ml/min. through the oxygen saturated adsorbent bed, counter- currently to the feed flow. FIG.7 shows the adsorption and desorption curves of oxygen described
15 above in this example.

Example 9

Breakthrough measurement of oxygen in the adsorbent system described in Example 7 was conducted with a feed concentration of 50% oxygen and 50% argon on volume basis at a flow rate of 50 ml/min. The concentration profile of oxygen with respect to time, at the
20 outlet of the adsorbent column is shown in FIG. 8.

Example 10

Breakthrough measurement of oxygen in the adsorbent system described in Example 7 was conducted with a feed concentration of 6.5% oxygen and 93.5% argon on volume basis at a flow rate of 107 ml/min. The column pressure was 4 atm (absolute) during the
25 adsorption measurements. The concentration profile of oxygen with respect to time, at

the outlet of the adsorbent column is shown in FIG. 9.

The starting temperature of all the oxygen breakthrough measurements was 303 K. The breakthrough measurements of oxygen in SrX(G) adsorbent showed that strontium exchanged zeolite X can be used as a oxygen selective adsorbent for the separation of argon-oxygen for the production of argon, either from the crude argon stream coming from the cryogenic air separation plant, or from the product stream of oxygen PSA where the product contains around 5 % argon on volume basis along with the oxygen gas.

We claim:

1. A process for the preparation of a molecular sieve adsorbent for the selective adsorption of oxygen from its gaseous mixture with argon, the process comprising the steps of:

- 5 (i) subjecting the zeolite X or zeolite Y taken in the form of powder, binderless pellets and/or granular beads to cation exchange by treating it with 0.01-1.0M aqueous solution of a divalent alkaline earth metal cation salts, at a temperature of 303 - 373 K for a period of 2 - 24 hrs;
- 10 (ii) filtering the above said solution as obtained in step (i) and washing the powder or pellets with copious amount of distilled water till the adsorbent is free from the anions;
- (iii) repeating the above said cation exchange process described in steps (i) & (ii) until the complete or above 90 percentage exchange of extra framework sodium cation present in zeolite X with divalent alkaline earth metal cations;
- 15 (iv) drying the above said resultant exchanged zeolite at a temperature of 350-360 K in a hot air oven for a period of 10-13 hrs and
- (v) activating the resultant cation exchanged zeolite by heating gradually from ambient temperature to 673 K and keeping it at this temperature for 4 - 8hrs, under an inert atmosphere of either helium, nitrogen, argon, oxygen or vacuum to
20 obtain the desired molecular sieve adsorbent.

2. A process as claimed in claim 1, wherein the divalent alkaline earth metal cation used in step (i) is selected from the group consisting of calcium, strontium and barium.

3. A process as claimed in claim 1, wherein the temperature used for cation exchange of

zeolite in step (i) is in the range of 303 K to 363 K.

4. A process as claimed in claim 1, wherein at least 30% of any exchangeable ion capacity of zeolite is exchanged with an alkaline earth metal cation or the mixture of alkaline earth metal cations thereof.
- 5 5. A process as claimed in claim 1, wherein the molecular sieve adsorbent obtained is useful for the selective adsorption of oxygen from its mixture with argon, for the production of highly pure argon from a feed gas consists of argon at varying concentration with other gases like oxygen.
6. A process as claimed in claim 1, wherein the molecular sieve adsorbent obtained is
10 useful for the preparation of chromatographic column for the analysis air samples, particularly for argon-oxygen mixtures.
7. A process as claimed in claim 1, wherein the molecular sieve adsorbent obtained is useful for the preparation of chromatographic column, which is selective towards oxygen and argon as in the order of oxygen > argon.
- 15 8. The process of claim 1 wherein the said cation exchanged zeolite adsorbent has an oxygen equilibrium adsorption capacity in the range of 5.0 - 8.0 cc/g and an equilibrium selectivity for oxygen over argon in the range of 1.4 - 2.0, at 303 K and 760 mmHg."

