A metal doped catalyst

Technical Field

The present invention relates to a metal doped catalyst and a method of preparing the same. In particular, the metal doped catalyst is a metal doped PAC catalyst.

Background

Industrial wastewater such as wastewater from food, pulp and paper, textile, cork boiling, petrochemical and pharmaceutical industries could contain high levels of toxic organic compounds and persistent micropollutants. Discharge of inadequately treated industrial wastewater could cause chemical pollution and ecotoxicity to receiving water bodies. Recently, the discharge of industrial wastewater is regulated by more stringent and specific guidelines. Achieving low chemical oxygen demand (COD) in industrial treated effluent is therefore desirable to increase the water recovery as well as to meet stringent discharge standard.

Some examples of wastewater treatment include biological methods, adsorption on activated carbon, reverse osmosis, separation by membranes, ozonation, photocatalysis, photo-Fenton, UV radiation, just to name a few. Thermal treatment at high temperature, although effective, is not economically feasible. Chemical treatments are not resolving as they require a post-treatment. Advanced oxidation processes (AOPs) are frequently selected as a water treatment option to remove refractory and toxic organic compounds present in water, however, the traditional AOPs, including photocatalysis and photo-Fenton can hardly meet the requirements of the practical applications, because the high cost and the low mineralization efficiency.

Heterogeneous catalytic ozonation has been attracting increasing interest due to its potentially higher effectiveness in the degradation, and mineralization of refractory organic pollutants and lower negative effect on water quality. So far, metal oxides and metal or metal oxides on supports have been reported as effective catalysts for ozonation processes. Heterogeneous catalysts with higher stability and lower loss can improve the efficiency of ozone decomposition, and be recycled and reused without further treatment. However, the current catalysts used for heterogeneous catalytic ozonation have low performance stability and cannot be recovered easily.

There is therefore a need for an improved catalyst for use in catalytic ozonation.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved catalyst for use in catalytic ozonation.

In general terms, the invention relates to a metal doped PAC catalyst. The catalyst of the present invention has many advantages, such as effective recovery following its use in catalytic ozonation processes and enhanced ozonation performance when the catalyst is utilised. The invention also relates to a method of making the metal doped PAC catalyst, as well as a catalytic ozonation system utilising the catalyst.

According to a first aspect, the present invention provides a metal doped powdered activated carbon (PAC) catalyst for catalytic ozonation. The catalyst may be a monometallic or a bimetallic doped PAC catalyst.

The metal comprised in the PAC catalyst may be any suitable metal. For example, the metal may be, but not limited to: iron (Fe), manganese (Mn), copper (Cu), magnesium (Mg), nickel (Ni), cobalt (Co), or a combination thereof.

According to a particular aspect, when the metal doped PAC catalyst is a bimetallic doped PAC catalyst, the catalyst may comprise, but not limited to: Fe-Mn, Fe-Ni, Fe-Co, Ni-Cu, Mn-Co, Mg-Cu, Mg-Ni, or Fe-Cu.

The catalyst may have any suitable size. For example, the catalyst may have an average size of 1-150 mm.

The catalyst may have any suitable form. For example, the catalyst may be in the form of a pellet.

According to a second aspect, the present invention provides a method of forming the catalyst according to the first aspect, the method comprising:

- mixing a metal ion solution in an acidic solvent to form a first mixture;
- adding powdered activated carbon (PAC) to the first mixture to form a second mixture;
- adding an organic solvent to the second mixture to form a xerogel;
- drying the xerogel; and
- calcinating the xerogel to form the metal-doped PAC catalyst.

The acidic solvent may be any suitable acidic solvent. For example, the acidic solvent may be, but not limited to: citric acid, acetic acid, formic acid, oxalic acid, propionic acid, lactic acid, or a combination thereof.

According to a particular aspect, the method may further comprise ultrasonicating the second mixture prior to the adding an organic solvent.

The organic solvent used for forming the xerogel may be any suitable organic solvent. For example, the organic solvent may be, but not limited to: ethylene glycol, glycerol, isopropanol, 1,2-propane diol, triethylene glycol, polyethylene glycol, or a combination thereof.

