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Heavy metals uptake by inorganic particles and activated sludge in WWTP

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ABSTRACT

In order to verify whether a conventional wastewater treatment process can provide sufficient protective screen of heavy metals, a long-term regular monitoring of the influent, effluent, and water at different stages of a domestic wastewater treatment plant was conducted, targeting As, Cd, Cr, Cu, Hg, Pb and Zn. For most of the heavy metals, more than 50%'s removal efficiency could be obtained by the whole treatment process, in which a fraction of heavy metals was removed by the primary settling tank, while the following biological unit made great contribution to heavy metal removal. Through a series of adsorption experiments using quartz sand, kaolin of known size distribution as inorganic adsorbents and laboratory-cultured activated sludge as organic adsorbent for adsorbing model of As and Cr, it was found that the adsorption of heavy metals by the inorganic adsorbents well followed by the Langmuir isotherm with the saturation capacity proportional to the specific surface area of the solid particles, indicating a single-layer adsorption property. However for the activated sludge, its adsorption isotherm showed a property of multilayer adsorption and the adsorption capacity was one order higher than the inorganic particles. The different behavior between the activated sludge and the organic particles for heavy metals adsorption explained the mechanism of heavy metals decay in the different stages of the conventional wastewater treatment plant and indicated that the activated sludge in the biological treatment plant played an important role for heavy metals removal. Models obtained from the adsorption experiment were practical, and can provide an approach to predicting the contents of heavy metals in the WWTP's effluent.

KEYWORDS

Activated sludge; Adsorption isotherm; Heavy metal; Inorganic particles.

INTRODUCTION

With the rapid development of economy and urbanization, there is an increased demand for water resource. As a consequence, large quantities of wastewater are discharged, carrying various contaminants including heavy metals into water environment[1]. Heavy metal pollution with the feature of concealment, bioaccumulation, chronicity and irreversibility, which makes it distinguished from other types of pollutants[2,3]. Heavy metals are easily soluble in water, and can be adsorbed by organisms. Heavy metals can be accumulated in the human body, once entering the food chain[4]. When the accumulation of heavy metals reaches a certain level, it will exert a toxic effect on bodies, which gives a serious threat to human health. For example, the excessive ingestion of zinc brings about serious toxicological concerns, including stomach cramps, skin irritations, vomiting, and so on[5]. Too much copper can cause obvious health problems, such as vomiting, cramps, convulsions, or even death[6]. The significant accumulation of mercury can do harm to central nervous system, the most prominent example of mercury poisoning is minamata disease. And the event of 'Itai-Itai Disease' in Japan was a result of chronic cadmium poisoning. In order to protect human health and environment from heavy metal pollution, many criteria have been proposed and passed to limit the emission of heavy metals. Many countries have made the control of heavy metal pollution an environmental priority in recent years. Facing the stricter limitations, it is imperative to remove heavy metals from the water.

People have been exploring new technologies to treat heavy metal wastewater for decades. Methods had been proposed and developed to remove heavy metals in wastewater, such as chemical precipitation (hydroxide precipitation and sulfide precipitation), ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc[7]. Though these methods have many advantages, they are poor in processing efficiency and expensive in cost when used to treat wastewater with low concentration of heavy metals, in addition, the disposal of sludge produced during treatment processing is another problem to be solved, so most of these methods are not eco-friendly[8]. Recently, microorganism has been considered to be an effective bio-adsorbent. Although it is a relatively new technology to use bio-adsorbents for heavy metal adsorption, its extensive sources, low cost, easy operation makes it a accepted method[9,10], and promising in the treatment of wastewater with low concentration of heavy metals. Activated sludge process in a wastewater treatment plant (WWTP) with microorganism at the core, can not only remove organic matters such as COD, BOD, NH^4-N and TP in wastewater effectively, but also reduce the content of heavy metals. by precipitation, adsorption or biodegradation with lower operating cost and similar even higher efficiency, which is considered to be a side benefit of activated sludge process[8,11,12]. Besides activated sludge process, other novel biological treatment technology for removing heavy metals had been developed rapidly in recent years[13,14]. At present, the research of heavy metal removal by activated sludge is mainly focused on: the occurrence of heavy metals during a WWTP[12,15], the modeling heavy metal uptake[16], the mechanism of adsorption[17], and the impact of heavy metal on the microorganisms[18-20], and so on.

