

Heavy Metal and Phosphorus Removal from Waters by Optimizing Use of Calcium Hydroxide and Risk Assessment

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Abstract

The optimizing using calcium hydroxide to remove dissolved heavy metal, phosphorus pollutants and algae was investigated. It was found that the concentration of calcium ion was minimal at pH 10.5 when a large amount of generated calcium carbonate increased the particle size of the precipitates and improved sedimentation of sludge and the removal efficiency of heavy metal and phosphorus significantly. Regardless of the initial heavy metals concentrations contained in the wastewater, the final treated concentrations were all extremely low. Risk assessment in alkaline environment of pH 10.5 was tested by fancy carp, daphnia, seed, luminescent bacterium Q67. The results showed that pH 10.5 had a little influence on the four tested organisms. Thus it is suggested that calcium hydroxide at pH 10.5 may be a potential method for treating wastewater and eutrophication water.

Keywords: Heavy metals, Phosphorus, Co-precipitation, Calcium hydroxide, Risk assessment

1. Introduction

Heavy metals-containing human, industrial and urban wastewaters, which were discharged into river systems, caused a serious problem that is a major concern worldwide (Tsai, Yu, Chen, & Kung, 2003). Heavy metals are harmful to both human and aquatic life (Stéphanie Lecomte & Ehrhardt, 2001). They are present in soluble form in the aqueous solution over a wide range of pH values and quite mobile in the natural environment (Baek & Yang, 2004). When wastewater containing higher concentration of heavy metals is discharged into the natural water bodies, it affects aquatic life and is destructive to the environment. Even trace amounts of heavy metal pollution, can produce bioaccumulation through the food chain. When people drink the water or eat the food contaminated by heavy metals, there will be high contents of heavy metals in the body, leading to a variety of incurable diseases.

Lead is a recognized environmental pollutant that acts as a cumulative poison. Inorganic Pb^{2+} is an enzyme inhibitor, which affects the nervous system. Once being mobile in the environment in the ionic form, it finds its way into the human body through drinking water, food and air, like many other toxic elements (Bhattacharjee, Chakrabarty, Maity, Thakur, & Bhattacharyya, 2003). As a trace element, zinc is essential for human health. It is important for the physiological functions of living tissues and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea

and anemia (Oyaro, Oyaro, Juddy, Murago, & Gitonga, 2007). Copper plays an important role in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Paulino, Minasse, Guilherme, Reis, Muniz, & Nozaki, 2006). Exceeding its critical level, nickel might cause serious lung and kidney problems, besides gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba, Guirardello, Silva, Veit, & Tavares, 2006). And it is known that nickel is a human carcinogen. Cadmium has been classified by the U.S. Environmental Protection Agency as a probable human carcinogen. Cadmium exposure will create severe risks to human health. Chronic exposure of cadmium can result in kidney dysfunction and high levels of exposure will result in death (Fu & Wang, 2011).

In some developing countries, drinking water resources are threatened by harmful algae blooms (HABs) (Chen, He, Huang, Kong, Lin, Li, & Zeng, 2009a). It is evident that nitrogen (N) and phosphorus (P) contained in agricultural effluents and industrial wastewaters are mainly responsible for eutrophication (Smith, Tilman, & Nekola, 1999) and it is necessary to reduce both N and P inputs for long-term eutrophication and cyanobacterial bloom control in hyper-eutrophic system (Paerl, Xu, McCarthy, Zhu, Qin, Li, & Gardner, 2011). Controlling aquatic nutrients especially phosphorus was emphasized as the chief measure to conquer HABs (Martin & Katrin, 2000).

To remove heavy metals, many techniques including ion exchange with a material possessing ion exchange capability, membrane filtration, reverse osmosis, and electrodialysis, etc. have been used. Meanwhile, various measures, including ultrasonic radiation, dissolved air flotation, chlorine or permanganate oxidation, have been adopted to remove algae. However, combined with the complicated operation process, the extremely high expenses of source control made these methods would not become highly effective until 10 years later or even longer.

By far, chemical precipitation is an effective and the most widely used process in industry, because it is relatively simple and inexpensive to operate (Ku & Jung, 2001). In the precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The most extensively employed chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH (Huisman, Schouten, & Schultz, 2006). Calcium hydroxide is an ideal precipitation agent because of the low cost of fabricating and high processing effects. But the precipitates of amphoteric metals, for example, zinc and lead, tend to re-dissolve as the pH changes beyond the optimal range. Consequently, pH must be controlled strictly.

In this study, sodium hydroxide and calcium hydroxide were used to adjust the pH. The objective of this work was to optimize the control condition in which the most important was the value of pH to remove heavy metals from solutions. The agglomeration of the precipitates during the treatment was investigated and characterized by scanning electron microscope (SEM). The additional experiment was carried out for removing the algae and P under the natural aerate-scale condition, as a part of this investigation, the degree to which the four aquatic organisms—fancy carp, daphnia, seed, Luminescent bacterium *Q67* were affected when living in the treated water with pH 10.5 was investigated.

2. Materials and Methods

2.1 Materials

All primary chemicals used were of analytical grade. Solutions (synthetic effluents) containing zinc, copper, manganese, nickel, lead, cadmium and di-hydrogen phosphate were prepared by dissolving the metals in deionized water at a concentration of 500 mg/L for precipitation studies.

2.2 Precipitation

2.2.1 Synthetic Wastewater

Samples for removal experiment of heavy metals and phosphate were taken randomly at three different time points. These samples were tested with the Jar test. In the Jar test, sodium hydroxide and calcium hydroxide were separately added to the samples to adjust the pH to different values. The pH was constantly monitored using a METTLER TOLEDO S20P-K pH meter with a glass electrode. In the process, the samples were stirred at 350 r/min with magnetic stirring apparatus. 15 mL of the samples were taken at every pH point with a pipette. Then, keeping the water samples static and the supernatants taken at a constant depth of 30 mm using the pipette from each vessel were collected. Then, a certain volume of each water sample was acidified by adding nitric acid. The concentration of Cd^{2+} was measured using graphite furnace atomic absorption spectrometry (AA-600, Perkin-elmer, USA). The concentrations of Cu^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Cd^{2+} and P were determined using

atomic emission spectrometry (ICP) (J-A1100, Jarrell-Ash, USA). The concentrations of heavy metal ions and P were measured, and how pH values affect the treatment effectiveness was investigated.

After calcium hydroxide was mixed with the synthetic heavy metal-containing wastewater under stirring at pH 10.5, the suspending substance precipitated in 30 min and was then washed with deionized water thoroughly. The sediments were characterized using SEM (S-3400N II, Hitachi, JP) micrograph analysis.

2.2.2 River Water

The water sample used was taken from the river in the Nanjing University. Different dosages of calcium hydroxide were added to adjust pH to 9.0, 10.0, 10.5, 11.0, 11.5. The concentrations of total phosphorus (TP), total dissolved phosphorus (TDP) and chlorophyll a in the treated water samples were measured.