The calcinating may be carried out at a suitable temperature. For example, the calcinating may be carried out at a temperature of 400-800°C.

According to a particular aspect, the method may further comprise pelletizing the catalyst to form a pellet.

According to a third aspect of the present invention, there is provided a catalytic ozonation system for wastewater treatment comprising:

- a wastewater inlet for receiving wastewater;
- an ozone inlet for receiving ozone gas;
- an ozone reactor for catalytic ozonation of wastewater, the ozone reactor in fluid communication with the wastewater inlet and the ozone inlet, wherein the ozone reactor is loaded with the catalyst according to the first aspect of the present invention; and
- a water outlet for discharging treated wastewater.

The system may further comprise a microbubble generator in fluid communication with the ozone inlet for forming ozone microbubbles.

There is also provided a method for catalytic ozonation comprising ozonising wastewater over the catalyst according to the first aspect of the present invention.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of a system for catalytic ozonation according to one embodiment of the present invention;

Figure 2 shows the x-ray diffraction (XRD) pattern of granulated activated carbon (GAC), powdered activated carbon (PAC), Fe-Mn doped GAC and Fe-Mn doped PAC catalysts;

Figure 3 shows the scanning electron microscope (SEM) images of (a) GAC, (b) PAC, (c) Fe-Mn doped GAC and (d) Fe-Mn doped PAC;

Figure 4 shows the energy dispersive X-ray (EDX) analysis results of (a) GAC, (b) PAC, (c) Fe-Mn doped GAC and (d) Fe-Mn doped PAC;

Figure 5 shows the chemical oxygen demand (COD) removal in reverse osmosis concentrate (ROC) with different ozonation processes;

Figure 6 shows the COD removal in ROC with different catalysts;

Figure 7 shows the COD removal in ROC with microbubble ozonation using Fe-Mn doped PAC pellet catalyst according to one embodiment of the present invention for six consecutive batch runs;

Figure 8 shows COD removal in ROC with microbubble ozonation using Fe-Mn doped GAC pellet catalyst for six consecutive batch runs; and

Figure 9 shows the influent and effluent COD levels in ROC during continuous operation of microbubble ozonation using Fe-Mn doped PAC pellet catalyst.

Detailed Description

As explained above, there is a need for an improved catalyst, particularly for use in catalytic ozonation.

In general terms, the present invention provides a catalyst which may be particularly suitable for use in catalytic ozonation. In particular, the catalyst of the present invention may have a high surface area and high performance stability. With a higher surface area, the catalyst of the present invention may have a faster oxidation rate. Further, the catalyst may be easily separated, thereby making it easier for catalyst recovery. This contributes to lowering the cost of catalytic ozonation, therefore being more cost effective.

The present invention also provides a system for catalytic ozonation, particularly for use in the treatment of wastewater, such as industrial wastewater. The system may utilise the catalyst of the present invention. The system may be retrofitted into an existing treatment train to enhance biodegradability of industrial wastewater. Alternatively, the system may be adopted as a standalone tertiary treatment to remove remaining recalcitrant chemical oxygen demand (COD).

There is also provided an improved method of catalytic ozonation using the catalyst of the present invention. The catalytic ozonation results in lower COD in various types of industrial wastewater. Further, the method of the present invention may have a high ozone mass transfer rate, and accordingly, a low ozone dose to COD removed ratio. This makes the method of the present invention more cost-effective as compared to a conventional ozonation process.

The present invention may be suitable for treating reverse osmosis concentrate (ROC) with high total dissolved solid and low biodegradability. The method of the present invention may effectively remove organics present in ROC to achieve a final COD below 50 mg/L to meet wastewater COD discharge standards adopted in many countries. The present invention may also be a pre-treatment solution for high organic loading wastewaters, and may achieve effective phenol removal and biodegradability enhancement in phenolic wastewater.

According to a first aspect, the present invention provides a metal doped powdered activated carbon (PAC) catalyst. The catalyst may be for any suitable use, such as for catalytic ozonation. In particular, the catalyst may be for use in heterogeneous catalytic ozonation.

The metal comprised in the PAC catalyst may be any suitable metal. For example, the metal may be, but not limited to: iron (Fe), manganese (Mn), copper (Cu), magnesium (Mg), nickel (Ni), cobalt (Co), or a combination thereof.

