

# In Acidic Porous Medium Under the Action of Humic Acid, Rice $\text{TiO}_2$ . Migration and Retention Mechanisms

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**Abstract:** Mechanisms. mobility, retention. titanium dioxide nanoparticles ( $\text{ntio}_2$ ). Well-defined Porous Media Composite of clean quartz sand in the presence of full acid (FA) and humic acid (HA) were studied under acidic conditions.  $\text{ntio}_2$  were immobile in the porous media in the absence of FA and HA at pH 4.0. FA and HA could be adsorbed onto the surface of  $\text{ntio}_2$ , changing the electrochemical properties of  $\text{ntio}_2$ . The transport of  $\text{ntio}_2$  increased from 0.01 and 0.94 to 0.91 and 0.88 with the increase of FA and HA from 1 mg/L to 10 mg/L, respectively. Compared to FA, more HA was adsorbed onto  $\text{ntio}_2$ , and the effect of HA on the transport of  $\text{ntio}_2$  was stronger.  $\text{Ca}^{2+}$  ions inhibited the mobility of  $\text{ntio}_2$ , and the effect of  $\text{CaCl}_2$  was greater than that of NaCl in the same concentration. The mobility of  $\text{ntio}_2$  was better in the presence of HA than FA. In addition, 7% ~ 56%  $\text{ntio}_2$  was preserved in the secondary energy minimum well in the presence of HA, higher than 4% ~ 17% in the presence of FA, which could be easily released when the environmental conditions have changed. High energy barriers between  $\text{ntio}_2$  and quartz promoted the mobility of  $\text{ntio}_2$ , while a combination of the secondary minimum energy, strain, diffusion and gravitational position were involved in the retention of  $\text{ntio}_2$ .

**Keywords:** Titanium Oxide Nanoparticles; Fulvic Acid; Humic Acid; Stability; Transport

## 1. Materials and Methods

### 1.1 Material

6.2. FA Since Fluka, Use deionized water as a measurement 1g/L solution. HA Since Sigma-Aldrich, Use deionized water as a measurement 1g/L solution, with 1mol/L NaOH pH to 10.0. Quartz Sand (40-40 ~ 70  $\mu\text{m}$ ) Chemistry, chemistry, Reference Litton and Olson Fang Surface Removal Method<sup>[10]</sup>.

### 1.2 $\text{Ntio}_2$ Qualitative

Accurate weighing 250 mg  $\text{ntio}_2$  scattered in 1L deionized water, ultrasonic dispersion 4 min (JY92-IIDN ultrasound cell Mill Ningbo xin zhi the same below), made 250 mg/L  $\text{ntio}_2$  mother liquor. Placed 4 Save 48 Small". To  $\text{Ntio}_2$  mother liquor in joint different FA, HA, NaCl or  $\text{CaCl}_2$  solution with water dilute 50 mg/L of  $\text{ntio}_2$  liquid 0.1mol/L HCl pH, ultrasonic dispersion 4 min, made different conditions under  $\text{ntio}_2$  liquid (Table 1). The particle size (Zetasizer nano ZS90 Malvern) set  $\text{ntio}_2$  the particle size distribution, Zeta A and quartz sand Zeta A.

### 1.3 $\text{Ntio}_2$ FA and HA Adsorption

In and 1.2 The same conditions under set FA and HA in  $\text{ntio}_2$  surface of adsorption capacity. Will different conditions under  $\text{ntio}_2$  liquid placed 150 rpm cyclotron-bed in room temperature shock 2 h. Use more times high-speed centrifugal methods (9600g natural 20 min) will  $\text{ntio}_2$  from liquid in separation<sup>[1]</sup> supernatant 0.22 antibody

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mMembraneLiquid points in275nmAnd300nmColorimetricFAAndHAOfFAAndHAQuasi-of van in0 ~ 100 mg/L,Related Coefficient0.999.Adsorption capacity General Formula(1)Count:  
-In:QAdsorption capacity(Mg/g ),C<sub>0</sub>Initial degree(Mg/L ),C<sub>E</sub>Balance(Mg/L ),CN<sub>tio<sub>2</sub></sub>Of(Mg/L ).  
1.4 N<sub>tio<sub>2</sub></sub>Of migration

With the diameter25mm 100mmOf glass column chromatographyBoth ENDS points with apertureNatural 20 antibody mOf, Network.Every time said to take a certain amount of quartz sand slow into analysis column inBe careful TampingRepeat more times until a column chromatography.Weight legal packed column of pore body(PV ),Pore0.40 ~ 0.47.