After digesting the water sample with $\text{H}_2\text{SO}_4\text{-HClO}_4$ directly, the TP contents were determined. The TDP contents were determined by filtrating the water samples through a $0.45\ \mu\text{m}$ membrane and then digesting the filtrate. The analysis method was both the molybdenum-antimony anti-spectrophotometric method (Murphy & Riley, 1962). The difference of TP and TDP was the concentration of particulate phosphorus (PP). Extracted with 90 % ethanol, the concentration of chlorophyll a was determined spectrophotometrically (ISO, 1992). The specific procedure is as follows: 500 mL of the samples were filtered through a $0.45\ \mu\text{m}$ Whatman GF/C filter and chlorophyll a was extracted with 90 % ethanol at $80\ ^\circ\text{C}$ for 5 min. After filtration of the extract, 10 mL of the filtrate was taken for acidification by 10 μL of 3 mol/L hydrochloric acid. The absorbances of the two filtrates were measured at 665 nm and 750 nm.

2.3 Bio-toxicity Detection of the Treated Water and Toxicity Test

2.3.1 Fancy Carp

The experimental fish, fancy carp were obtained from a fish hatchery in Nanjing. The fish were fed for 15 days in an aquarium, with an average weight of $50 \pm 8\ \text{g}$ and length of $12 \pm 1\ \text{cm}$. Then fish were transferred to 3 glass aquaria (18 individuals/ aquarium) with 200 L of freshwater via a continuous system of water filtration and aeration. Temperature was maintained at $21 \pm 2\ ^\circ\text{C}$ and dissolved oxygen values at $7.0 \pm 0.5\ \text{mg/L}$. Mean values for additional parameters of water quality were: pH 7.8 ± 0.2 , conductivity $305\ \mu\text{S/cm}$, Ca^{2+} $0.6\ \text{mmol/L}$ and Mg^{2+} $0.3\ \text{mmol/L}$.

Fish treatment groups consisted of control group (aquarium 1), the group exposed to the constant pH value 10.5 (aquarium 2) and the group of the initial pH 10.5 under natural aeration (aquarium 3). All experimental fish were fed once a day and the exposure solutions were completely not changed. Calcium hydroxide emulsion was used to adjust the pH value of water to 10.5. The pH of the water in aquaria 2 was controlled every day to keep the pH value stable, and the control condition of aquarium 3 were kept the same as that of the control group. The fish were sampled on the days 0.5, 1, 2, 4, 8, 12, and antioxidant enzymatic activities (SOD), lipid peroxidation (MDA) and catalase (CAT) were measured.

All tests of bio-marks were conducted the day after the preparation of tissues. According to results from the preliminary experiments, we chose 0.9 % NaCl solution as the dilution. Liver samples were homogenized with ice-cold 0.9 % NaCl and then centrifuged at 4000 r/min at $4\ ^\circ\text{C}$ for 17 min. The resulting supernatants were used for the determination of SOD, MDA and CAT levels.

The activities of SOD, MDA and CAT were measured using the Diagnostic Reagent Kit, purchased from Nanjing Jiancheng Bioengineering Institute (Jiancheng, China), according to the manufacturer's instructions.

2.3.2 Daphnia

Daphnia, originally isolated from Lake Taihu, in the city of Wuxi, were maintained in parthenogenetic cultures in our laboratory. The cultures were acclimated at $25 \pm 1\ ^\circ\text{C}$ under a 14 h light/10 h dark cycle before the experiment. EC_{50} values for daphnia exposed to the alkaline environment were determined according to ISO method (ISO 6341, 1996). For each treatment, ten daphnia aged 6-24 h were placed in 150 mL glass beakers containing 100 mL of exposure solutions. All the groups were set to four parallel tests and repeated twice. The daphnia were not fed during the test.

2.3.3 Seed Germination

In this part, the toxic effects of alkalinity on Huaxing early V Chinese cabbage were assessed, based on seed germination. The mature, full seeds with similar sizes were chosen and sown in the glass culture dishes. 15 seeds contained in the rolled filter paper with 5 mL of respective test solutions are cultivated in each dish. The seeds cultured in distilled water were served as a control. The germination test was conducted under the condition of darkness with a temperature of $25 \pm 1\ ^\circ\text{C}$ in the culturing box (SPX-250, Fuma, China). The number of

germinated seeds was counted three days later. All the treatments were replicated 3 times in order to minimize experimental error. A seed was considered to be germinated when the emerging radicle elongated to 2 mm.

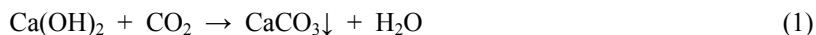
2.3.4 Luminescent Bacterium *Q67*

Freshwater Photobacterium phosphoreum *Q67* were provided by the Biology Department of the East China Normal University (ECNU). The cultured slant was diluted with distilled water in proper amount (luminous density of the blank control tube was controlled within the measurement range of the luminescence apparatus). The testing medium was composed of distilled water and a certain amount of calcium hydroxide and the blank solution was 2ml of distilled water. Before each test, the relative light unit (RLU) of *Q67* suspension was adjusted to around 50 % by adding test mediums to let determined concentration be in the appropriate range. Three parallel samples were taken for each concentration group with 2.0 mL in the colorimetric tubes, and 2 mL of distilled water was set as the blank control group. The assays of *Q67* were carried out by adding 0.5 mL of bacterial suspension and 2.0 mL of test medium to a colorimetric tube. The mixture was thoroughly mixed and the RLU was recorded by a luminometer (BHP9511, Binsong Photonics, China). The final RLU was recorded after 15 min incubation at 22 ± 1 °C.

3. Results and Discussion

3.1 Golden Point

Initial treatment runs was added calcium hydroxide solution in the river water which never joined any other heavy metals. The pH of river water was adjusted stable to 7.9, 8.4, 8.9, 9.4, 9.9, 10.5, 10.8, and 11.3, respectively. Figure 1 showed that the calcium concentration increased mildly at first, and then dropped slowly until the pH value was 10.5. After this Golden point, the concentration of calcium increased obviously. The lowest concentration of calcium in the solutions during the process was 24.83 mg/L, a half of the initial concentration. It is possible that abundant carbonate ions exist in the water when calcium hydroxide was added in:



There were generating a large amount of calcium carbonate, with no need to add sodium carbonate or aerate carbon dioxide into the water.

During the experiment, we also recorded the conductivity, which presented the similar variation to the calcium concentration. The reduction of the ion content at pH 10.5 brought about the decrease of the conductivity. There is no question that the point of pH value 10.5 is very significant. Though the turbidity of the solution was very high due to the generated large amount of calcium carbonate, the suspensions were soon settled down after 30 min. All the evidence suggested that the golden point is worth to research.