According to a particular aspect, the catalyst may be a monometallic or a bimetallic doped PAC catalyst. The monometallic doped PAC catalyst may comprise any suitable metal. For example, the metal may be as described above.

The bimetallic doped PAC catalyst may comprise any suitable combination of metals. For example, the metals comprised in the bimetallic doped PAC catalyst may be selected from the metals described above. According to a particular aspect, the bimetallic doped PAC catalyst may comprise metal combinations selected from, but not limited to: Fe-Mn, Fe-Ni, Fe-Co, Ni-Cu, Mn-Co, Mg-Cu, Mg-Ni, or Fe-Cu. Even more in particular, the metal doped PAC catalyst may be Fe-Mn doped PAC catalyst.

The catalyst may have any suitable size. For example, the catalyst may have an average size of 1-150 mm. For the purposes of the present invention, the average size may refer to at least one of the height of the catalyst or the width of the catalyst. In particular, the average size of the catalyst may be 5-120 mm, 10-100 mm, 15-95 mm, 20-90 mm, 25-85 mm, 30-80 mm, 35-75 mm, 40-70 mm, 50-60 mm. Even more in particular, the average size of the catalyst may be about 10 mm.

The catalyst may have any suitable form. For example, the catalyst may be in the form of, but not limited to, a pellet, sphere, cube, hollow cube, solid cylinder, hollow cylinder, four-hole cylinder, single ring, cross web, ribbed ring, trilobe, quadralobe, and the like. In particular, the catalyst may be in the form of a pellet. When the catalyst is in the form of a particular structure such as those described above, the catalyst may be easily separated and recovered for re-use in further wastewater treatment processes.

According to a second aspect, the present invention provides a method of forming the catalyst according to the first aspect, the method comprising:

- mixing a metal ion solution in an acidic solvent to form a first mixture;
- adding powdered activated carbon (PAC) to the first mixture to form a second mixture;
- adding an organic solvent to the second mixture to form a xerogel;

- drying the xerogel; and
- calcinating the xerogel to form the metal-doped PAC catalyst.

The metal ion solution may comprise ions of any suitable metal for the preparation of the doped metal PAC catalyst. For example, the metal ion solution may comprise ions of the following non-limiting metals: iron (Fe), manganese (Mn), copper (Cu), magnesium (Mg), nickel (Ni), cobalt (Co), or a combination thereof.

In particular, for the preparation of a monometallic doped PAC catalyst, the metal ion solution may comprise ions from one metal. For the preparation of a bimetallic doped PAC catalyst, the metal ion solution may comprise ions from two metals. According to a particular aspect, the metal ion solution may comprise iron and manganese ions.

The acidic solvent may be any suitable acidic solvent. In particular, the acidic solvent may be a weak organic acid solvent. For example, the acidic solvent may be, but not limited to: citric acid, acetic acid, formic acid, oxalic acid, propionic acid, lactic acid, or a combination thereof. According to a particular aspect, the acidic solvent may be citric acid. The mixing may be carried out in distilled water.

The mixing may be carried out under suitable conditions. For example, the mixing may be carried out for a suitable duration, at a suitable temperature and/or pH. According to a particular aspect, the temperature may be 60-120°C. Even more in particular, the temperature may be 80°C. According to a particular aspect, the mixing may be carried out for 1-5 hours. Even more in particular, the mixing may be carried out for about 3 hours. According to a particular aspect, the mixing may be carried out at a pH of 5-7. Even more in particular, the pH may be 6.

The adding PAC may be carried out under suitable conditions. For example, the adding of the PAC into the first mixture to form a second mixture may further comprise ultrasonicating the second mixture comprising a metal-PAC solution. The ultrasonicating may be at a suitable temperature and for a suitable period of time. For example, the ultrasonicating may be at a temperature of 60-90°C. In particular, the ultrasonicating may be at a temperature of about 70°C. The ultrasonicating may be carried out for 10-40 minutes. In particular, the ultrasonicating may be for about 30 minutes.