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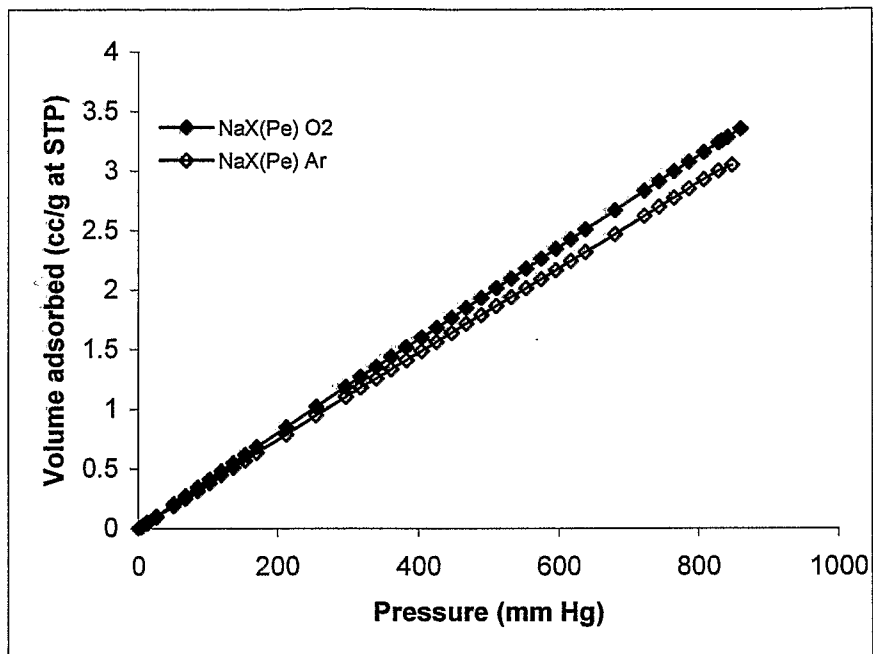


FIG. 1

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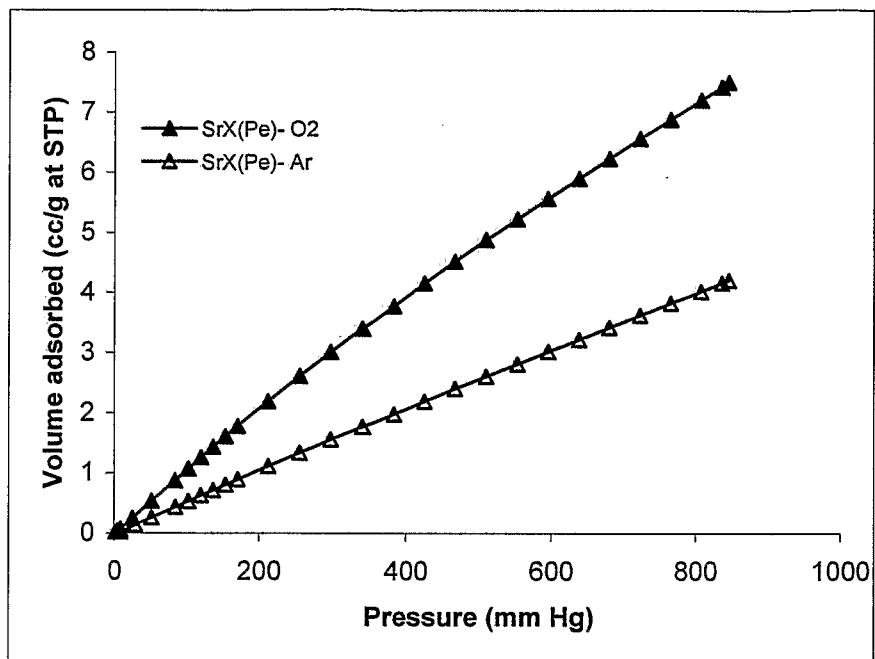