Fill column after the specific process is as follows:( 1)With stay conditions(Table1)The backgroundSolution(Does not containN<sub>tio<sub>2</sub></sub>)BalancePacked Column; (2)Creep(BT100-2),Baoding Lattice)Accurate3PVAnd background solution same conditionsN<sub>tio<sub>2</sub></sub>Liquid; (3) 4PVBackground solution packed column; (4)The above steps beam afterThen3PVOnly containsFAOrHAOf background solution(Does not contain ion andN<sub>tio<sub>2</sub></sub>)Flushing packed column(Table1In serial number10 ~ 23 ).AllA processSolution andN<sub>tio<sub>2</sub></sub>To0.81 ~ 0.89/minSpeed bottom-up into the cylinderEffluent with self-part collector(BS-100A,Shanghai, Huxi)CollectionEffluent N<sub>tio<sub>2</sub></sub>Du yong UV spectrophotometry(Genesys 10 s uv-Vis Thermo Fisher)In wave343nmColorimetric legalQuasi-of van in0 ~ 80 mg/L,Related Coefficient0.999.EveryRepeat two timesTwo followed by poor<3%,Take one of the fruit.

## 1.5 Data Analysis Methods

### 1.5.1 ExhibitionDLVO (xdlvo)MechanismCode

DLVOMechanism count of anti-Can including two surface each other close to there of Van der gravitational energy and doubleStatic exclusion can sum<sup>[11]</sup>.M-M of Department of Van der gravitational energy( $V_{vdW_{NN}}$ )And doubleStatic exclusion force( $V_{EDL_{NN}}$ ), M-Quartz Sand Department of Van der gravitational energy( $V_{vdW_{NS}}$ )And doubleStatic exclusion force( $V_{EDL_{NS}}$ )Of a reference literature[11].

In surface adsorption humic acid of MTest In addition two kind of empty exclusion anti-of Role:Penetration and spiral<sup>[12]</sup>.Penetration is due to each other close to of cause of coincidence regional in polymer degree of increase caused Penetration exclusion can( $V_{OSM}$ )Count the literature<sup>[12 13]</sup>;Surface Adsorption of humic acid(H<D)Will cause of lossOf of repellent force( $V_{Elas}$ )Of StudentsIts a reference literature[14].

1.5.2 Colloidal MechanismColloidal ManagementFloating on the pore fluid of grain main3A mechanism and porous Mediated surface contact:Powder, interception and gravity settlement.In the world of contact efficiency $\eta_0$ Can expression<sup>[15]</sup>:

Adsorption efficiency $\alpha$ Said the most of adsorption of grain and collector of the collision of RatioAlso is phase collector Removal Efficiency $\eta$ And phase collector contact efficiency $\eta_0$ Ratio:

The parameters of specific count the literature[9].

## 2. Fruit and

### 2.1 N<sub>tio<sub>2</sub></sub>FAAndHAOf Adsorption

By1CanN<sub>tio<sub>2</sub></sub>FAThe adsorption capacity with the solution in the initialFADegree of increased and increasePH 4.0,Adsorption capacity from1 mg/L FAOf5.93 mg/gIncrease10 mg/LOf54.3 mg/g (1a). n<sub>tio<sub>2</sub></sub>Of zero6.2,AndFAInPH 2 ~ 8UnderZetaA were.SoCan inference static attractive in adsorption role to important role.In additionN<sub>tio<sub>2</sub></sub>Surface of base andFAOf of base and base of ligand pay is also important of Adsorption Mechanism<sup>[1,8]</sup>.AndFAComparedHAInN<sub>tio<sub>2</sub></sub>Surface of adsorption capacity more

