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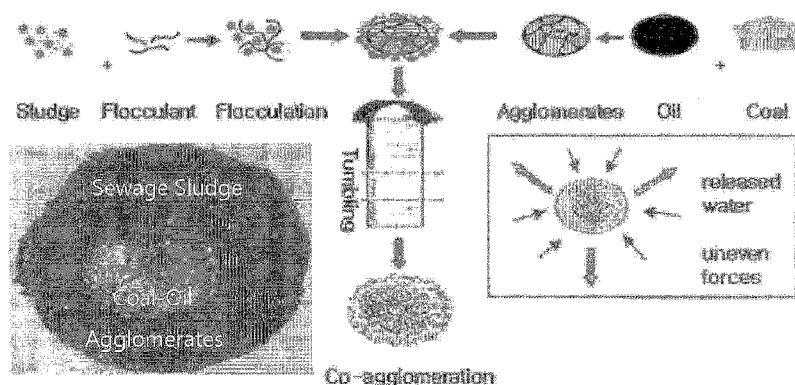
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(54) Title: CHITOSAN-NIPAM THERMOSENSITIVE POLYMER COAGULANT AND METHOD FOR THE PREPARATION THEREFOR

[Fig. 1]



(57) Abstract: Provided are thermosensitive polymer coagulant comprising chitosan and N-isopropylacrylamide and a process for preparing the same. More specifically, chitosan-NIPAM thermosensitive polymer coagulant having both hydrophobicity and hydrophilicity is prepared by polymerizing chitosan, a type of biomolecule existing abundantly in the nature, with NIPAM (N-isopropylacrylamide) as monomer for poly (N-isopropylacrylamide), a type of thermosensitive polymer.

【DESCRIPTION】**【Invention Title】**

CHITOSAN-NIPAM THERMOSENSITIVE POLYMER COAGULANT AND
METHOD FOR THE PREPARATION THEREFOR

5

【Technical Field】

The present invention relates to chitosan-NIPAM
thermosensitive polymer coagulant and a process for preparing
the same. According to the present invention, provided are
10 chitosan-NIPAM thermosensitive polymer coagulant which
selectively separates and coagulates organic sludge
exclusively during wastewater treatment to improve dewatering
effect, as well as providing excellent effects on
purifying/recovering the organic substances, and a process for
15 preparing the same.

【Background Art】**【Disclosure】****【Technical Problem】**

Some sewage treatment plants make landfill or reuse the
20 final products from the final process of treating the sludge.
However, landfill has been preferentially carried out before
drying, thereby causing the problems of leaching water.
Recently, there are trends to prohibit landfill or sea-
dumping, while incineration is rather in the spotlight as an

appropriate way to treat sewage in a large scale.

Incineration comprises burning combustible material by the use of oxygen in the air. Incineration has been currently used for processes for reducing wastes (owing to the
5 difficulties of landfill) and stabilizing treatment of corruptible material by using inorganization of organic materials. Further, wasteheat generated during the combustion may be reused for generating electric power or warming indoor (being applied to treatment of urban waste). In case of
10 harmful waste, reduction of the amount of sludge in order to overcome the limitation of ground for landfill is preferentially considered rather than the matter of stabilization and safety, when incineration is progressed from large cities. In advanced nations, treatment of sewage has a
15 tendency of conversion from conventional landfill into incineration.

Incineration has advantages including ability of hygienic treatment of sewage, no corruption, less abomination as compared to dewatered cake, and reduction of sludge volume by
20 by 10~20% on the basis of the initial volume.

Concentrated sludge slurry produced from a sewage treatment plant usually contains not less than 98% of moisture. For incineration of the sludge, dehydration must be carried out. By using ordinary mechanical dewatering process, one can

dewater 75~85% of the moisture content. The sludge after dewatering is subjected to drying process, and then incinerated.

For the process of treating sewage sludge as described
5 above, dehydration and purification are to be readily carried out with reduced cost required for the treatment of sludge. Further, it is required that the relevant facilities have to be simplified and effectuated, with less trouble of unpleasant odor or air pollution, and that the dehydrated sludge is to be
10 utilized as fuel of high quality.

In the process of raw/waste water treatment, ~~dehydration~~ dewatering would be difficult because of closure of ~~bubbles~~ filter media due to mucous microorganisms, during the course of dewatering of sludge obtained by coagulation/precipitation
15 of activated sludge or anaerobic digestion sludge which is generated with decomposition of organic substances by microorganisms. As a proposal of pretreatment, inorganic or organic coagulant for adjusting physical properties of sludge for the next step of filtration is added in order to improve
20 the dewatering efficiency.

