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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

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学位論文題目：
Title of Dissertation　　Energy Saving Technology Development for the Treatment of Reverse Osmosis Concentrate Using a Rotating Advanced Oxidation Contactor （回転円板型促進酸化装置を用いた逆浸透濃縮排水の省エネルギー型処理技術の開発）

学位論文要約：
Dissertation Summary

Reverse osmosis is a well-established and widely used technology for wastewater reclamation. With the purification of the treated wastewater, the RO process produces a concentrate which reported to be about 15–20 % of the influent volume. The RO concentrate contains concentrated levels of rejected pollutants originating from the source water. The emerging pollutants persistent in wastewater, such as pharmaceuticals and personal care products (PPCPs), have raised awareness of the environmental risk of the direct discharge of the RO concentrate. Recent developments in analytical technology have allowed a wide range of PPCPs to be detected in environmental water samples. Some of the PPCPs have been reported to cause toxic effects in the environment at concentrations of micrograms per litre and there is concern that the presence of these chemicals in the environment could cause drug resistant bacteria to develop. Many pharmaceuticals used to treat humans and livestock are excreted in urines and feces, and various pharmaceuticals have been found in sewage effluent, which is a potential source water of RO concentrate. There is therefore an urgent need for advanced treatment technologies to be developed to allow PPCPs to be removed for the aquatic environment protection. In addition, with the increase in global water demand, the scale of RO plants has been getting larger for several decades. Therefore, it is necessary to develop suitable technology to treat RO concentrate before discharging into receiving water or recycling for other purposes.

In a number of recent studies, TiO_2 photocatalysis has been used to treat pharmaceuticals in wastewater. The nonselective oxidation ability of hydroxyl radicals enables effective degradation of various organic pollutants. However, the photocatalysis of target compounds can be inhibited by coexisting materials, such as inorganic ions and organic matter, in the wastewater. In addition, toxic intermediates may be produced during photocatalysis, and the effects of pharmaceutical degradation products in the environment are of concern. Furthermore, when TiO_2 or nano-TiO_2 powder in water is exposed to ultraviolet (UV) radiation, radicals that are harmful to aquatic organisms are produced. Therefore, the effective recovery of catalyst powder after wastewater treatment should be taken into consideration. Wastewater treatment frequently involves adsorption processes, and various types of adsorbents have been developed to remove different pollutants. However, after adsorption, the contaminants are permanently transferred to the sorbent and not destroyed, which can lead to problems with saturation of the adsorbent. In addition, attempts have been made to synthesize TiO_2-adsorbent composites that allow both photocatalysis and adsorption processes to work to treat pharmaceuticals in wastewater

In this thesis, the removal of organic matters especially PPCPs in RO concentrate from a ultrafiltration/RO system of the municipal wastewater reclamation facility has been researched by using coagulation and a laboratory-scale RAOC equipped with TiO_2-zeolite composite sheets. Crotamiton is a scabicide and antipruritic agent that has frequently been detected in sewage effluent in Japan because of its stable nature and wide consumption. Like many other advanced oxidation processes, TiO_2 photocatalysis is generally considered to be high cost and energy intensive, and therefore, it is more suitable to integrate these processes with an appropriate pretreatment process to make the treatment more feasible for application. Coagulation is an effective pretreatment because it not only removes large molecular weight organic matter, but it also improves UV transmittance, which is beneficial for TiO_2 photocatalysis.

The immobilization of powder materials into the composite sheet effectively solves the problem of the catalyst and adsorbent recovery after treatment, and the development of the RAOC reactor makes the composite material more feasible for practical application. In addition, the photocatalytic decomposition process makes it possible to regenerate the adsorbent during treatment. To develop an energy saving treatment scheme, coagulation pretreatment was applied for the solar irradiated RAOC treatment of the RO concentrate. The treatment performances of powdered TiO_2-zeolite composite and sole TiO_2-zeolite composite sheet were investigated to reveal the mechanism of crotamiton removal in practical water matrix. The effect of the water matrix on removing crotamiton using different materials is discussed. Meanwhile, the behavior of the main degradation intermediates was monitored to clarify the treatment mechanism. To achieve a more energy saving treatment scheme, the applicability of solar irradiation was discussed for the sequence of the TiO_2-zeolite composite sheet-coupled RAOC with the coagulation pretreatment. And as an indispensable step for the development of a water treatment technology, the energy consumption of the proposed treatment for RO concentrate was evaluated.

Firstly, in this thesis, the synthesized TiO_2-high silica zeolite (HSZ-385) composites powder had been applied for the treatment of crotamiton, a scabicide and antipruritic agent persistent during biological treatment processes and frequently detected in secondary effluent in Japan, potential source water of wastewater reclamation plants. Titanium dioxide (TiO_2) and high-silica zeolite (HSZ-385) composites were synthesized and applied for the treatment of crotamiton in secondary effluent. Crotamiton was rapidly adsorbed by HSZ-385, and the adsorption performance of crotamiton in the secondary effluent was quite close to that in the test using ultrapure water. Even though the TiO_2–zeolite composites showed lower adsorption rates than that of HSZ-385, similar crotamiton adsorption capacities were revealed using both test materials. The photocatalytic decomposition of crotamiton was significantly inhibited by the water matrix at low initial concentrations. The TiO_2–zeolite composites rapidly adsorbed crotamiton from secondary effluent, and then the crotamiton was gradually decomposed under UV irradiation. Importantly, when using TiO_2–zeolite composites, coexisting material in the secondary effluent did not markedly inhibit crotamiton removal at low initial crotamiton concentration. The behaviors of the main intermediates during treatment demonstrated that the main degradation intermediates of crotamiton were also captured by the composites.