3.2 Heavy Metal Removals

Chemical precipitation is widely used for heavy metal removal from inorganic effluent. After the pH is adjusted to the basic condition (pH 10.5), the dissolved metal ions are converted to the insoluble solid phase via a chemical reaction with a precipitant agent. Usually, the precipitation will be suspended in the water. Therefore, the remove effect is not satisfactory.

The results of the precipitation experiments are shown in Table 1. It was found that the optimum pH for chemical coagulation and precipitation by sodium hydroxide and calcium hydroxide were larger than 10.5, at which point the Zn^{2+} , Mn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} levels in the micro-polluted water could be decreased significantly. The mechanism of heavy metal removal by chemical precipitation is presented in Eq. (2) (Wang, Vaccari, Li, & Shammass, 2005):



Where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while M(OH)_2 is the insoluble metal hydroxide.

The testing revealed that calcium hydroxide could be successfully removed from the synthetic water by the formation of calcium carbonate at the golden point. The removal efficiencies showed that the treatment effect was strongly dependent upon pH, and pH value 10.5 was the optimal control point. In the pH region above 10.5, the removal rate of Mn^{2+} almost reached to 100 %, Cd^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and Pb^{2+} were respectively 96.48 %, 99.76 %, 86.74 %, 96.76 % and 89.67 % precipitated, and the residual concentration satisfied the following provision stipulated in Limits Environmental Quality Standards for Surface Water of China: Mn 0.1 mg/L, Cd 0.005 mg/L, Zn 0.05 mg/L, Cu 1.0 mg/L and met the discharge limit stipulated in The Integrated Wastewater Discharge Standard of China for Ni^{2+} 1.0 mg/L. Improving the pH value, the Cd^{2+} , Mn^{2+} , Ni^{2+} and Cu^{2+}

concentrations reduced further while the concentration of Pb^{2+} decreased. The amphoteric heavy metals tend to re-dissolve as the pH changes beyond the optimal range. The mass of calcium carbonate reduced the re-dissolution degree of Pb^{2+} into the solution.

It can be seen that the removal efficiency of calcium hydroxide was better than that of sodium hydroxide except for Zn^{2+} . The initial concentrations of Zn^{2+} in the sodium hydroxide group were all lower than those in the calcium hydroxide group and the remove efficiency of Zn^{2+} by these two reagents was all 99.76 %. What's more, the deficiency of sodium hydroxide was the higher cost than calcium hydroxide.

Then we used calcium hydroxide to treat the heavy metal of the higher concentration in the synthetic wastewater (Table 2). The results indicated that the concentration of the six heavy metals all dropped a lot with the removal efficiency more than 95 %. We controlled the pH value to 6-11, the residual concentrations of copper reduced to 0.948 mg/L, 0.748 mg/L, 0.066 mg/L and 0.085 mg/L when the initial concentration was 150 mg/L, 40 mg/L, 10 mg/L and 2.3 mg/L, respectively (Figure 2). It is suggested that calcium hydroxide has a strong ability to remove the heavy metals in wastewater.

The effect of the treatment may depend on calcium carbonate as precipitant/ flocculant during the process, improve the removal effect. During the coagulation/flocculation a part of the calcium ions precipitated as calcium carbonate. These precipitates form an important part of the produced flocs. The amount of calcium carbonate precipitated may influence the concentration of heavy metals in the effluent. Calcium hydroxide is better used in complex wastewater than simulated single-metal wastewater because a lot of precipitates are generated during the treatment process of complex wastewater. As a seed material, various sediments including calcium carbonate make the heavy metal ions co-precipitated.

Calcium hydroxide also excellently removed most of heavy metals in the electroplating wastewater. The results have been summarized in Figure 3. The concentration of Ni^{2+} , Zn^{2+} , Cu^{2+} and Mn^{2+} in the untreated wastewater were 198.55 mg/L, 13.69 mg/L, 116.54 mg/L and 0.68 mg/L, respectively. From the experimental results it can be concluded that at pH about 10.5, calcium hydroxide could make the concentrations of heavy metals extremely low. Especially, Mn^{2+} and Ni^{2+} concentrations in the treated water appeared to below the detection limit (< 0.001 mg/L). More than 99 % of Cu^{2+} and Zn^{2+} were removed, the residual metal levels, Cu 0.12 mg/L and Zn 0.124 mg/L, are far below the Chinese discharge limits (Cu 0.5-2 mg/L, Zn 2-5 mg/L). Consequently, calcium hydroxide had better effect on the real wastewater than the simulated wastewater.

The pH working value for each metal is given by the solubility product constant at each pH, which shows an idea of the quantity of the metal dissolved and the quantity in the solid form. Solubility product constants of Mn^{2+} and Ni^{2+} hydroxides are known to be 1.9×10^{-13} and 2.0×10^{-15} , respectively (Dean, 2004). It should be very difficult to calculate the solubility of these compounds in the electroplating wastewater exactly. The large amount of impurities, such as organic matter, turbidity, hardness, etc. makes the solubility of the metals become higher, primarily due to the interactions between organic matter and metal (Beltrán & Sánchez, 2009). Under the premise that the hydroxides are dissolved in the distilled water, the Mn^{2+} and Ni^{2+} concentration were 0.1045 mg/L and 0.0012 mg/L when the concentration of these two compounds in the treated water at pH 10.5 were all < 0.001 mg/L. The removal of metal ions under these experimental conditions was dominated by effective co-precipitation.

Nowadays, heavy metals are the environmental priority pollutants, which are faced with more and more stringent regulations. The only way to remove them is to change their chemical and physical states by oxidation/reduction and precipitation. So far, there have been a number of researches that used physical and chemical methods to treat heavy metals-containing wastewater (Table 3-4).

Cu^{2+} , Zn^{2+} , Cr^{3+} , Pb^{2+} ions were successfully removed by using fly ash as a seed material to enhance precipitation with lime (Chen, Luo, Hills, Xue, & Tyrer, 2009b). They controlled the pH value to 7-11, the residual concentrations of chromium, copper, lead and zinc in effluents listed in Table 3 showed that the method was successful in reducing the level of soluble heavy metals in solution. In this study, we found the special phenomenon that at pH 10.5 a large amount of calcium carbonates were generated in the solution. By adjusting the pH to 10.5 with calcium hydroxide, instead of fly ash in the method mentioned above the calcium carbonates generated acted as the seed material, and the Zn^{2+} and Pb^{2+} concentrations were decreased to a third. Charentanyarak (Charentanyarak, 1999) employed chemical coagulation and precipitation by lime and Na_2S to treat synthetic wastewater. He found if coagulant was added, the residual concentration of heavy metal can be decreased further. However, there are potential dangers in applying precipitation with sulfide. Heavy metal ions are often in acid environment while sulfide results in the evolution of toxic H_2S fumes easily.