Since sewage sludge is negatively charged in general, the polymer coagulant used for the purpose is usually cationic. However, anionic or nonionic polymer coagulants may be applied depending on the type of sludge (such as wastewater from

leather treatment). The application of coagulant depends on interfacial charge of the flocculation: for example, if the interfacial charge is anionic, a cationic polymer coagulant (having opposite charge) is preferably applied.

5 In order to dewater not only sewage sludge but also the third additional substance at the same time, the role of the polymer coagulant would become further complicated. Polymer coagulant for general use is water soluble, but if sewage sludge is to be dewatered by coagulation with coal-oil
10 agglomerate by incorporating a hydrophobic substance such as coal-oil agglomerate as well, a polymeric substance containing both hydrophilic group and hydrophobic group has to be used, or any operation to provide such functions step by step is needed.

15 According to Korean Patent Publication No. 2005-0093731, chitosan/cationic acrylamide copolymer is prepared, and incorporated to a process for manufacturing paper to increase the bonding force between pulp fibers (as dispersion stabilizer) and inorganic filler to improve the strength
20 properties and physical properties of the paper. Thus the copolymer can be applied as sludge coagulant in wastewater from paper manufactory. However, the disclosed patent has disadvantages in that the process for preparation is relatively complicated and less economic.

In addition, Korean Patent Publication Nos. 1989-0005942, 1991-0006742, 1999-0052023, 2005-0093731 and 1999-0002798 disclose copolymers using chitosan as a coagulant for wastewater treatment. However, the coagulants introduced by those patent publications are prepared through complicated processes, and the coagulated material has disadvantage for being reused as fuel because of high moisture content. Due to such drawbacks in terms of the performances, the coagulants must be further improved in coagulation efficiency for the purpose of practical use.

Currently, coagulants used for wastewater treatment preferentially include polyacrylamide coagulants, polyacrylic acid coagulants, and derivatives thereof. Those coagulants should have large molecular weight to provide coagulating ability, so that they can be hardly dissolved, and their molecular chains are cleaved by mechanical dissolution with stirring to reduce the viscosity down to 1/3, which deteriorate the performances as coagulant. In order to solve such disadvantages, prepared were coagulants such as starch-arylamide copolymer and cellulose-acrylamide copolymer, which exhibited excellent effect with relatively low molecular weight as compared to polyacrylamide coagulants. However, they lack economic efficiency to be applied to industry, but only showing insufficient coagulating effect.

Chitosan used for the present invention is environmentally friendly polymeric substance obtained via deacetylation of chitin which constitutes shells of Crustacea such as crabs and crawfish. The polymers of NIPAM (N-isopropylacrylamide), i.e. poly(N-isopropylacrylamide) show lower critical solution temperature (LCST) at about 32°C. Thus, poly(N-isopropylacrylamide) shows inherent property in that it is dissolved at a temperature not more than 32°C, but precipitates at a temperature higher than 32°C. Taking advantage of such a property, efficient coagulant can be provided for wastewater treatment.

【Technical Solution】

In order to solve the problems described above, the present invention provides polymer coagulant having far more excellent coagulating performance than that of conventional commercially available cationic polymers, as well as enhanced dewatering effect (particularly by coagulation), effect of separation/purification of inorganic substances and that of recovering organic substances at the same time, and a simple process for preparing the coagulant. Further, the present invention is to provide such an excellent polymer coagulant that the sewage sludge can be used as fuel, and a process for preparing the same.

The present invention relates to thermosensitive polymer coagulant comprising chitosan and N-isopropylacrylamide and a process for preparing the same. More specifically, chitosan-NIPAM thermosensitive polymer coagulant having both
5 hydrophobicity and hydrophilicity is prepared by polymerizing chitosan, a type of biomolecule existing abundantly in the nature, with NIPAM (N-isopropylacrylamide) as monomer for poly(N-isopropylacrylamide), a type of thermosensitive polymer.