FIG. 2

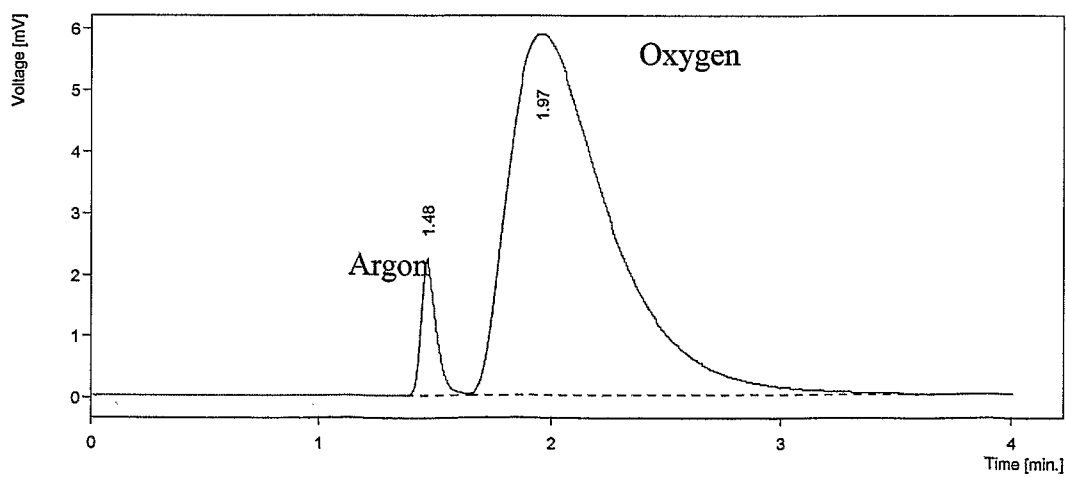


FIG. 3

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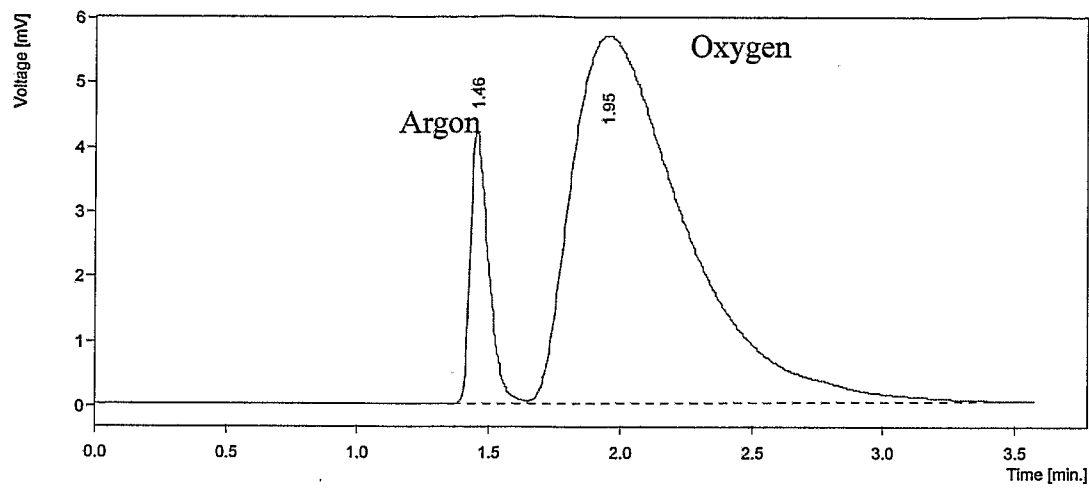