Membrane technology is one option for the separation of heavy metals from wastewater without generating any

pollution. The membrane process used to remove metals from wastewater includes reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF) and electrodialysis (ED). Mohsennia et al. (2007) successfully removed Cu^{2+} and Ni^{2+} ions by RO process. By using Na_2EDTA , the removal efficiencies of Cu^{2+} and Ni^{2+} were more than 99 %. The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes. As a result, RO has not been widely applied yet. In recent years, Murthy and Chaudhari (Murthy & Chaudhari, 2008) reported the application of NF-300 membrane for the elimination of Ni^{2+} from aqueous wastewater. They also investigated the separation capability of NF-300 membrane for binary heavy metals (cadmium & nickel) from aqueous solutions (Murthy & Chaudhari, 2009). And these two reports all indicated the removal efficiency of Ni^{2+} and Cd^{2+} decreases with concentration increase in influent at constant flow rate. Much smaller than 1.4 mg/L and 4.02 mg/L for the treated electroplating wastewater in this study, the final concentration of copper and nickel ions were just 0.12 mg/L and 0.0003 mg/L for an initial concentration of 116.54 mg/L and 198.55 mg/L, the removal rate reached to 99.89 % and 99.99 %, respectively. Whatever the initial concentrations were, the final heavy metals concentrations were all extremely low for the method by Murthy and Chaudhari.

Generally, coagulation-flocculation can't remove the heavy metals from wastewater completely (Chang & Wang, 2007). Coagulation-flocculation must be followed by other treatment techniques. So Beltrán and Sánchez (Beltrán & Sánchez, 2009) tested a new commercial tannin-based flocculant to remove Zn^{2+} , Ni^{2+} and Cu^{2+} by coagulation-flocculation process. Yuan et al. (2008) investigated the potential of ion flotation for the elimination of Cd^{2+} , Pb^{2+} and Cu^{2+} from dilute aqueous solution with a plant-derived bio-surfactant tea saponin. Its disadvantages involve high initial capital cost, high maintenance and operation costs. The electrochemical (EC) system with aluminium electrodes was used for removing Mn^{2+} ion and the process which combined the EC system with electroflotation (EF) / electrocoagulation (EC) cell was investigated on the removal of zinc from synthetic solutions (Casqueira, Torem, & Kohler, 2006; Shafaei, Rezayee, Arami, & Nikazar, 2010). The results of their study revealed that Mn^{2+} removal rate decreased with the initial concentration of the contaminant. Electrochemical treatment techniques, which require fewer chemicals, provide good removal efficiencies and produce less sludge, are regarded rapid and well-controlled. However, the relatively large capital investment and the high electricity supply lead to the limited application of electrochemical wastewater technologies. Due to its selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} , clinoptilolite is one of the most frequently studied natural zeolites (Babel & Kurniawan, 2003). It can be seen from Table 4 that Doula and Dimirkou (Doula & Dimirkou, 2008) employed Clin and the Clin-Fe system to simultaneously remove Cu^{2+} , Mn^{2+} and Zn^{2+} from drinking water. Compared with the synthetic resin, the use of zeolites as ion-exchange resin is limited at present since ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. Moreover, the cost is expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration. Consequently, ion-exchange resins cannot be used at large scale.

Although all the above-mentioned treatment techniques can be employed to remove heavy metals from wastewater, each of them has its inherent advantages and limitations. In general, the methods possess high removal efficiency require high capital cost and complex operations. For both the synthetic wastewater and the electroplating wastewater, calcium carbonate generated during the treatment process can serve as a coagulant to greatly remove the heavy metal ions by precipitation, and the ultimate concentrations all could meet the corresponding regulations.

3.3 Characterization of Sediment

As is known to all, the crystal particles of CaCO_3 are rectangular prisms. Its surface is smooth and the edges and angles are sharp and clear (Figure 4). Many rectangular prisms aggregate and wedge each other together.

In Figure 4 there are some substances with rough surface, attaching on the outside surface of CaCO_3 . The floccules were also wrapped in various rectangular prisms. Without doubt, the floccules are hydroxides, which have been adsorbed on the outside surface of CaCO_3 and wrapped in it. The large amount of CaCO_3 generated increased the particle size of the precipitate, improved sedimentation of sludge and the removal efficiency of Pb.

3.4 Phosphorus and Alga Removal

3.4.1 Phosphorus

Influx of Phosphorus (P) into freshwater ecosystems is the primary cause of eutrophication which has many undesirable effects. Without significant commercial or industrial loads, the influent concentration of total phosphorus in waste water treatment plant (WWTP) effluent may range from 6-8 mg/L as P (Sengupta & Pandit, 2011). In this study, the removal efficiency of phosphorus by calcium hydroxide was also investigated in the

synthetic wastewater. The concentration of P was initially 10.8 mg/L and finally decreased to 0.379 mg/L, which met the regulatory requirements (< 0.5 mg/L).

Calcium hydroxide was effective to remove the various forms of P in the river water (Figure 5). Experimental results show that most of the phosphorus was removed. The removal rates of TDP and PP were, respectively, 57.05 % and 78.53 %, and the final concentration of TP was 0.124 mg/L, for an initial concentration of 0.445 mg/L. The water quality on TP was improved from worse than class V to class II water.

3.4.2 Alga

As a photosynthetic pigment integrating all types of algae, chlorophyll a is a measurable parameter for whole algal production. When the pH value was decreased to 10.5, the concentration of chlorophyll a reached 0.009 mg/L (Figure 6). According to the fix boundary Chl a criteria system of OECD (1982), after removal, the quality of original water was enhanced from serious eutrophication to mid-eutrophic state.

3.5 Bio-toxicity Detection

The purpose of this part was to investigate the effect of exposure to alkalinity on the four organisms which were fancy carp, daphnia, seed, Luminescent bacterium *Q67*.

There are two key antioxidant defense systems found in many organisms to prevent oxidative stress and maintain health. One consists of antioxidant enzymes including SOD, CAT, et al. SOD plays an important role in the scavenging of superoxide free radicals, which helps to maintain a balance between oxidant and antioxidant. CAT act cooperatively in the liver as scavengers of hydrogen peroxide. MDA is one of the main manifestations of oxidative stress induced by various hepatotoxins (Li, Chung, Kim, & Lee, 2005).

To investigate the potential impacts of alkaline environment on fancy carp, SOD, CAT and MDA were investigated by two different groups of the fancy carp, one of which was exposed to constant pH 10.5 and the other under natural aeration-scale. MDA, CAT, SOD activities in the liver of the fish after exposure to the natural aerated alkaline environment for 0.5, 1, 2, 5, 8, 12 days are shown in Figure 7. The Figure 7A showed SOD activities in the test group were all lower than the control group. The performance of inhibition on SOD could be seen after 12 hours exposure, which indicated the fancy carp soon produce the stress of oxidation but antioxidant enzymes need a lagging process to react to the stress of oxidation. The activities of antioxidant enzyme (CAT) significantly increased in the livers of the 2th day of alkalinity-exposed fancy carp, as compared to the control fish (Figure 7B). This indicated that toxin-induced oxidative stress activates these antioxidant enzymes to eliminate reactive oxygen species (ROS) and protect cells from lesions. Increased lipid peroxidation was detected from the first day to the fourth day in the present study (Figure 7C). This is probably caused by the environment in which fish lived. But in the eighth day the MDA began to fall, indicating that the damage levels of the body's cells attacked by free radicals were not as serious as the original.