The organic solvent added to the second mixture for forming the xerogel may be any suitable organic solvent. For example, the organic solvent may be, but not limited to: ethylene glycol, glycerol, isopropanol, 1,2-propane diol, triethylene glycol, polyethylene glycol, or a combination thereof. In particular, the organic solution may be ethylene glycol. Following the addition of the organic solvent, the mixture of the organic solvent and the second mixture may be continuously mixed at a suitable temperature until a xerogel is formed. For example, the temperature may be 100-150°C. In particular, the temperature may be about 120°C.

Following the formation of the xerogel, the drying of the xerogel may be under suitable conditions. For example, the drying may comprise drying the xerogel at a temperature of 80-150°C. In particular, the temperature may be about 100°C. The drying may be for a suitable period of time. For example, the drying may be for 12-24 hours. In particular, the drying may be for about 18 hours.

The calcinating of the dried xerogel may be at a suitable temperature. For example, the calcinating may be a temperature of 400-800°C. In particular, the temperature may be about 550°C. The calcinating may be for a suitable period of time. For example, the calcinating may be for 2-4 hours. In particular, the calcinating may be for 3 hours.

Following calcinating the metal doped PAC catalyst is formed. The catalyst may be in the form of a powder. The method may further comprise forming the catalyst into a suitable form such as a pellet, sphere, cube, hollow cube, solid cylinder, hollow cylinder, four-hole cylinder, single ring, cross web, ribbed ring, trilobe, quadralobe, and the like. According to a particular aspect, the method may further comprise pelletizing the catalyst to form a pellet. Any suitable pelletizing method for the purposes of the present invention may be used.

According to a particular aspect, pelletizing may comprise mixing the powdered metal doped PAC catalyst with a binding agent to form a paste, followed by pelletizing the paste. The binding agent may be any suitable binding agent. The binding agent may comprise, but is not limited to, polytetrafluoroethylene, silica colloidal, sulfonated tetrafluoroethylene based fluoropolymer-copolymer, or combinations thereof. In particular, the polytetrafluoroethylene may be Teflon®, and the

sulfonated tetrafluoroethylene based fluoropolymer-copolymer may be Nafion® solution. Even more in particular, the binding agent may be a polytetrafluoroethylene.

The pelletizing may be by using a hydraulic press, 3D printing, pellet making machine, and the like. The pelletizing may enable the formation of the metal doped PAC catalyst into a suitable shape and size.

The method may further comprise calcinating the pellets formed from the pelletizing. The calcinating may be at a suitable temperature. For example, the calcinating may be at a temperature of 150-250°C. In particular, the calcinating may be at a temperature of about 180°C. The calcinating may be for a suitable period of time. For example, the calcinating may be for 3-8 hours. In particular, the calcinating may be for about 5 hours.

An embodiment of the method of the present invention will now be described. An iron salt solution, such as for example iron nitrate, iron chloride, and/or iron sulfate, and a manganese salt solution, such as for example manganese nitrate, manganese chloride and/or manganese sulfate may be mixed with citric acid in distilled water. The iron salt solution and the manganese salt solution may have the same anions, and the molar ratio between the iron and manganese ions may be 1 to 1. The metal solution may be mixed at 60-90°C for 1-3 hours, with pH maintained at 6.5-7.5.

PAC may be added into the metal solution and mixed under ultra-sonication for 10-40 min at 60-90°C. Ethylene glycol may then be added into the metal-PAC solution, mixing continuously at 100-150°C until a xerogel mixture is formed. The xerogel mixture may be dried at a temperature of 100-150°C for about 12-24 hours, and the resultant mixture may be calcinated at 400-600°C for 2-4 hours to produce Fe-Mn doped PAC powder.

The Fe-Mn doped PAC powder may be mixed with Teflon® solution into a thick paste. The mass of the Fe-Mn doped PAC powder may be 5-50 g, and the volume of the Teflon® solution may be 1.5-15 mL. Pelletizing may then be performed, for example with a hydraulic press, and the pelleted catalyst may be made into any shape with any size. The pressed pellet may be subsequently calcinated at 150-250°C for 3-8 hours.