In a process using sewage sludge as fuel, efficient
10 performance can be expected only with the coagulated substance having large specific area. Thus, the shape of coagulated substance should be small with low moisture content, in order to provide coagulating core having low moisture content. According to the present invention, coal-oil agglomerate are
15 prepared to be used for coagulating core. When sewage sludges are coagulated on the surface of the hydrophobic agglomerates, polymer coagulant must have the role of crosslink between the coagulation and sewage sludge. If the object of dehydration is difficult to get spherical agglomerates by simple agitation
20 method, additional dewatering operation such as tumbling is required (Fig. 1).

First, the polymer coagulant which serves as crosslink between the agglomerates and sewage sludge must be hydrophilic in order to sufficiently wet the surface of the sewage sludge

(Fig. 2 and 3). Then, the surface of the sewage sludge becomes hydrophobic by applying heat, to form coagulation between the sewage sludge and agglomerates of the third core substance, coal-oil agglomerate. Water (H_2O) molecules are then disposed
5 out of the surface of the coagulation, to be removed or to be converted to a readily removable state.

It is the object of the present invention to selectively separate and dewater only organic substances from sewage sludge by using polymer. The target polymer is chitosan-NIPAM
10 copolymer.

A first embodiment of the process for preparing the polymer comprises (a) dissolving chitosan (the starting material) and N-isopropylacrylamide in aqueous acetic acid; and (b) incorporating a redox initiator to the solution in
15 aqueous acetic acid, and carrying out polymerization.

A second embodiment of the process comprises (a) dissolving chitosan (the starting material) and N-isopropylacrylamide in aqueous acetic acid; (a₁) additionally incorporating thereto tetramethylethylenediamine (TMEDA) as
20 reaction catalyst and (b) incorporating a redox initiator to the solution in aqueous acetic acid, and carrying out polymerization.

A third embodiment of the process according to the invention comprises (a) dissolving chitosan (the starting

material) and N-isopropylacrylamide in aqueous acetic acid;
(a₁) additionally incorporating thereto
tetramethylethylenediamine (TMEDA) as reaction catalyst; (a₂)
incorporating thereto additional acetic acid or water; and (b)
5 incorporating a redox initiator to the solution in aqueous
acetic acid, and carrying out polymerization.

Now, the present invention is described in more detail.

Used were chitosan and N-isopropylacrylamide as the
starting materials for preparing chitosan-NIPAM
10 thermosensitive polymer coagulant, tetramethylethylenediamine
as the reaction catalyst, ammonium persulfate (APS) as the
reaction initiator, and aqueous acetic acid solution as the
solvent for polymerization.

In the preparation of chitosan-NIPAM thermosensitive
15 polymer coagulant according to the present invention, aqueous
acetic acid solution as solvent was in a concentration of 0.5
to 20% by weight. On the basis of 100 parts by weight of the
aqueous acetic acid solution, total amount of the starting
materials, the reaction catalyst and the reaction initiator
20 would be advantageously from 0.5 to 15 parts by weight. In
order to obtain thermosensitive polymer coagulant having
excellent coagulating ability, it is advantageous to
incorporate 5~1000 parts by weight of N-isopropylacrylamide,
0.5~30 parts by weight of tetramethylethylenediamine, 0.1~10

parts by weight of ammonium as the starting material, reaction catalyst and reaction initiator to 100 parts by weight of chitosan for the polymerization.

When preparing chitosan-NIPAM thermosensitive polymer
5 coagulant according to the invention, polymerization is carried out with stirring at ambient temperature for 0.5 to 6 hours, preferably for 0.5 to 1 hour.

Chitosan-NIPAM block copolymer obtained by the process as described above, which comprises 5~95% by weight, preferably
10 50% by weight of chitosan, and 95~5% by weight, preferably 50% by weight of N-isopropylacrylamide, is advantageous for thermosensitive coagulant. When chitosan-NIPAM copolymer comprising 2 parts by weight of chitosan and 2 parts by weight of N-isopropylacrylamide on the basis of 100 parts by weight
15 of the reaction solution of the process was prepared, the viscosity was from 35 to 40 cP. On the other hand, in case of chitosan-NIPAM copolymer comprising less than 2 parts by weight of chitosan and N-isopropylacrylamide, respectively, or NIPAM polymer comprising only N-isopropylacrylamide on the
20 basis of 100 parts by weight of the reaction solution, the viscosity was from 20 to 25 cP.

While thermosensitive polymer is water-soluble since it is hydrophilic at a low temperature, it becomes hydrophobic and insoluble at a higher temperature than the critical

solution temperature. Thus, the thermosensitive polymer undergo reversible conversion of hydrophilicity/hydrophobicity. Chitosan-NIPAM block copolymer obtained via polymerization process as described above is characterized by having the
5 critical solution temperature of 34°C.