Secondly, the two powdered materials TiO_2 and HSZ-385 have been effectively immobilized into a paper-like composite sheet, which is easy to handle and to recover the photocatalyst and adsorbent during the treatment process. The removal of the antipruritic agent crotamiton from RO concentrate was studied using the TiO_2/zeolite composite sheet. The effect of coexisting matters in the wastewater matrix on inhibition of the crotamiton degradation was evaluated. In addition, the behavior of crotamiton degradation intermediates during the photocatalysis was investigated. Excellent adsorption performance of crotamiton by the TiO_2/zeolite composite sheet has been found without obvious inhibition by other components in the RO concentrate. With application of UV irradiation, crotamiton was simultaneously removed by adsorption and photocatalysis. The photocatalytic decomposition of crotamiton in the RO concentrate was significantly inhibited by the water matrix at high initial crotamiton concentrations, whereas rapid decomposition was realized at low initial crotamiton concentrations. In addition, the behavior of crotamiton degradation intermediates during the photocatalysis was investigated. The peak area for main crotamiton degradation intermediates P219 was higher in the composite sheet during treatment than that in the aqueous phase when using the HSZ-385/P25 composite sheet. Even if the efficiency of desorption of the intermediates from the sheet could not be confirmed without the standard of every detected intermediate, the high peak areas for the intermediates provide direct evidence of the adsorption of intermediates on the composite sheet. In conclusion, the HSZ-385/P25 composite sheet is effective not only for removing crotamiton, but also for adsorbing degradation intermediates produced by photocatalysis. This provides a mechanism to mitigate the negative impact on the environment of harmful degradation intermediates produced by advanced oxidation processes. What's more, the cyclic use of the HSZ-385/P25 composite sheet had also been checked. The efficiency of removing crotamiton from RO concentrate achieved by the HSZ-385/P25 composite sheet after 24 hr ultraviolet irradiation in three circles of reuse were all over 95%. The crotamiton amount in the composite sheet after three cycles of reuse was 0.40 mg, which was ca. 27% of the total amount of three cycles of treated crotamiton, demonstrating continuous crotamiton photocatalytic degradation. The TOC removal efficiency slightly decreased with an increase in the cycles of reuse. It can be concluded that the HSZ-385/P25 composite sheet is feasible for the cyclic removal of crotamiton in RO concentrate.

Furthermore, a novel rotating advanced oxidation contactor (RAOC) equipped with the composite TiO_2-zeolite sheet was used for the treatment of RO concentrate. The removal of organic matters was studied as well as the variation of biodegradability of the reverse osmosis concentrates. We analyzed the concentration of various kinds of PPCPs in the raw RO concentrate and the removal efficiency of PPCPs under the RAOC treatment was revealed. With or without UV irradiation, the adsorption and photocatalytic decomposition of the organic matters was indicated through the variation of the BOD_5/COD_{Cr} ratio, A_{365} and $SUVA_{254}$. It was found that the RAOC reactor is effective for the removal of PPCPs and the improvement of the biodegradability of the RO concentrate. And judging from the improved biodegradability, after a short time UV applied RAOC treatment, the residual organic matters in the RO concentrate might be easily removed by a post biological process.

Next, removing the antipruritic agent crotamiton from RO concentrate using the RAOC with or without coagulation pretreatment process have been studied. The polyaluminum chloride (PAC) coagulation was applied as a pretreatment process of the RO concentrate. In terms of the TOC, COD_{Cr}, A_{365} and A_{254} variations, the coagulation performance was assessed and the optimum operation conditions were confirmed. The adsorption and photocatalytic decomposition of crotamiton using the RAOC was investigated, and the effect of coexisting matters in the RO concentrate was discussed. The behaviors of the main degradation intermediates of crotamiton during RAOC treatment were also monitored. Coagulation followed by the RAOC process was effective in the removal of the organic matter in the RO concentrate as well as the photocatalytic degradation of crotamiton. The effect of the coagulation on the removal of crotamiton was indicated by the performances of the tests with or without coagulation pretreatment.

Last but not the least, based on all the above mentioned research, a simple treatment scheme of the combination of coagulation and a solar light irradiated RAOC equipped with TiO_2-zeolite composite sheets was proposed for the removal of organic matters in the RO concentrate. Since the RO concentrate from the secondary effluent reclamation plants have already gone through the effective biological treatment in wastewater treatment facilities and some other treatment processes, the organic matters contained in the RO concentrate are usually recalcitrant to biological treatment. Through advanced oxidation treatment, these organics can be mineralized and then the assimilable organic carbon can be produced. In addition, it was reported that photocatalytic oxidation coupling pretreatment of coagulation could be a synergistic treatment process specifically for the treatment of RO concentrate. The coagulation pretreatment improved the removal performance of organic matters by the RAOC from the RO concentrate. With the improved biodegradability after a few hours RAOC photocatalytic decomposition, it is possible to introduce a post biological treatment to further remove the residual organic matters in the RO concentrate. The energy consumption and economic cost were assessed during the treatment of RAOC. The applicability of solar light for the treatment in the treatment scheme largely reduced the economic cost. With the improved biodegradability after a partial oxidation by RAOC with coagulation process, it might be possible to introduce a post biological treatment to further remove the residual organic matters.

For the future research, full-scale or pilot scale studies integrating coagulation pretreatment, the solar light irradiated RAOC as well as a post biological treatment are necessary for a more realistic evaluation of the combined process even though biodegradability tests provide useful information for the effect of coagulation pre-treatment and RAOC treatment on subsequent biological degradation of RO concentrate.