FIG. 4

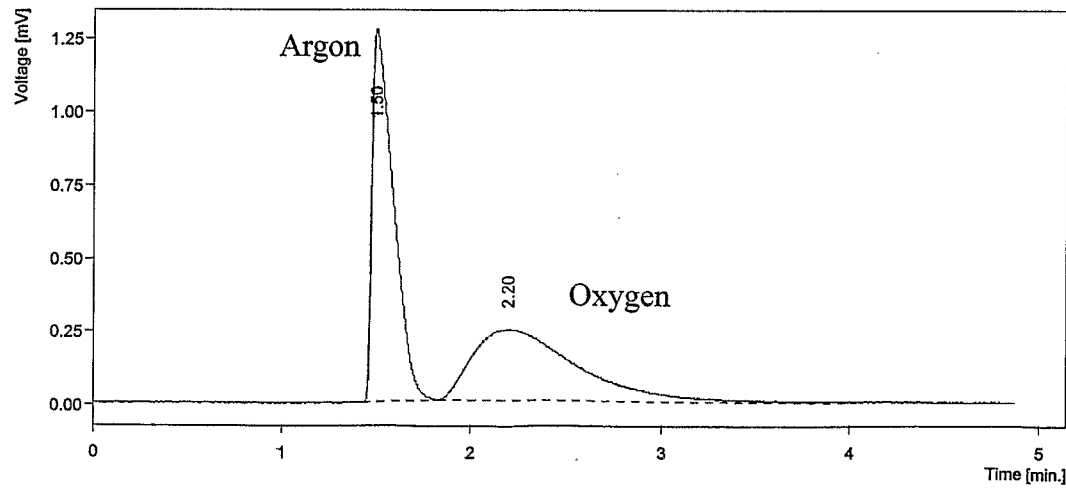


FIG. 5

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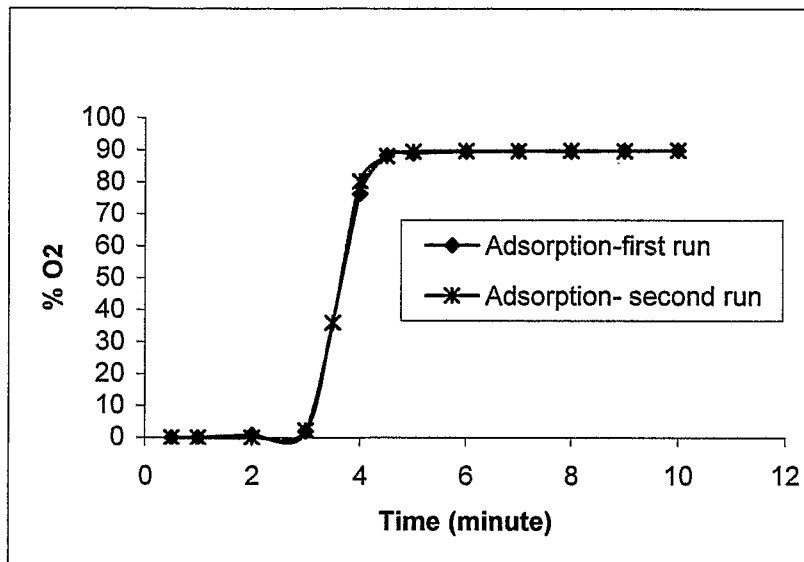


FIG. 6

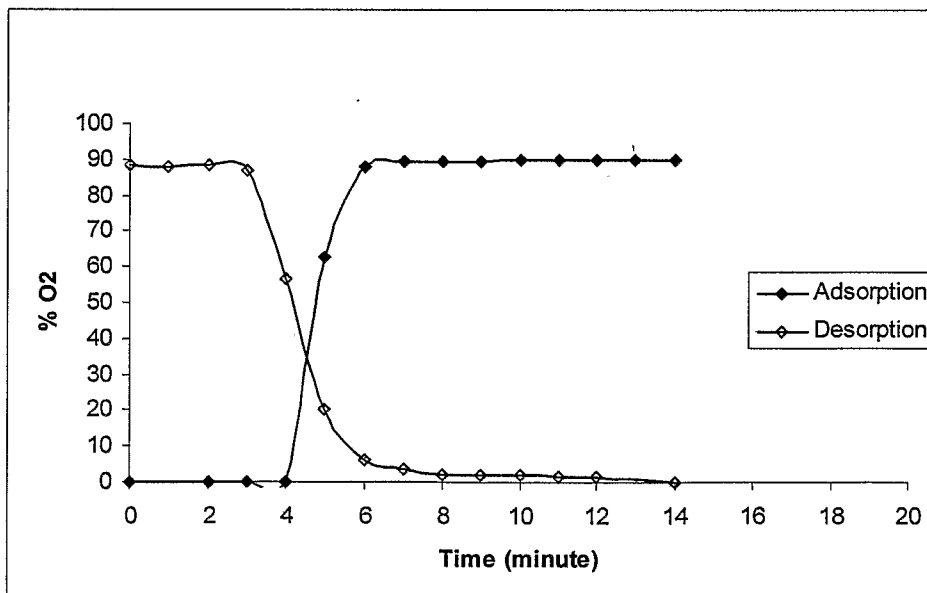


FIG. 7

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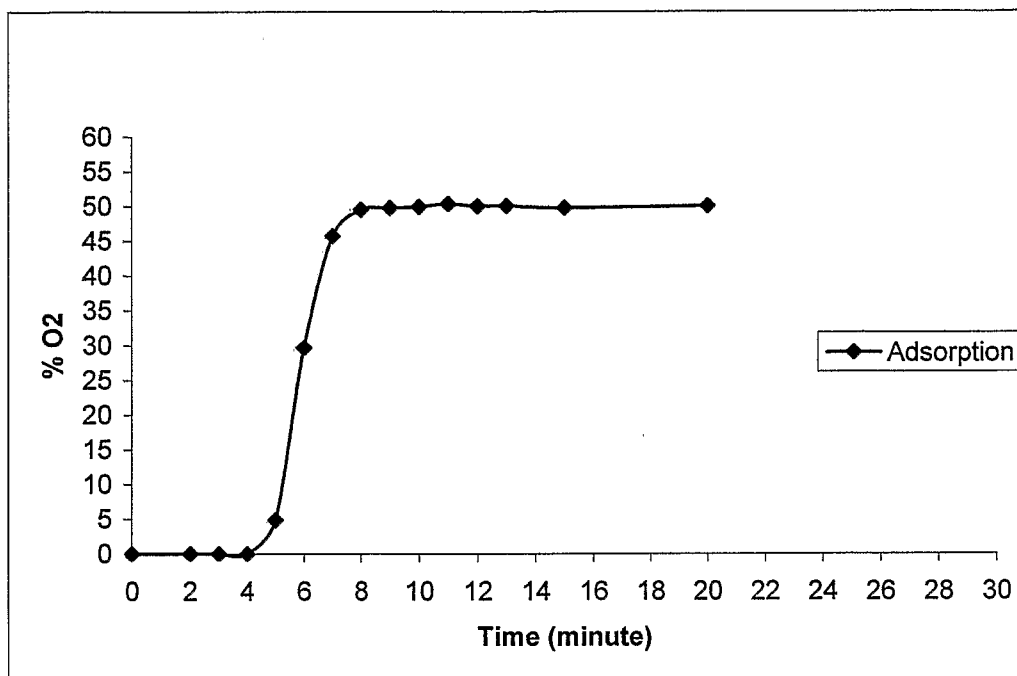