According to a third aspect of the present invention, there is provided a catalytic ozonation system for wastewater treatment comprising:

- a wastewater inlet for receiving wastewater;
- an ozone inlet for receiving ozone gas;
- an ozone reactor for catalytic ozonation of wastewater, the ozone reactor in fluid communication with the wastewater inlet and the ozone inlet, wherein the ozone reactor is loaded with the catalyst according to the first aspect of the present invention; and
- a water outlet for discharging treated wastewater.

The system may further comprise a microbubble generator in fluid communication with the ozone inlet for forming ozone microbubbles.

An example of the system of the present invention is provided at Figure 1. Figure 1 shows a catalytic ozonation system 100 according to one embodiment of the present invention. The system 100 comprises a wastewater inlet 102 for receiving wastewater and an ozone inlet 104 for receiving ozone gas. The wastewater inlet 102 and the ozone inlet 104 are in fluid connection with an ozone reactor 106. The ozone reactor 106 may be packed with metal doped PAC catalyst pellets 108. The ozone reactor 106 is also in fluid connection with a water outlet 110 for discharging treated wastewater.

The system 100 may also comprise an ozone generator 112 and an optional microbubble generator 114. The microbubble generator 112 may be in fluid communication with the ozone generator 112, with the microbubble generator 112 further in fluid communication with the ozone inlet 104 to feed ozone microbubbles into the ozone reactor 106 via ozone inlet 104.

The system may further comprise an ozone destruction unit 116 in fluid connection with an ozone outlet 118. The ozone outlet 118 may be in fluid connection with the ozone reactor 106. There is also provided a pump 120 to pump water from a wastewater supply source to the wastewater inlet 102.

There is also provided a method for catalytic ozonation comprising ozonising wastewater over the catalyst according to the first aspect of the present invention.

A method of catalytic ozonation comprising ozonising wastewater over the catalyst will now be described in relation to the system 100 as shown in Figure 1.

Ozone gas may be produced by the ozone generator 112 using pure oxygen or oxygen enriched air, and subsequently introducing the ozone gas into the microbubble generator 114 to produce ozone microbubbles. Ozone microbubbles may enter the ozone reactor 106 from the bottom of the ozone reactor 106 through ozone inlet 104 and mixing with the incoming wastewater entering the ozone reactor 106 through wastewater inlet 102. Introducing the ozone gas in the form of microbubbles from the bottom of the ozone reactor 105 enhances the ozone mass transfer rate. In particular, when the ozone is introduced into the ozone reactor 105 in the form of microbubbles, a high gas to liquid ozone transfer rate is achieved.

The ozone reactor 106 may be loaded with metal doped PAC catalysts 108, for example, Fe-Mn doped PAC pellets. The ozone microbubbles, wastewater and catalyst pellets 108 initiate heterogeneous catalytic ozonation within the ozone reactor 106. Hydroxyl radicals (OH°) can be generated through both microbubble shrinking and catalytic ozone decomposition. During the oxidation process, OH° radicals play the key role for recalcitrant COD removal and biodegradability enhancement of the wastewater. Treated wastewater may flow out from the water outlet 110 at the top of the ozone reactor 106, and off-gas ozone may be removed from the ozone reactor 106 via ozone outlet 118 by the ozone destructor 116.

The ozone reactor 106 may be an airtight ozone resistant column with a working pressure less than 0.05 MPa. The ozone reactor 106 may be made of any suitable material such as, but not limited to, glass, polycarbonate, or stainless steel.

The ozone microbubbles may be of any suitable size. For example, the size of the ozone microbubbles may be ≤ 100 μm.

The liquid phase ozone dose may be varied according to wastewater characteristics. For the purpose of tertiary treatment, the applied ozone dose may be ranging from 5-35 mg/L. To achieve biodegradability enhancement in raw industrial wastewaters, the ozone dose may be varied from 35-100 mg/L.

The hydraulic retention time (HRT) of the catalytic ozone reactor 106 may be based on influent characteristics and effluent quality required. Typically, the HRT may be ≤ 120 minutes.

The metal doped PAC catalyst pellets 108 comprised in the ozone reactor 106 may be packed or freely fluidized within the ozone reactor 106. The catalyst loading range may be 1-10g/L, depending on the wastewater characteristics and effluent quality required.