When chitosan-NIPAM thermosensitive polymer coagulant according to the present invention is used along with coal-oil agglomerate disclosed in Korean Patent Publication 2007-0025493 by the present inventors as the core for coagulating
10 sludge in sewage, coagulation of sludge is facilitated. Chitosan-NIPAM thermosensitive polymer coagulant having hydrophilicity at low temperature coagulates only organic sludge in the sewage. When coal-oil agglomerate is incorporated thereto, and heat the mixture above the critical
15 solution temperature of the thermosensitive polymer coagulant, chitosan-NIPAM thermosensitive polymer coagulant and the surface of the sludge become hydrophobic, so that moisture will be disposed outside. Chitosan-NIPAM thermosensitive polymer coagulant-organic sludge and coal-oil agglomerate,
20 being now hydrophobic, are coagulated each other and converted to a state wherein they can be readily dehydrated. Conventional sewage treatment comprises incineration process including dehydration stage and drying stage.

When both thermosensitive polymer coagulant and coal-oil

agglomerate are used according to the present invention, moisture content is noticeably lowered to facilitate and promote dehydration, thereby simplifying the relevant facilities. Due to selective coagulating ability of chitosan-
5 NIPAM thermosensitive polymer coagulant separates and purifies inorganic substances to recover only organic substances. Thus the process according to the present invention has less concern about unpleasant odor or air pollution, while the dehydrated sludge can be utilized as fuel of high quality.

10

【Advantageous Effects】

In sewage sludge treatment, dehydration and purification can be rapidly and easily achieved by using chitosan-NIPAM thermosensitive polymer coagulant according to invention. In
15 the sludge treatment, generic cost can be reduced, and the relevant facilities can be essentially simplified and effectuated according to the present invention. Thus, the process according to the present invention has less concern about unpleasant odor or air pollution, while the dehydrated
20 sludge can be utilized as fuel of high quality.

【Description of Drawings】

The above and other objects, features and advantages of the present invention will become apparent from the following

description of preferred embodiments given in conjunction with the accompanying drawings:

Fig. 1 shows the process wherein sewage sludge is coagulated with chitosan-NIPAM thermosensitive polymer coagulant and coal-petroleum agglomerate and dehydrated.

Fig. 2 shows the coagulation mechanism wherein chitosan-NIPAM thermosensitive polymer coagulant, having both hydrophilicity and hydrophobicity, coagulates the sludge, and responses to heat to change the property from hydrophilic to hydrophobic.

Fig. 3 shows the process wherein chitosan-NIPAM thermosensitive polymer coagulant responses to heat with being changed from hydrophilic to hydrophobic to separate water molecules from the molecular structure to result in dehydration.

【Best Mode】

Hereinafter, the present invention will be described in detail with reference to Examples, which are give as illustration of the invention only, but not intended to restrict the scope of the invention.

[Preparation Example 1]

Chitosan (2 g) was dissolved in 100 ml of water, and the

mixture was stirred while adding 4 ml of acetic acid to obtain complete dissolution. To the solution, added was N-isopropylacrylamide (2 g). As tetramethylethylenediamine (about 0.5 ml) was added thereto with stirring, precipitation
5 occurs. Acetic acid was additionally added dropwise until the precipitate disappeared, or about 50 ml of water was added to dissolve it. Ammonium persulfate (0.2 g) was added thereto as an initiator at ambient temperature, and the resultant mixture was stirred about 1 hour.

10 Viscosity of the thermosensitive polymer coagulant thus obtained was measured by using digital viscometer (Brookfield; DV-III ULTRA Rheocalc V 2.4; spindle:SC4-18). The result showed viscosity of 36.70 cP at 20°C.

15 [Example 1]

Coal-oil agglomerate was previously prepared according to the same condition described in Korean Patent Publication No. 2003-0031796. To concentrated sewage sludge, added were chitosan-NIPAM thermosensitive polymer coagulant obtained from
20 Preparation Example 1 and a commercially available cation coagulant (CP700: molecular weight of about 7,000,000), respectively, as thermosensitive polymer coagulant, and the mixtures were stirred for about 10 minutes while maintaining the temperature condition of ambient temperature or 36°C. Same

amount of coal-oil agglomerate was then added to each mixture, and they were stirred at about 300 rpm for about 5 minutes. After separating by filtration through a 60 mesh sieve, the products from each mixture were examined. The coagulation on
5 the sieve was taken after about 5 minutes and analyzed in terms of moisture content and ash content. The dehydrated solution under the sieve was analyzed by COD (chemical oxygen demand), which was compared with that of the sewage sludge before treatment to calculate the recovery(%) of organic
10 substances.