9Of Ruichang such as: humic acid role under acid porous mediated in m<sub>tio<sub>2</sub></sub>Of migration and Retention 10.3%,LessHAMolecular in content28.1%.By1BCanPH 4.0 NaClAndCaCl<sub>2</sub>Of adsorption capacity were no influence

Same ion of underHAInN<sub>tio<sub>2</sub></sub>Surface of adsorption capacityFA

### 2.2 FAAndHARole UnderN<sub>tio<sub>2</sub></sub>Of of and aggregation Characteristics

Adsorption inN<sub>tio<sub>2</sub></sub>Surface of humic acid will influence mAnd M of each other roleTo influence m grain in Liquid in qualitative.M of qualitative is influence its migration and settlement line of the Factors.The conditions underN<sub>tio<sub>2</sub></sub>

ZetaA such2Shown in.By2aWe can know thatPH 4.0,Does not exist

FAN<sub>tio<sub>2</sub></sub>OfZetaA+ 33. 0mV,There1 mg/l fa zetaA drop+ 15. 9mV; faOf2 mg/L zeta

A positive-13. 3mV;WhenFAOf10 mg/L n<sub>tio<sub>2</sub></sub>OfZetaA drop-34.7mV.HA n<sub>tio<sub>2</sub></sub>And Quartz SandZetaA of influence andFASimilar(2B ).Different of isPH 4.0,BecauseHAInN<sub>tio<sub>2</sub></sub>Surface adsorption capacity greaterMake N<sub>tio<sub>2</sub></sub>OfZetaYuzheng'sHaDu 0.8 mg/L,LessFaThe degree1.5 mg/L;Low, low(<2 mg/L), haExistenceN<sub>tio<sub>2</sub></sub>OfZetaBit lessFaBits of existence(Bigger).Influence of humic acidN<sub>tio<sub>2</sub></sub>OfZetaThe mechanism3.Aspects(1)Adsorbed onN<sub>tio<sub>2</sub></sub>Base in surface humic acid molecule, neutralizing positive charge on Particle Surface,ZetaBit drop(2) n<sub>tio<sub>2</sub></sub>.The coordination between the base group on the surface and humic acid decreased.,Possible dropN<sub>tio<sub>2</sub></sub>.Positive surface charge<sup>[8,17]</sup>(3)The organic anion of humic acid can increase the charge density on the grain surface.,Section location, off-grain surface,Will also be reducedN<sub>tio<sub>2</sub></sub>Of ZetaBit<sup>[8,18]</sup>.

By2cCan, 5 mg/L FA,PH 4.0 n<sub>tio<sub>2</sub></sub>OfZeta

Position along the solution NaCl The degree of rise and rise (Jiang), By 5 mmol/L NaCl of -33. 6mV Sheng Gao Zhi 50 mmol/L NaCl of -22. 5mV, The charge shielding effect and double effect are NaCl Cause Zeta The main cause Yin<sup>[1,19]</sup>. Same PH and NaCl Du, With Fa Compare, Ha Under existing conditions Nt<sub>2</sub>O<sub>2</sub> Of Zeta Bit, bigger (2d). In addition to the charge shielding effect and double effect, CA<sup>2-</sup> Nt<sub>2</sub>O<sub>2</sub>. SURFACE ADSORBED Fa The role of certain sets in the molecule also lowers the particle size Surface Charge (Zeta Bit elevation)<sup>[20,21]</sup>. Therefore, Same degree CaCl<sub>2</sub>. Zeta The Influence of BIT is greater NaCl (2E).

Same as literature, Road<sup>[1,20]</sup>, Static and repulsive forces of the presence of charged quartz sand and Humic Acid, Can the adsorption capacity of humic acid on quartz sand be ignored? Therefore, Humic Acid quartz sand in Solution Zeta No influence (3AB). But NaCl With CaCl<sub>2</sub> Of Presence lowers Quartz Sand Zeta Bit (Zeta Bit elevation), And CaCl<sub>2</sub>. The role of more (3def).