The changes of MDA, CAT, SOD concentration in the experimental fish group exposed at the constant pH 10.5 were shown in Figure 8. The general variation trend of CAT and MDA were similar to the natural aerated group in addition to change very quickly. But there were obvious changes in the absolute concentrations of CAT and MDA. This might be because that the constant pH value of the water environment made fancy carp greater stress. What's more, Figure 8A showed that SOD declined at 12h and completely recovered at the 4th day. The reason was the active oxygen began to inspire, arousing the generation of antioxidant enzymes. With the extension of exposure time, the enzyme activity was down again, since there appears poisoning in the experimental fish owing to the excessive exposure.

What discussed above indicated that the alkalinity had some impact on the fancy carp. Because the aeration made the pH value fall sharply, the pH value could decrease to the normal level about 8 in four hours. With the decrease of alkalinity, the damage on the tissue of fish was also weakened.

In the beginning of the daphnia experiment, the test solution with different pH value was prepared. As shown in Figure 9, the survival rate of daphnia in 24 h was 100 % when pH value was not more than 10.5. Decreased survival rate (75 % and 37.5 %, respectively) was observed at the pH value of 10.8 and 11.0 after 24 h. These phenomena indicated that the solution with pH less than 10.5 had a little adverse effect on the daphnia. When the pH of the solution was adjusted to 11.3 with calcium hydroxide, daphnia was all dead. This may be caused by the joint toxicity of calcium ion and alkalinity. Along, the concentration of calcium ions increased rapidly after pH 10.6 with the continuous addition of calcium hydroxide.

It was suggested from Figure 9 that the relationship between inhibition rate of seed germination and the pH value appeared to be positively correlated. The GC_{50} of the cabbage seeds was found at pH 12.05.

The pH value at which the relative luminance was 50 %, also regarded as the pH value of half luminescence inhibition against *Q67* (EC_{50}), was obtained with linear interpolation method. The standard errors of three parallel experiments for each pH value were less than 10 %. The EC_{50} value for *Q67* was 11.13, respectively.

In summary, alkalinity had a poisonous effect on the four tested organisms and the different effect among pH values was significant. It can be thought that the toxicity of the alkaline solution at the adjusted pH value of 10.5, as well as the smaller pH under natural aeration, on the living beings was slight. 100 % seed germination was observed at the pH value 10.5. Both *Daphnia* and *Q67* did not show the poisoning symptoms. Consequently, pH 10.5 adjusted by calcium hydroxide had little influence to the organisms under natural aeration.

4. Conclusions

In this study, we found a phenomenon that the concentration of calcium ion was minimal when pH was adjusted to the golden point of 10.5 with calcium hydroxide. The precipitation of heavy metals with calcium hydroxide which adjusted the pH value of wastewater to 10.5 was shown to be successful in reducing the concentration of soluble heavy metals. The generated calcium carbonate improved the removal efficiency of heavy metals from the synthetic wastewater and electroplating wastewater, making the residual concentration meet regulatory requirements. Compared with the conventional methods, the precipitation with calcium hydroxide adjusting the pH to 10.5 has several advantages: high removal efficiency, low operating cost, production of more concentrated sludge and little influence to the aquatic organisms. What's more, the method also has very good effect on the removal of algae and P. Precipitation, coagulation, flocculation with calcium hydroxide for the adjustment of the pH value to 10.5 can also be used to remove algae from eutrophication water. It was, therefore, apparent that the method would be robust for application in treating the problem water, for example, micro-polluted water, heavy metal-containing industrial wastewater and eutrophication water.

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Table 1. Jar tests with simulation wastewater by calcium hydroxide and sodium hydroxide

pH	Heavy metal concentration (mg/L)											
	Sodium hydroxide						Calcium hydroxide					
	Cd	Mn	Zn	Ni	Cu	Pb	Cd	Mn	Zn	Ni	Cu	Pb
7	NA	4.664	4.589	NA	2.059	NA	NA	4.653	5.012	NA	2.037	NA
8	NA	3.748	0.664	1.910	1.482	0.147	NA	3.964	0.945	1.954	1.303	0.155
9	0.031	2.974	0.092	1.740	1.349	0.114	0.034	1.732	0.040	1.454	0.941	0.135
10	0.006	0.615	0.0008	0.648	1.107	0.043	0.002	0.422	0.021	0.700	0.566	0.028
10.5	0.002	0.204	0.011	0.453	0.815	0.023	0.001	0.082	0.012	0.259	0.066	0.016
11	0.003	0.005	0.013	0.428	0.854	0.041	0.0008	ND	0.027	0.091	0.033	0.017

NA: not available; ND: not detect.

Table 2. Jar tests with simulation wastewater by calcium hydroxide

pH	Heavy metal concentration (mg/L)					
	Cd	Mn	Zn	Ni	Cu	Pb
6	NA	NA	NA	NA	150	NA
7	NA	NA	NA	NA	2.723	NA
8	NA	65.040	14.020	10.210	1.258	NA
9	0.079	48.680	0.874	6.160	1.170	0.688
10	0.012	2.192	0.267	1.220	0.917	0.388
10.5	0.002	0.416	0.093	0.451	0.948	0.020
11	0.003	0.071	0.185	0.200	1.128	0.014

NA: not available.

Table 3. A list of some selected examples of heavy metal removal by chemical precipitation, membrane filtration, coagulation and flocculation, flotation, electrochemical treatment

Methods	Species	Conditions	Ultimate metal conc.	Removal efficiency	Ref.
chemical precipitation	Cu ²⁺ , Zn ²⁺ , Cr ³⁺ , Pb ²⁺	fly ash-lime-carbonation treatment	0.14, 0.45, 0.08, 0.03 mg/L	99.37-99.6	(Chen et al., 2009b)
	Zn ²⁺ , Cd ²⁺ , Mn ²⁺ , Mg ²⁺	Na ₂ S-lime	0.4, < 0.1, 0.7, 5 mg/L	50-99.59	(Charemtanyarak, 1999)
membrane filtration	Cu ²⁺ , Ni ²⁺	RO- EDTA -operation pressure 5 atm	1.4, 4.02 mg/L	99.14-99.72	(Mohsennia et al., 2007)
	Cu ²⁺	NF-transmembrane pressure(1-3bar)	236.8-339.2 mg/L	47-66	(Chaabane et al., 2006)
	Cu ²⁺	RO+NF-combination of flotation and membrane filtration, 3.8 bar	0.15-0.75 mg/L	95-99	(Sudilovskiy et al., 2008)
coagulation and flocculation	Zn ²⁺ , Cu ²⁺ , Ni ²⁺	Tanfloc with an optimum value in 7, 6 and 8	5, 2, 6 mg/L	75, 90, 70	(Beltrán & Sánchez, 2009)
flotation	Cu ²⁺ , Cd ²⁺ , Pb ²⁺	ion flotation when the ratio of collector to metal was 3:1	0.121 mg/L, 0.323 mg/L, 0.208 mg/L	81.13, 71.17, 89.95	(Yuan et al., 2008)
	Cu ²⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺	colloidal ferric hydroxide precipitate- a modified column flotation	0.4, 0.8, 0.9, 0.2 mg/L	90-99	(Capponi et al., 2006)
electrochemical treatment	Mn ²⁺	EC process with aluminium electrodes, current density of 6.25 mA/cm ²	21.7 mg/L	78.2	(Shafaei et al., 2010)
	Zn ²⁺	electroflotation - sodium dodecyl sulfate (SDS) as collector in the stoichiometric ratio 1:3, current density of around 8 mA/cm ²	0.8 mg/L	96	Casqueira et al., 2006
	Ni ²⁺ , Cu ²⁺	Electroflotation: Current 0.3 mA	1 mg/L	98-99	(Khelifa et al., 2005)