But, few studies by far have systematically investigated heavy metals fading at different stages of wastewater treatment, and there isn't enough sufficient information or knowledge on the characteristics of interaction between heavy metal and inorganic particles versus that between heavy metals and activated sludge particles. The present work was thus aiming at clarifying these actions and related mechanisms by conducting both field investigation and laboratory experiment.

MATERIALS AND METHODS

Sample collection and analysis

Sample collection

According to the process flow (Figure 1) of one urban wastewater treatment plant in Xi'an, Shaanxi province in China, four sampling points were picked, which were fine screen, primary settling tank, oxidation ditch and secondary sedimentation settler. The designed capacity of the WWTP treatment was about 100 000$m^3 \cdot d^{-1}$, with Orbal Oxidation Ditch and reuse system. Samples were weekly

collected between May 18, 2008 and July 6, 2009, from the end of four facilities and brought back to the laboratory immediately for water quality analysis.

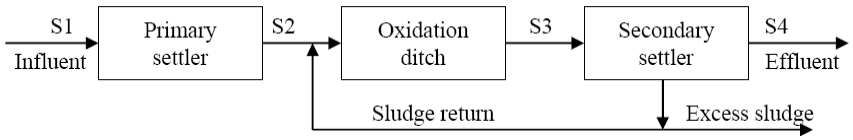

Figure 1 : Schematic flow diagram and sampling point of the WWTP

Sample pretreatment

The sample preparation procedure was as follows: The samples were centrifuged at 10,000 rpm for 30 minutes (SORVALL RC 6 Plus, Thermo) to separate the sludge from the supernatant. The supernatant were filtrated through 0.45μm filter membrane and the filtrates were chosen as aqueous phase. Then the aqueous phase was stored at 4°C before analysis. Then the sediment was air dried at room temperature, which was treated as solid phase. It was then crushed by the agate mortar, following be sieved through 100 mesh nylon sieve. Then the sludge gathered were digested using the ISO method.

Heavy metal analysis

In this study, seven metals were targeted: Cu, Zn, Pb, Cd, Cr, Hg and As, among which Cu, Zn, Cd and Pb were analyzed using atomic absorption spectroscopy (Avanta PM, GBC), Hg and As were determined by hydride generation atomic adsorption spectrometry (WHG-103 Peking Hanshi Manufacturing), while Cr was analyzed using ICP-MS (Elan DRC-e, PE). All the vessels were immersed in 20% analytical grade nitric acid for several hours and then flushed with ultrapure water for three times (Elix, Milli-Q). All experiments were performed in triplicate.

Adsorption experiment

Adsorbents

In this study, quartz and kaolin purchased from Sinopharm Chemical Reagent Co., Ltd. were chosen as inorganic adsorbents with different diameter and different specific surface area, and stabilized activated sludge was chosen as organic adsorbent. Each inorganic adsorbent was air dried, lightly grained by sieving through 100 mesh nylon sieve, and the particle size distribution was measured using a laser particle size analyzer (LS230/SVM+, Beckman Coulter), while the specific surface area was determined by BET method using a Micromeritics Gemini analyzer (Norcrocc). The size distributions and specific surface area of quartz sand and kaolinite used in this investigation were shown in Tab. 1. It is clear that quartz was about 2 times larger than kaolinite, and quartz has less specific surface area. Lab-scale reactors were operated in a computer-controlled sequencing batch mode according to the following sequence: unaerated feed, aerated reaction, settling, unaerated sludge withdrawal. The activated sludge used for adsorption experiment was cultured in it using synthetic wastewater to obtain sludge with identical characteristics during the experiment. The reactor was regulated sampled (usually once a day) at the end of the reaction for determination of the biomass. In addition, scanning electron microscope (S-3400N, Hitachi) was conducted for morphological observation of the sludge particles, the SEM pictures were shown in Figure 2.