By combining microbubble ozonation and heterogeneous catalytic ozonation, a high ozonation efficiency may be achieved by the present invention. Fr example, the ratio between ozone consumption and COD removal is less than 1.5:1.

Having now generally described the invention, the same will be more readily understood through reference to the following embodiment which is provided by way of illustration, and is not intended to be limiting.

Example

Fe-Mn doped PAC pellet catalyst and Fe-Mn doped granulated activated carbon (GAC) pellet catalyst preparation

A sol-gel method was adopted to prepare Fe-Mn doped PAC catalyst. 0.015 M iron nitrate, 0.015 M manganese nitrate and 0.09 M citric acid were firstly added into distilled water with a total volume of 10 mL. The metal solution was mixed with magnetic stirrer for 2 hours at 80°C, and pH of the metal solution was maintained at 6.5-7.5 with ammonium hydroxide. 30 g PAC was subsequently added into the metal solution and ultra-sonicated for 15 minutes. Another 15 minutes mixing of the metal-PAC solution was conducted at 80°C. In the next step, ethylene glycol was introduced into the metal-PAC solution, and continuous mixing at 150°C was performed until xerogel mixture was formed. The resultant xerogel mixture was then dried at 105°C for 12 hours and calcinated at 550°C for 3 hours to produce Fe-Mn doped PAC powder.

In order to make the Fe-Mn doped PAC catalyst into a pellet form, 10 g prepared Fe-Mn doped PAC powder was firstly mixed with 3 mL binder Teflon solution into a thick paste. The catalyst paste was added into a 1 cm diameter stainless steel mold and compacted at 5 kN load for 10 min. The prepared Fe-Mn doped PAC pellet had a diameter of 1 cm and thickness of 0.5 cm, and they were subsequently calcinated at 200°C for 5 hours.

Fe-Mn doped GAC pellet was prepared with the same experiment procedures, except for using GAC as the carbon substrate.

Ozonation operation conditions

The ozone reactor was an airtight Perspex column with an inner diameter of 50 mm, height of 100 mm, and working volume of 2 L. The oxygen flow rate for ozone generation was 1 L/min, average size of ozone microbubbles ranges from 50 to 100 μm, and the liquid phase ozone dose was 30 mg/L. The hydraulic retention time (HRT) of the catalytic ozonation reactor was 60 min. Fe-Mn doped PAC pellets occupy 1/3 of the reactor working volume and they were freely fluidized within the reactor. The total catalyst loading was 2 g/L.

Characterization of Fe-Mn doped PAC pellet catalyst and Fe-Mn doped GAC pellet catalyst

X-ray diffraction (XRD) analysis of Fe-Mn doped PAC pellet catalyst and Fe-Mn doped GAC pellet catalyst was firstly conducted to confirm successful doping of Fe and Mn metal ions on the two carbon substrates. Figure 2 demonstrates the XRD patterns of PAC, GAC, Fe-Mn doped PAC and Fe-Mn doped GAC. Both bare PAC and GAC shows a characteristics 2θ broad peak at 25°, which corresponds to a typical activated carbon reflection. Small diffraction peaks at 37° and 50° is detected in Fe-Mn doped GAC and Fe-Mn doped PAC XRD patterns, indicating deposition of Fe and Mn metal ions on the carbon substrates, respectively. It was also noted that diffraction peaks of carbon substrates at 25° had reduced intensity after successful doping of Fe and Mn metal ions.

A scanning electron microscope (SEM) was used to scan the surface GAC, PAC, Fe-Mn doped GAC and Fe-Mn doped PAC, the produced SEM images are shown in Figure 3. Through SEM analysis, it was found that pure PAC and GAC possessed uniform flaky appearance without any metal deposition on the carbon surface (Figure 3a and 3b). Due to FeO and MnO deposition, inhomogeneous sized particles were found on the surface of Fe-Mn doped GAC and Fe-Mn doped PAC (Figure 3c and 3d).