Table 4. Heavy metal removal using chemical ion-exchange

Species	Ion-exchange	Adsorption capacity	Removal efficiency	Ref.
Cu ²⁺	Clin and the Clin-Fe system	13.6 mg/g, 37.5 mg/g	NA	(Doula & Dimirkou, 2008)
Pb ²⁺	clinoptilolite	0.21-1 meq/g	20-40	(Inglezakis, 2003)
N ⁱ²⁺	clinoptilolite	0.11 meq/g	93.6	(Argun, 2008)

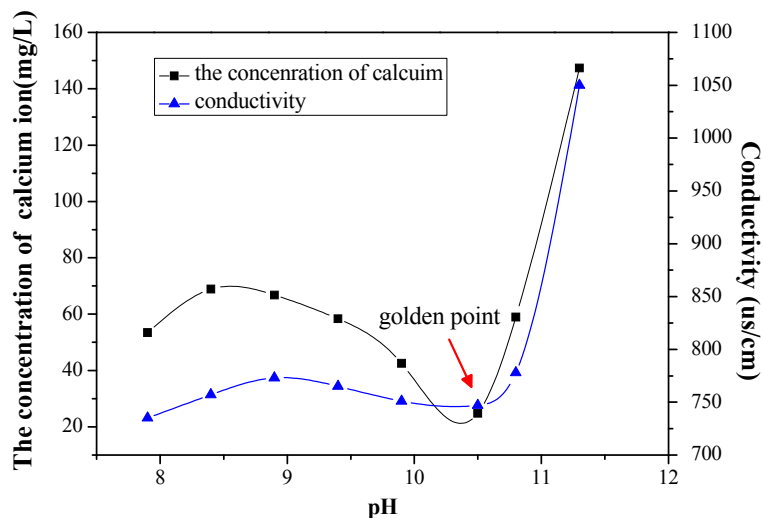


Figure 1. The effect of pH on the concentration of calcium ion and the conductivity

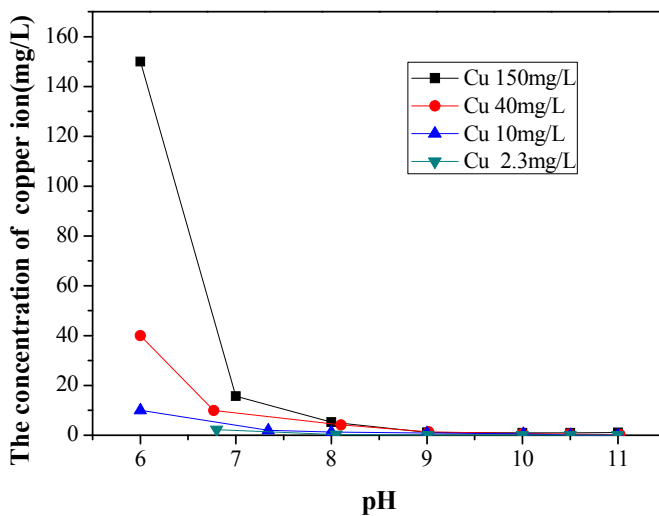
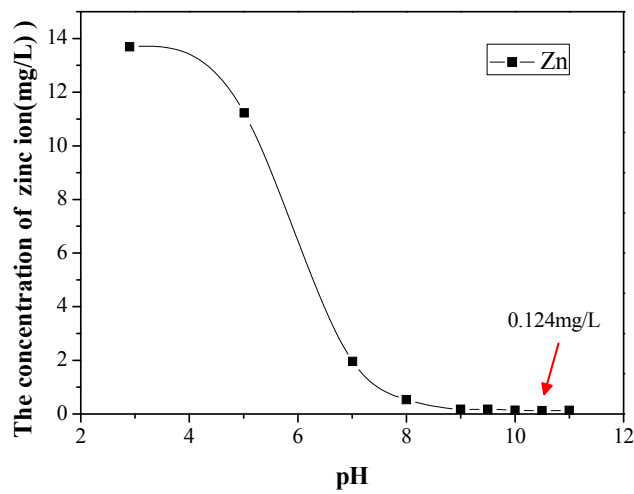
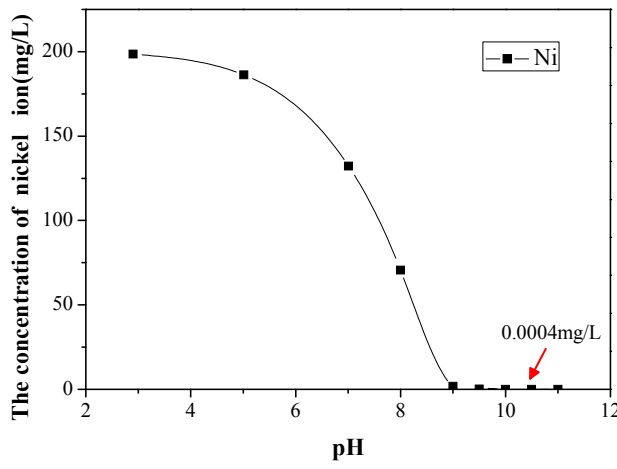
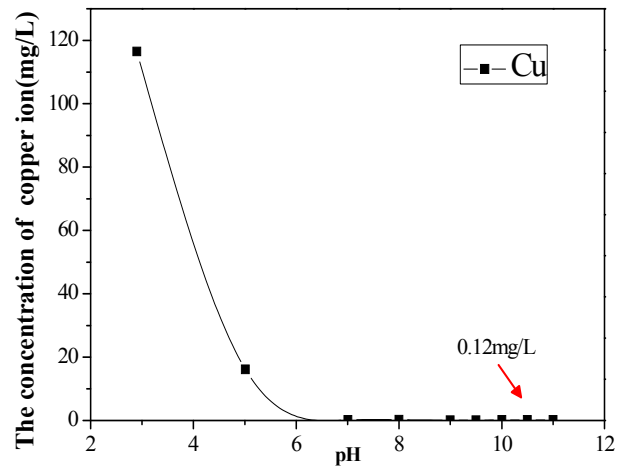