Table 1. Shown, Under all conditions Nt<sub>2</sub>O<sub>2</sub>. Integrated homogenized particle size greater 400nm Of aggregates. Product Metal Oxide m of usually to powder of form In water with liquid after don't is original m grain of there But students gathered generation da ju collective<sup>[22]</sup>. Counted among the conditions under Nt<sub>2</sub>O<sub>2</sub> Of XDLVO Anti-

Can in 2.4 ~ 40.4kT. Usually Greater 20kT Can prevent grain for collision and students Aggregation<sup>[23]</sup>. [And Research Product Nt<sub>2</sub>O<sub>2</sub> Dispersion in ultra-water after forming flat Particle Size 1430nm Of da ju collective Ultrasound 10 min After can will da ju collective damage generation average particle size 521nm Of aggregates But the ultrasound or join Na<sub>3</sub>PO<sub>4</sub>, Twelve-based sulfonic acid or C and scattered can't dispersion aggregates reduce aggregation Particle Size<sup>[22]</sup>. So In high (> 20KT) Also can't dispersion generation of aggregates But low of aggregates step Aggregation. For example PH 4.0, 1 mg/L FA Conditions under XDLVO Anti-can

### 2.3 Fa And Ha Under the Action Nt<sub>2</sub>O<sub>2</sub> Migration

Different Humic Acids Nt<sub>2</sub>O<sub>2</sub>. The penetrating song, 3. Shown. Does not exist Fa, Because Nt<sub>2</sub>O<sub>2</sub>. With Quartz Sand Surface Zeta The opposite, Quiet, attractive Nt<sub>2</sub>O<sub>2</sub>. All stranded in porous media, column. PH 4.0, Fa Du 1 mg/L, nt<sub>2</sub>O<sub>2</sub>. Surface Zeta Bit still, positive (2), nt<sub>2</sub>O<sub>2</sub>. Almost all stay in porous media, column, Outflow rate 0.01, xdlvo It's an elephant, None under this condition Existence (4). When Fa Degree, rise Nt<sub>2</sub>O<sub>2</sub>. Surface Zeta Bit, Its reaction to quartz sand > 150kt Of, Table, exclusion, Not good Nt<sub>2</sub>O<sub>2</sub>. Settling into porous medium<sup>[4]</sup> Nt<sub>2</sub>O<sub>2</sub>. Rising outflow rate, By 2 mg/L FA Of 0.53 Add To 10 mg/10f 0.91. 1 ~ 10 mg/l ha, nt<sub>2</sub>O<sub>2</sub>. Outflow rate 88% ~ 94%, Higher than the same, degrees Fa Under the Action Nt<sub>2</sub>O<sub>2</sub>. Outflow rate.

Bundle after increase 7 ~ 10pv Flushing process of background solution without ion, Reduced degree of ion retention in porous media Nt<sub>2</sub>O<sub>2</sub>. Line. A lot of research, When pore water ionicity, zero, Because double, The second minimum, the energy zone disappears, Settlement in the second minimum, energy area and quartz sand, not solid

Rice, Grain Weight<sup>[24]</sup>, 7 ~ 10pv The re-release process can be put 4% ~ 17% (Zhan Nt<sub>2</sub>O<sub>2</sub>. Quantity) Of Nt<sub>2</sub>O<sub>2</sub>.