As a result, dehydrating effect was noticeably enhanced when the thermosensitive coagulant according to the present invention worked under the condition of forming hydrophobic coagulation, as well as exhibiting higher moisture absorption
15 and COD. On the other hand, the results showed poor formation of coagulation under hydrophilic condition to give lower coagulation effect. The thermosensitive coagulant according to the invention also showed higher dehydration effect as compared to conventional coagulant CP700 (which is
20 commercially available), as well as better effect of recovery of organic substances and purification of ashes.

[Table 1] Dehydration effect of chitosan-NIPAM thermosensitive polymer coagulant (as compared to CP700)

Coagulant	Temperature (°C)	Moisture content (%)	Ash (%)	COD (ppm)	Recovery of organic substances (%)
Chitosan-NIPAM thermosensitive coagulant	Ambient	72.4	4.36	2,849	50.55
	36	51.1	5.08	122	97.81
CP700	Ambient	69.5	5.11	189	96.83
	36	71.7	4.94	212	96.42

[Example 2]

At 36°C, the chitosan-NIPAM thermosensitive polymer coagulant according to the invention was subjected to experiments with different load on the basis of suspended solids (SS). As a result, if the amount of the coagulant (based on SS) was less than 3%, insufficient formation of coagulation occurred to lower the efficiency. Under the condition of higher amount of the coagulant, no significant difference was found in coagulating effect. The results are shown in Table 2.

[Table 2] Effect of coagulation depending on the load of chitosan-NIPAM thermosensitive polymer coagulant

Amount of coagulant SS (%)	Moisture content (%)	Ash (%)	COD (ppm)	Recovery of organic substance (%)
1	69.4	5.23	2,342	60.53
3	54.3	5.65	179	96.95
5	51.5	5.14	122	98.82
7	51.4	5.38	146	98.43

【Industrial Applicability】

Chitosan-NIPAM thermosensitive polymer coagulant according to the invention can be advantageously used in

sewage treatment plant in order to coagulate and dehydrate sewage sludge, thereby facilitating the treatment of the sludge via incineration with reduced cost and increased efficiency.

【CLAIMS】**【Claim 1】**

A process for preparing chitosan-NIPAM thermosensitive polymer coagulant, which comprises

- 5 (a) dissolving chitosan and N-isopropylacrylamide in aqueous acetic acid; and
- (b) incorporating redox initiator to the solution in aqueous acetic acid, and carrying out polymerization.

【Claim 2】

- 10 The process for preparing chitosan-NIPAM thermosensitive polymer coagulant according to claim 1, which further comprises adding tetramethylethylenediamine as reaction catalyst.

【Claim 3】

- 15 Chitosan-NIPAM thermosensitive polymer coagulant which is prepared according to the process of claim 2, wherein the process further comprises incorporating acetic acid or additional amount of water after adding tetramethylethylene diamine in order to dissolve the precipitate.

20 **【Claim 4】**

Chitosan-NIPAM thermosensitive polymer coagulant prepared according to the polymerization process of claim 1, by incorporating 5~1000 parts by weight of N-isopropylacrylamide, 0.5~30 parts by weight of tetramethylethylenediamine, and

0.1~10 parts by weight of ammonium persulfate as reaction initiator to 100 parts by weight of chitosan at ambient temperature, and stirring the resultant mixture at the same temperature for 0.5~6 hours.