Figure 2. The effect of pH on the concentration of copper ion with different initial concentration



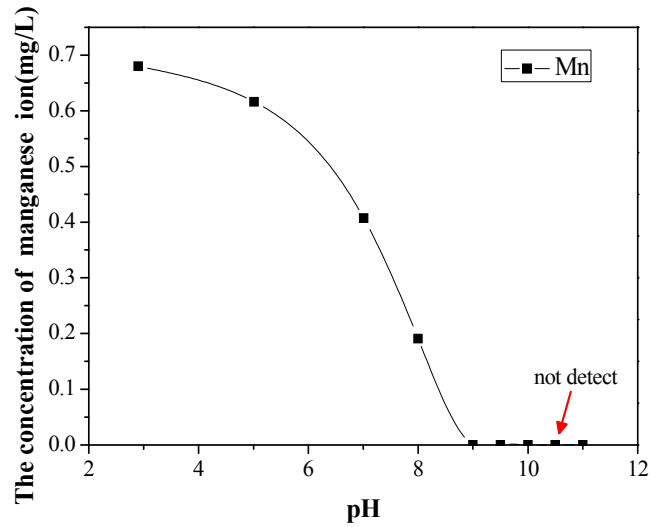


Figure 3. The relationship between pH and the concentration of Cu, Ni, Zn and Mn ion

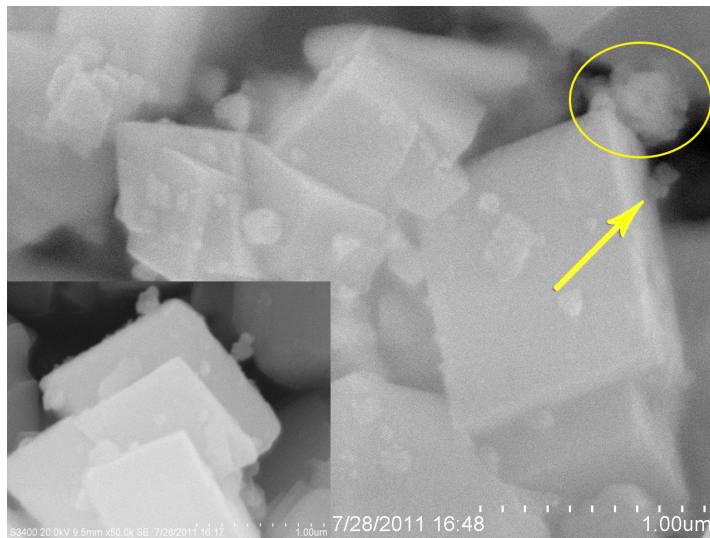


Figure 4. SEM images of Pb as hydroxide attached on CaCO₃

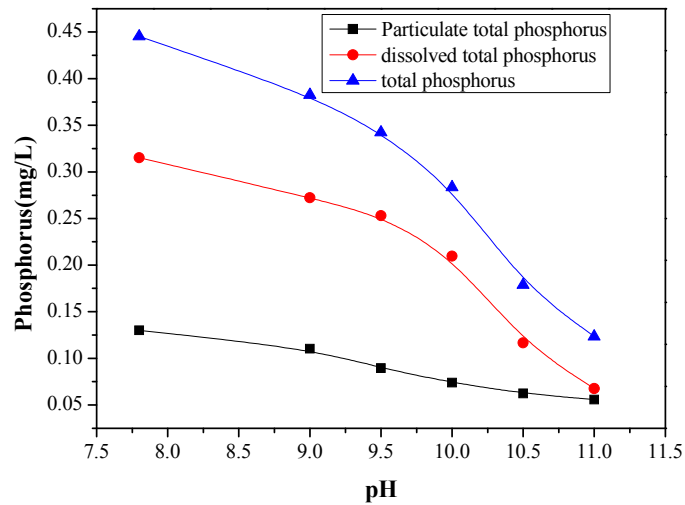


Figure 5. The concentration varying trends of TP, TDP and PP at different PH value

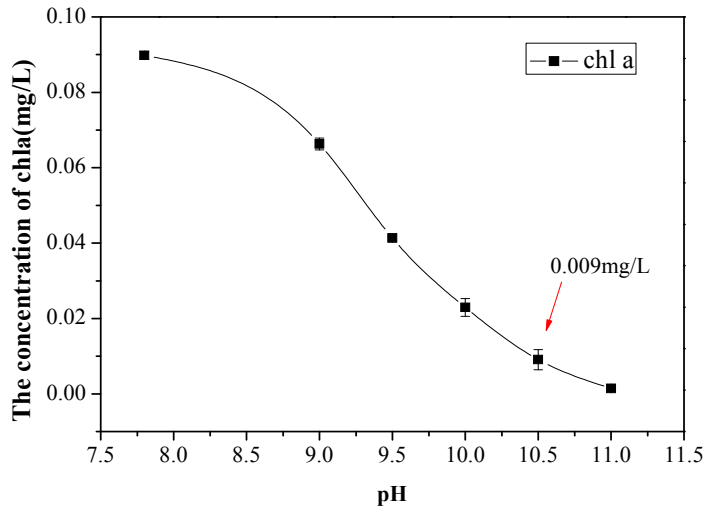
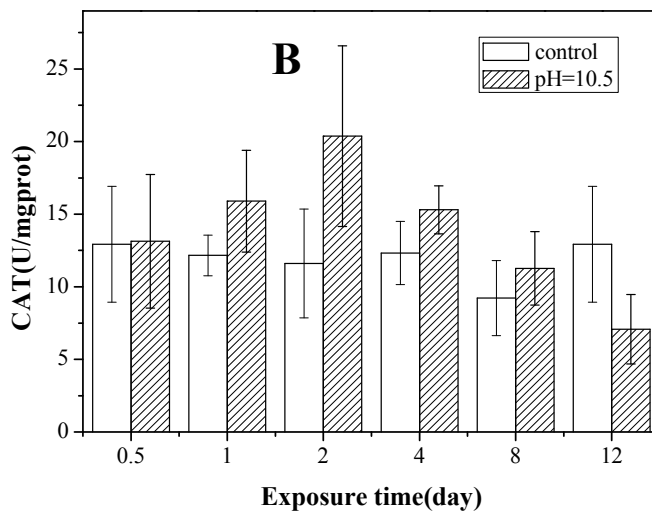
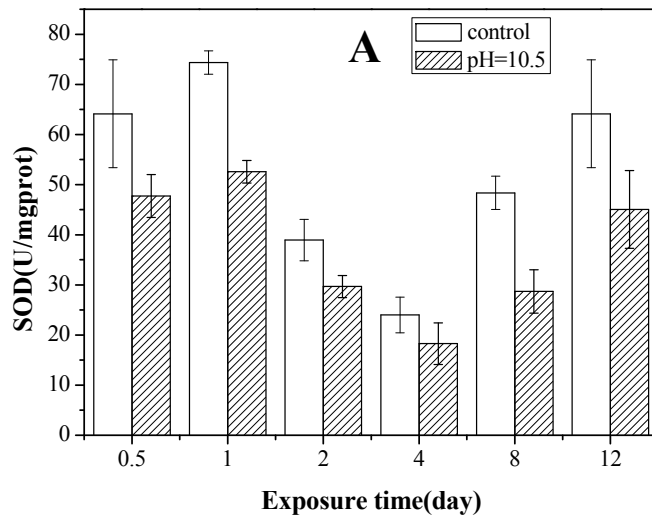