FIG. 8

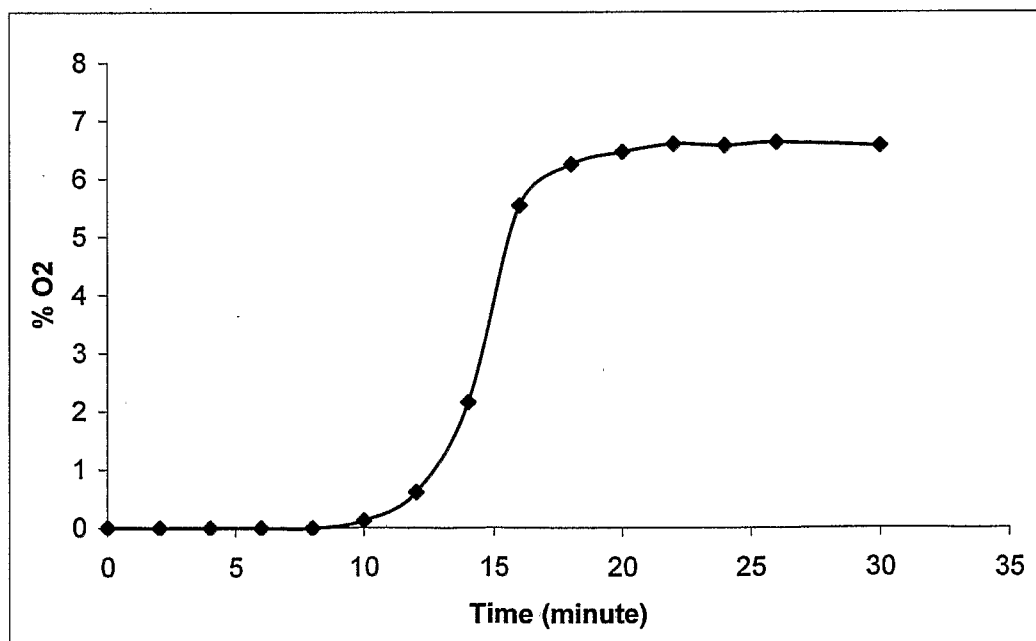


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2009/000399

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J20/18 B01D53/00
ADD. B01J29/08

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)

B01J B01D

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

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

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 744 805 A (MAROULIS PETER J [US] ET AL) 17 May 1988 (1988-05-17) examples 28-30 column 18, line 12 - line 16 tables I,II	1-8
X	US 2 882 244 A (MILTON ROBERT M) 14 April 1959 (1959-04-14) column 6, line 49 - column 7, line 19 column 10, line 40 - line 45 column 14, line 1 - line 17 column 14, line 38 - line 43 ----- -/--	1-8

☒ 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

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Date of the actual completion of the international search

17 December 2009

Date of mailing of the international search report

28/12/2009

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2009/000399

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 087 289 A (CHOUDARY NETTEM VENKATESHWARLU [IN] ET AL) 11 July 2000 (2000-07-11) abstract column 4, line 23 - line 27 examples 12,14 table 2	1-8
A	WO 2005/039755 A (COUNCIL SCIENT IND RES [IN]; JASRA RAKSH VIR [IN]; CHUDASAMA CHINTANSI) 6 May 2005 (2005-05-06) abstract examples	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2009/000399

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