Adsorption experiments

Batch sorption tests were carried out with 100mL of monometallic solutions to a 150mL beaker flask. To start the experiment, 100mg of the individual sorbents (Kaolinite or quartz sand) were introduced to a 100 ml solution containing heavy metals (10-100 $mg \cdot L^{-1}$). The flask was then transferred to a SHA-B model constant temperature shaker with a thermostat (Changzhou Guohua instrument Co., Ltd, China) and shaken under 160 oscillations per minute for 24h at 298K to ensure the sorption process can reach equilibrium. HNO_3 (1.0 M) was used to adjust the pH of solution throughout the experiment

when necessary. For the analysis of unadsorbed metal concentration, the acidification of the solution was not necessary since the pH was always lower than the precipitation values for all metals. The amount of each heavy metal loaded on the sorbent was calculated by conducting a mass balance before and after the test. After shaken, the suspensions were centrifuged at 10,000 rpm for 15min (Sorvall RC 6 Plus, Thermo). The determination of initial and equilibrium concentrations of Cu and Zn was the same as that mentioned above. The amounts of metals adsorption were calculated from the difference between their concentrations in solutions before (initial concentration) and after (equilibrium concentration) adsorption experiments. pH was also determined in the initial and centrifuged equilibrium solutions. All experiments were performed in triplicate and the average of the results is presented.

TABLE 1 : Characteristics of inorganic adsorbents

Adsorbents	TOC (%)	Mean particle size (μm)	Specific surface area ($m^2 \cdot g^{-1}$)
Quartz sand	0.0065	3.674	6.38
Kaolin	0.0111	1.918	15.63

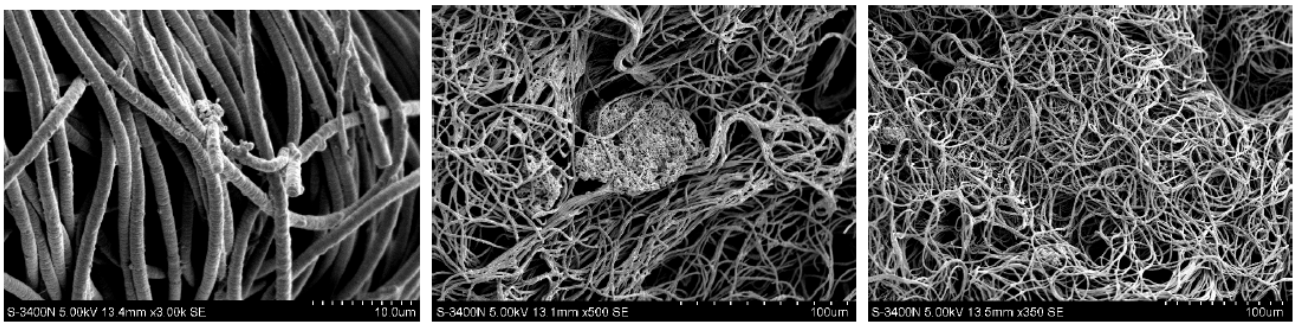

Figure 2 : SEM image of the activated sludge

RESULTS AND DISCUSSION

Distribution of heavy metals and their removal characteristics in WWTP

Occurrence of dissolved heavy metals in WWTP

Generally in a WWTP, primary settling tank is designed to remove suspended solid with diameter less than 0.1mm, while oxidation ditch is supposed to remove organic matters like COD, BOD, NH_4-N and T-P, in which the aeration causes a drop in pH. Finally the residual contaminants, especially the heavy metals, are further removed in secondary sedimentation settler since the pH in secondary settler is a little higher than that in oxidation ditch (See Figure 3).