Energy dispersive X-ray (EDX) analysis was used for the elemental analysis of GAC, PAC, Fe-Mn doped GAC and Fe-Mn doped PAC. The EDX patterns as shown in

Figure 4 confirm the presence of Fe, Mn and C elements in the Fe-Mn doped GAC and Fe-Mn doped PAC catalysts. The mass percentages of Fe and Mn in Fe-Mn doped GAC were calculated as 7.3% and 2.1%, respectively. Higher mass percentages of Fe and Mn were found in Fe-Mn doped PAC, with 10.3% for Fe and 4.7% for Mn. The prepared PAC catalyst obtained higher metal content than GAC catalysts.

Impact of microbubble and heterogeneous catalyst on ozonation system performance

Lab-scale batch studies were conducted to evaluate the performance of different ozone technologies for reverse osmosis concentrate (ROC) treatment. Figure 5 demonstrates COD removal in ROC with three types of ozonation processes, including conventional ozonation, microbubble ozonation and catalytic-microbubble ozonation coupled with Fe-Mn doped PAC pellet catalyst (O_3/Fe-Mn doped PAC catalyst). Ozone dosage in the three ozonation processes were all 30 mg/L, catalyst loading used in catalytic-microbubble ozonation was 2 g/L. Reaction time and pH for all processes were 60 minutes and 8, respectively. The operating principle behind the ozone technologies involved the oxidation of organic compounds by direct and indirect ozonation, in which gas to liquid phase ozone transmission and hydroxyl radical (OH°) generation occurred. Ozone microbubbles with an average size of 5 mm were used in the conventional ozonation, which obtained the lowest COD removal efficiency (28%) due to limited ozone transmission rate. Microbubble has the advantages of small bubble size (<100 μm), huge interfacial area, long stagnation time, lower bubble rising speed, and high interior pressure. Implementation of microbubble ozonation provided high ozone dissolution and fast mass transfer rate, thus microbubble ozonation achieved higher COD removal efficiency (52%) in ROC.

In catalytic-microbubble ozonation, Fe-Mn doped PAC pellets were introduced as the catalyst to decompose dissolved ozone into highly active oxidation species (OH°), and /or an adsorption site for organics that could directly react with dissolved ozone. OH° is a non-selective oxidant with much stronger oxidation capacity. Both microbubbles and heterogeneous catalytic ozonation were adopted as the optimization methods in the present system, and the results demonstrated highest COD removal efficiency (83%) in ROC with catalytic-microbubble ozonation process.

Impacts of different catalysts on ozonation system performance

Lab-scale batch studies were also conducted to assess the enhancement of ozonation system performance with different catalysts. Figure 6 illustrates the COD removal in ROC with various catalytic-microbubble ozonation processes. The applied ozone dosages were all 30 mg/L, catalyst loading used in catalytic ozonation processes was 2 g/L. Reaction time and pH in all ozonation processes were 60 minutes and 8, respectively. As previously indicated, pure microbubble ozonation (O_3 alone) process achieved 52% COD removal in ROC, and GAC addition did not exhibit significant performance enhancement as the COD in ROC was only reduced by 54% with O_3/GAC process. O_3/PAC process achieved higher COD removal (62%) compared to both O_3 alone and O_3/GAC processes. Addition of Fe-Mn doped GAC catalyst into the microbubble ozonation process (O3/Fe-Mn/GAC) resulted in 71% COD removal in the ROC, while addition of Fe-Mn doped PAC catalyst (O3/Fe-Mn/PAC) into the microbubble ozonation process showed the highest COD removal efficiency of 83%.

This shows that metal doped carbon catalysts are able to induce more efficient catalytic ozonation than pure carbon catalysts. The reason for higher COD removal with Fe-Mn doped carbon catalyst is due to higher reactivity between Fe/Mn ions and ozone molecules for hydroxyl radical (OH°) generation. For the comparison of carbon substrate, PAC consistently demonstrated better performance than GAC, which is due to higher surface area of PAC as compared to GAC, resulting in more organic adsorption and better interaction between ozone and the doped metal ions.

The system of the present invention uses Fe-Mn doped PAC catalysts to perform effective catalytic-microbubble ozonation process. Furthermore, Fe-Mn/PAC catalyst was introduced into the system in a pellet form, which allowed for easy catalyst recovery.