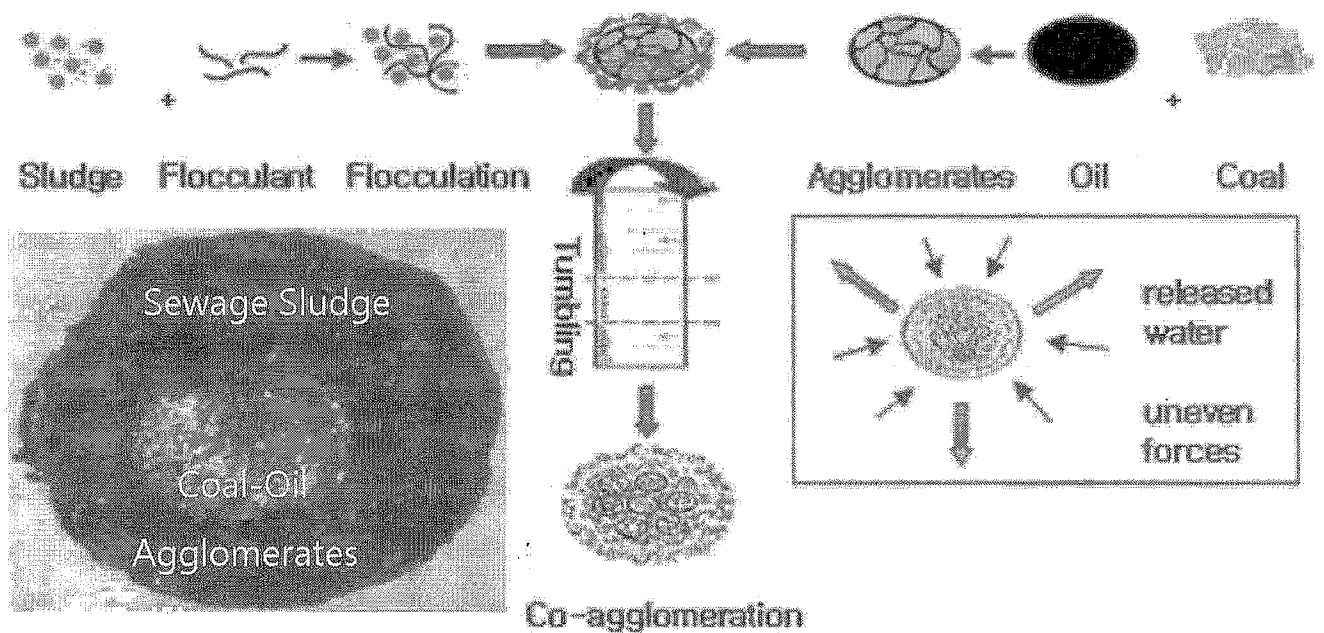
5 **【Claim 5】**

Chitosan-NIPAM thermosensitive polymer coagulant which essentially comprises chitosan and N-isopropylacrylamide.