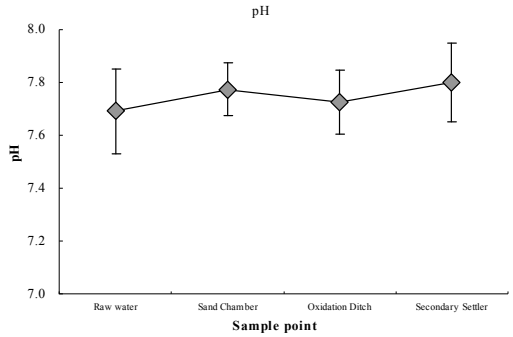

Figure 3 : Vibration of pH in different stages in WWTP

With about one year's consistent monitoring between May 18, 2008 and July 6, 2009 from the WWTP in Xi'an, the distribution of these seven heavy metals in dissolved states at different stages is shown in Figure 4. As shown in Figure 4, the contents of these seven metals in untreated water were in order of Zn>Cr>Cu>As>Cd>Hg>Pb, and most metals entered the WWPT at trace levels ($\mu g \cdot L^{-1}$), among which zinc generally at relatively high concentrations, with 59.8$\mu g \cdot L^{-1}$ approximately, indicating that urban wastewater in that area was not polluted by heavy metals seriously. Figure 4 also shows that all the heavy metals were progressively reduced along the treatment process, indicating that four wastewater treatment facilities in WWTP own a certain capacity for removing heavy metals, with leaving about several microgram per liter in the effluent. And the effluent of WWTP was safe for landscape reuses and municipal greening.