Performance stability of Fe-Mn doped PAC pellet catalyst

Stability of Fe-Mn doped PAC pellet catalyst performance was evaluated in terms of COD removal in ROC. Figure 7 shows the COD reduction through six consecutive batch runs using catalytic-microbubble ozonation coupled with Fe-Mn doped PAC pellet catalyst (O3/Fe-Mn/PAC). The ozone dosage was 30 mg/L, total reaction time of each batch testing was 60 min, catalyst loading was 2 g/L, and natural pH of ROC (pH of 8) was adopted in the catalytic-microbubble ozonation.

As shown in Figure 7, O3/Fe-Mn/PAC process exhibited stable COD removal throughout the six batches. The average COD removal efficiency was 69% with a standard deviation of 2, which shows stable performance of the O3/Fe-Mn/PAC pellet catalyst. For comparison purpose, another six-batch catalytic-microbubble ozonation was conducted for COD removal in ROC with addition of Fe-Mn doped GAC catalyst.

Figure 8 shows the COD removal efficiencies with O3/Fe-Mn/GAC process for six consecutive batch runs. The COD removal efficiencies were found to be gradually decreasing along the six batch runs. COD removal in the first batch was 68%, and it was 52% in the sixth batch. Reduced catalyst performance in O3/Fe-Mn/GAC process was due to the surface oxidation of catalyst and leaching of the doped metal ions. With higher surface area, PAC provided larger active site for interaction with metal ions than GAC, and sol-gel doping method allowed for stronger binding with the doped metal ions through complexation process.

Continuous catalytic-microbubble ozonation was also conducted to test the performance stability of Fe-Mn doped PAC pellet catalyst. ROC with an average influent COD level of 116 mg/L was continuously fed into the ozone reactor loaded with Fe-Mn doped PAC pellet catalyst. The HRT of ozone reactor was 60 minutes, catalyst loading was 2 g/L and total ozone dosage was 30 mg/L. Figure 9 summarizes the influent and effluent COD levels in four-phase operations of O3/Fe-Mn/PAC.

In each phase, the catalytic-microbubble ozonation of ROC was continuously operated for 8 hours, and the effluent COD level was found to be stable. According to the continuous data presented in Figure 9, the average COD removal efficiency of the ozone reactor for ROC treatment was 71%, and all effluent COD levels in the four operation phases were below 50 mg/L. The ratio between ozone consumption and COD removal for ROC treatment was calculated as 1.5:1.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A method of forming a metal doped powdered activated carbon (PAC) catalyst for catalytic ozonation, the method comprising:
   - mixing a metal ion solution in an acidic solvent to form a first mixture;
   - adding powdered activated carbon (PAC) to the first mixture to form a second mixture;
   - adding an organic solvent to the second mixture to form a xerogel;
   - drying the xerogel; and
   - calcinating the xerogel to form the metal-doped PAC catalyst.

2. The method according to claim 1, wherein the acidic solvent is: citric acid, acetic acid, formic acid, oxalic acid, propionic acid, lactic acid or a combination thereof.

3. The method according to claim 1 or 2, further comprising ultrasonicating the second mixture prior to the adding an organic solvent.

4. The method according to any of claims 1 to 3, wherein the organic solvent is: ethylene glycol, glycerol, 1,2-propane diol, triethylene glycol, polyethylene glycol, or a combination thereof.

5. The method according to any of claims 1 to 4, wherein the calcinating is at a temperature of 400-800°C.

6. The method according to any of claims 1 to 5, wherein the method further comprises pelletizing the catalyst.

7. A catalytic ozonation system for wastewater treatment comprising:
   - a wastewater inlet for receiving wastewater;
   - an ozone inlet for receiving ozone gas;
   - an ozone reactor for catalytic ozonation of wastewater, the ozone reactor in fluid communication with the wastewater inlet and the ozone inlet, wherein the ozone reactor is loaded with a metal doped powdered activated carbon (PAC) catalyst having an average size of 5-150 mm; and
   - a water outlet for discharging treated wastewater.

8. The system according to claim 7m, wherein the system further comprises a microbubble generator in fluid communication with the ozone inlet for forming ozone microbubbles.

9. A method for catalytic ozonation comprising ozonising wastewater over a metal doped powdered activated carbon (PAC) catalyst having an average size of 5-150 mm.