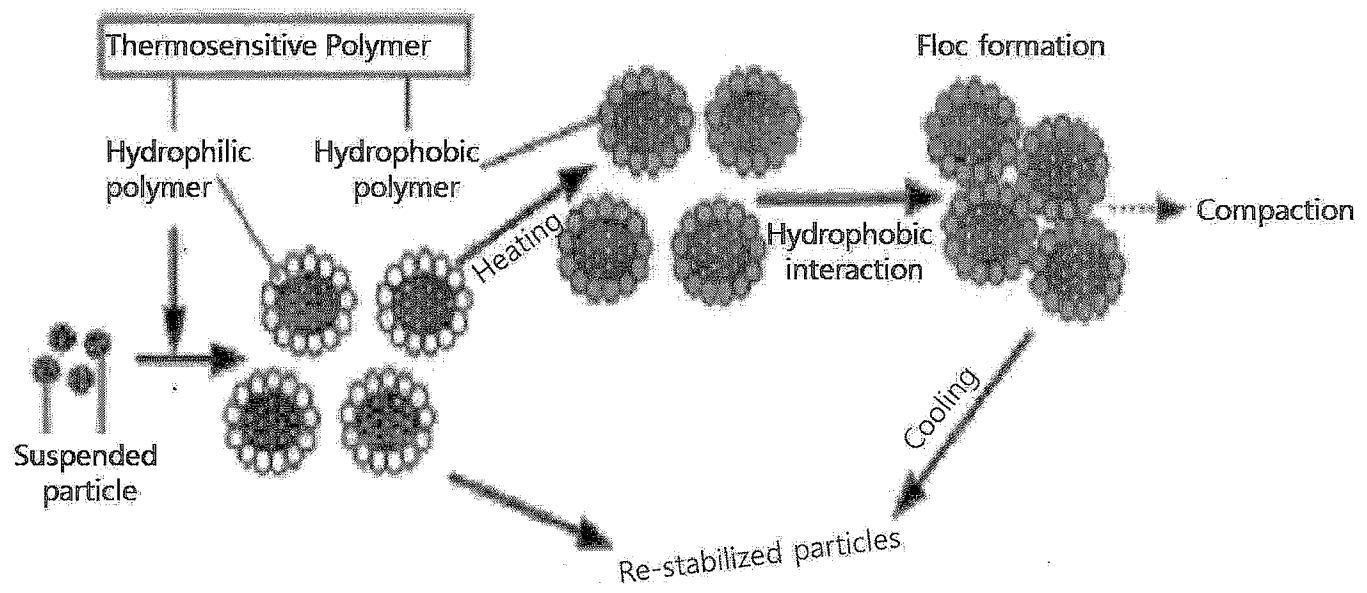
【Claim 6】

10 The chitosan-NIPAM thermosensitive polymer coagulant according to claim 5, which is prepared by polymerization of chitosan and N-isopropylacrylamide in a ratio of 5~95:95~5 (w/w).

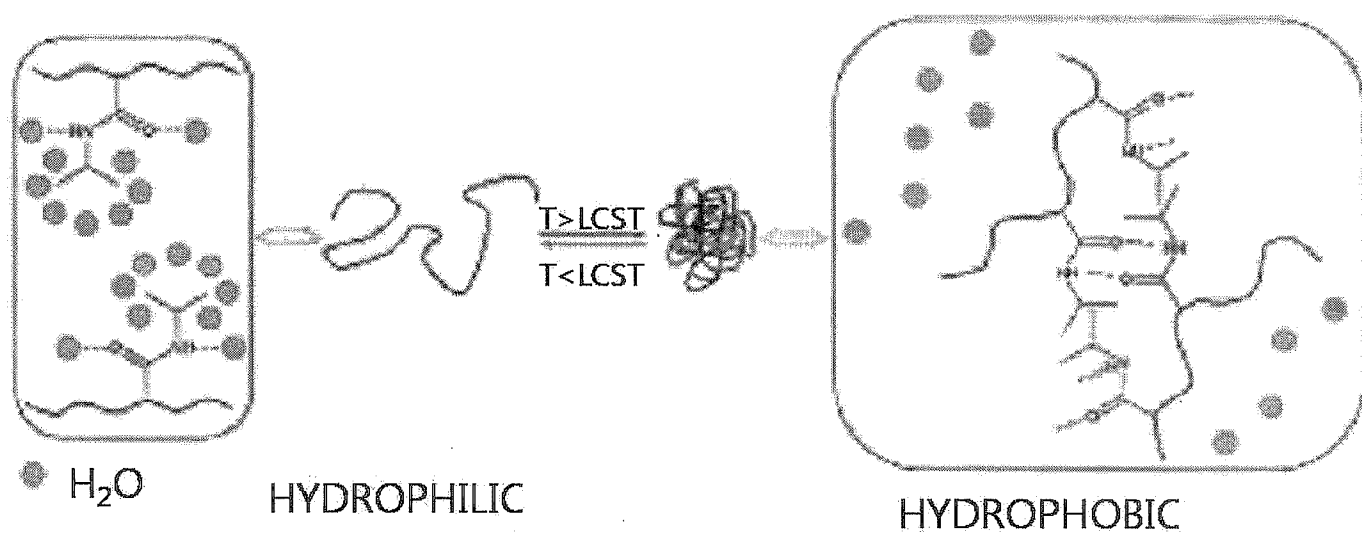
[Fig. 1]



[Fig. 2]



[Fig. 3]



A. CLASSIFICATION OF SUBJECT MATTER*C08L 5/08(2006.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : C08L 5/08

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

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

eKOMPASS(KIPO internal) & keywords: chitosan, acrylamide, coagulant, flocculant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1236748 A 1 (ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE) 04 Sep. 2002 See the abstract; and the claims.	1-6
A	KR 10-2005-0093731 A (EYANG CHEMICAL CO., LTD.) 23 Sep. 2005 See the abstract; and the claims.	1-6
A	KR 10-1991-002358 B1 (SAM YOUNG ELECTRONICS IND. CO. et al.) 20 April 1991 See the whole document.	1-6
A	WANG, JIAN-PING et al. "A chitosan-based flocculant prepared with gamma-irradiation-induced grafting". Bioresource Technology. 2008, 99, pages 3397-3402 * See the whole document. Note: * document is available online 20 September 2007	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/KR2008/007670Patent document
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EP 1236748 A1

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None

KR 10-2005-0093731 A

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None

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20.04.1991

None