With Fa Compare, Ha With a greater molecular weight and a more complex space

Construction, The empty will play a bigger role<sup>[16]</sup>, So in NaCl Same degree, Ha Under the Action Nt<sub>2</sub>O<sub>2</sub>. The migration, Settling in the second minimum, the energy area, the grain size is more (7% ~ 56%). If the grain is deposited in the second minimum, the energy region, the grain is considered as a potential migration. So 5 mg/l ha Existence, NaCl Toyoo 5 mmol/L Add 50 mmol/L, nt<sub>2</sub>O<sub>2</sub>. The potential migration is just a slight decline, Outflow rate (0 ~ 0 ~ 10pv) By 0.87 Drop 0.78, In this study, Although Nt<sub>2</sub>O<sub>2</sub>. The reverse energy of quartz sand > 150kt, There's still a lot Nt<sub>2</sub>O<sub>2</sub>. Stranded in porous media. For example, PH 4.0, 5 mg/L FA, 25 mmol/L NaCl Under existing conditions 187kt, But Nt<sub>2</sub>O<sub>2</sub>. Outflow rate 0.17. Ming except grain-Suke Xdlvo Anti-Energy, Has its Caused by a resistance effect of reasons: (1) Mediated surface adsorption site yin neng And of the existence of exclusion can<sup>[4,25]</sup>. This study conditions under The decrease caused by the decrease of the sedimentation rate of rice and Grain<sup>[25]</sup> (2) The attraction of hysteresis particles and dielectric particles and the rejection of grains cannot be rereleased without the same particles remaining in the medium.<sup>[26]</sup> Steric Effect, And Pierce out, trailing, like, Therefore, Retention, grain surface, with the increase of pore body, Outflow rate increased (Re-release is the main reason causing the steric effect. Blocking is in 3, 5). The first reason is mainly in grain- There is a small pore in the direction of the water absorption flow, and the particles can not be connected.

By table 1. You can see, Under most conditions Nt<sub>2</sub>O<sub>2</sub>. Aggregate size 595nm. Even if the average aggregation size is less, Due to aggregation Particle Size Distribution, The particle size of some aggregates has exceeded. Such The pH 4.0, 5 mg/L FA Under Conditions, 32.3% Of Nt<sub>2</sub>O<sub>2</sub>. Aggregate size greater 595nm (6). So, The blocking effect in this study is Nt<sub>2</sub>O<sub>2</sub>. An important mechanism of retention in quartz sand column. Also, Xu 100 1000 Particle Size (Nm) 6 pH 4.0, 5 mg/L FA, 0.1 mmol/L NaCl Under Conditions Nt<sub>2</sub>O<sub>2</sub>. Of Particle Size Distribution

Colloid, mechanism, commonly used in solution, colloid in porous media, RETENTION MECHANISM OF PARTICLES<sup>[15,29]</sup>. According to the conditions  $\eta_D, \eta_1, \eta_G, \eta_0$  And Alpha Equal Parameter table 1. Alpha < 1 Shows a certain amount Nt<sub>2</sub>O<sub>2</sub>. Migrate from Column. On the body, Alpha With PH and humic acid degrees rise

With NaCl With CaCl<sub>2</sub>. Reduce, Yu Zhong Nt<sub>2</sub>O<sub>2</sub>. Consistent outflow rate. Under all conditions,  $\eta_D$  Zhan  $\eta_0$  Of 42% ~ 83%.  $\eta_D$  With the liquid in Nt<sub>2</sub>O<sub>2</sub>. The aggregation size, Such Nt<sub>2</sub>O<sub>2</sub>. Aggregate

size 860 nm,  $\eta_D$  3.4 × 10<sup>-2</sup>; When  $\text{TiO}_2$  Particle size reduced 434 nm,  $\eta_D$  Grow 5.9 × 10<sup>-2</sup>. Research, Scattered is particle size less 100 nm. The most important sedimentation mechanism of particles in porous media<sup>[29-30]</sup>. Because of  $\text{TiO}_2$ . Large particle size, Gravity subsidence plays a very important role.,  $\eta_C$  Zhan,  $\eta$  Of 17% ~ 58%.  $\eta_D$  Contrary,  $\eta_C$  Increases with increasing particle size. For example, Liquid Medium  $\text{CaCl}_2$  Toyoo 0.5 mmol/L ( $\text{TiO}_2$  Aggregate size 450 nm) Add 5 mmol/L ( $\text{TiO}_2$  Poly SET SIZE 718 nm),  $\eta_C$  Added 2.6 Times. Under Various Conditions,  $\eta_D$  Zhan,  $\eta$  The ratio is less 0.2%, Can ignore?. In the porous medium, small  $\text{TiO}_2$ , Dispersion is the main Settlement Mechanism, And in the aggregate size, large, grain, Gravity subsidence is the main sink Drop Mechanism.

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