Figure 6. The relationship between pH and the concentration of chl a



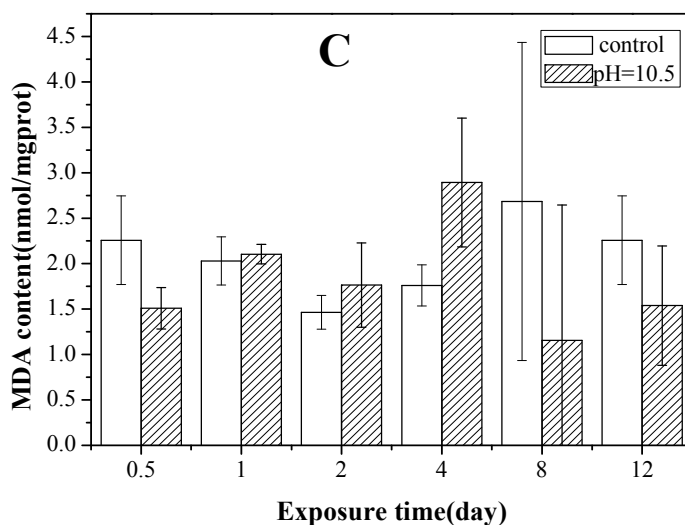
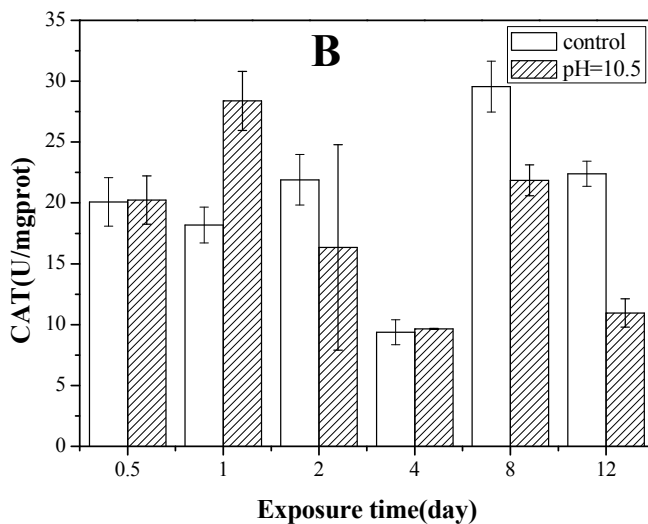
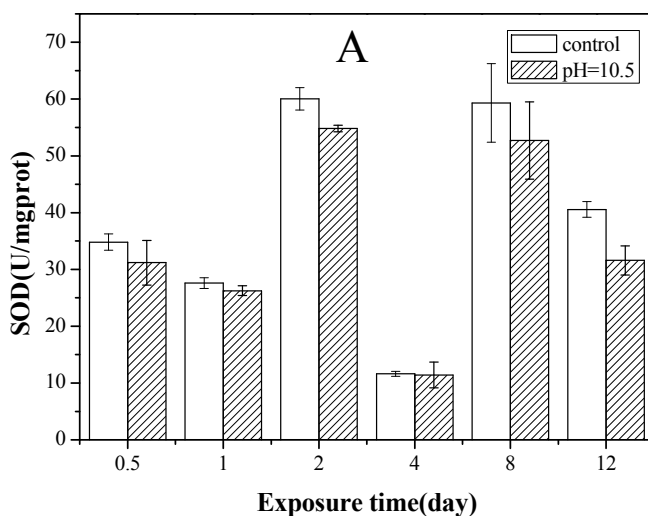


Figure 7. The level of SOD, CAT and MDA in the liver of fish which were exposed to alkalinity under natural aeration-scale in different time. Values were presented as the mean of three individual fish



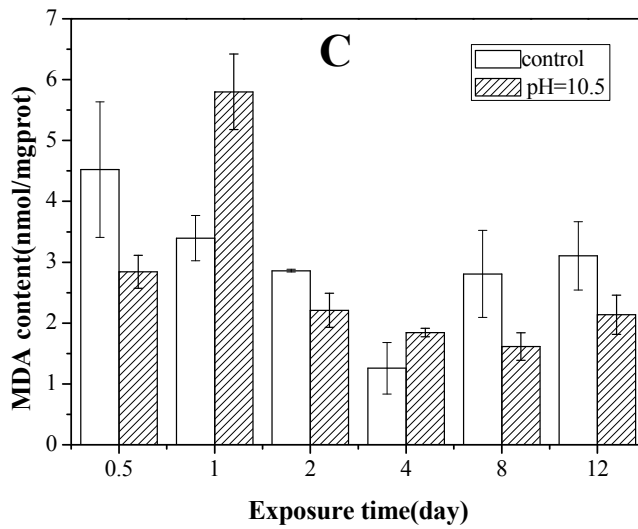


Figure 8. The SOD, CAT and MDA level in the liver of fish after different exposure time to alkalinity at the constant pH 10.5. Values were presented as the mean of three individual fish

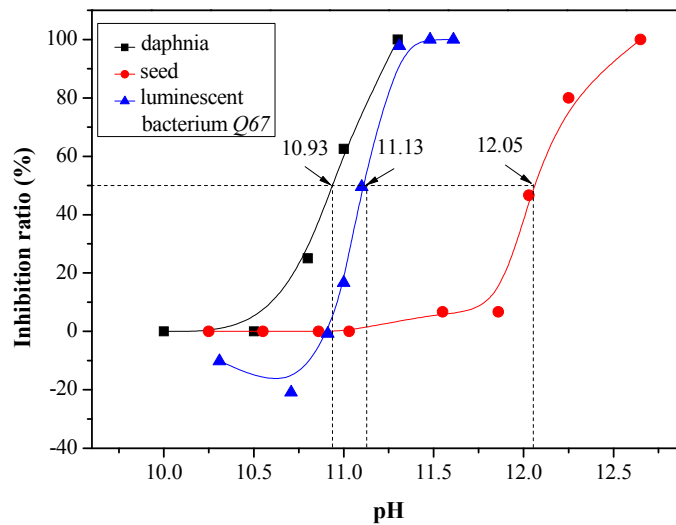


Figure 9. The impact of high pH values on the four tested organisms