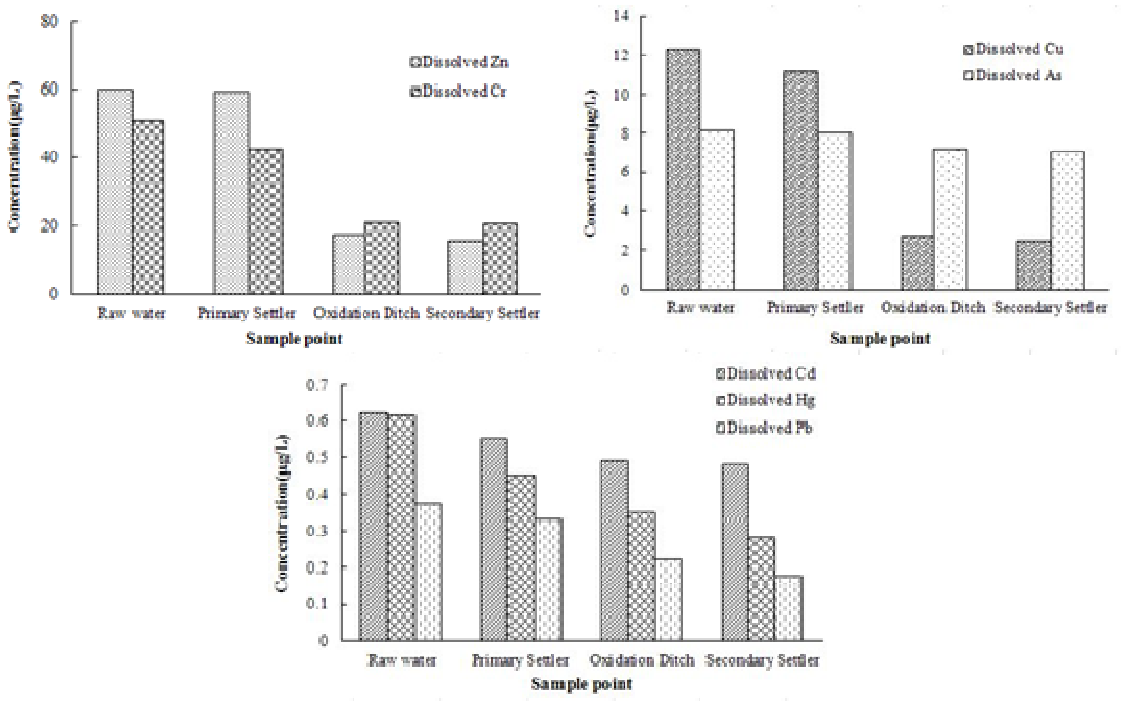

Figure 4 : Average distribution of the dissolved Cu, Zn, Pb, Cd, Hg and As in the different stages

Removal efficiencies of heavy metals in each stage and the whole treatment process

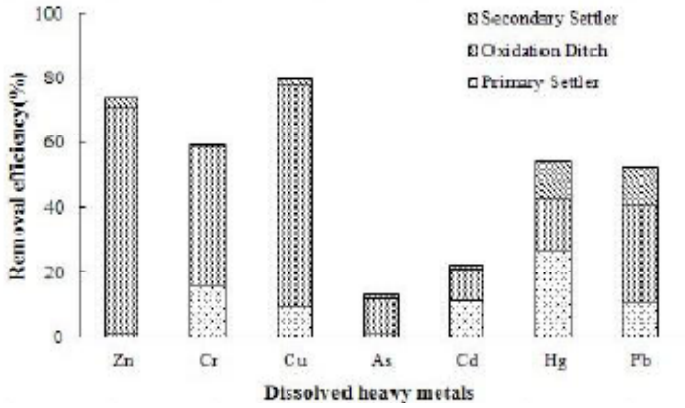

Figure 5 : Separate removal efficiency of the dissolved heavy metals

It can be found from Figure 5 that different removal efficiencies could be achieved in such a WWTP, ranging from 13% for As to 80% for Cu, and each facility was capable of removing heavy metals. Figure 5 shows that the process of WWTP could remove effectively Cu and Zn in aqueous phase with about 80%'s removal efficiencies, and nearly 60%'s removal efficiency could be obtained for Cr, Hg and Pb, but there were less removal efficiencies for both As and Cd. For each treatment stage, the oxidation ditch played a major role in removing Pb, Cu, Cr and Zn. Most of Pb, Cu, Cr and Zn was transferred to the activated sludge in oxidation ditch, which reduced their content in aqueous phase, indicating that the removal of Pb, Cu, Cr and Zn depended mainly on biochemical function. As shown in Figure 5, the primary settling tank and secondary sedimentation settler made great contribution to the removal of Cd, Hg and Pb, which means physical precipitation could remove these three metals in aqueous phase with effect, especially for Hg.

Removal efficiencies interrelate with the hydrate-radius of heavy metal and hydrolyzation. The adsorption of metal ions was closely related with their hydration radius and hydrolysis. The smaller hydration radius and the larger charge density per area of cation, the easier approaching to the surface of colloid. Cd, Pb, Hg, Cu and its major hydrolysis product with smaller hydration radius were positively charged, so the adsorption effect is obvious. On the contrary, As which were negatively charged with larger hydration radius, is difficult to be adsorbed on suspended solid, and has less removal efficiency during wastewater treatment.

The distribution of Cu, Zn, Cd, Pb, Cr, Hg and As in solid phase

The distribution of these heavy metals in solid phase was also investigated in this study, as summarized in Tab.2. All data was calculated by average, and 95% confidence interval was picked. It could be found that Zn appeared to be the most abundant metal with 1677.9 mg $Zn \cdot kg^{-1}$ sludge, which may have something to do with the widely use of galvanized pipe, while Hg exhibited the lowest abundance, and their contents were Zn, Cr, Pb, Cu, As, Cd and Hg in decreasing order, which was slightly different from those in aqueous phase. As mentioned above, Pb entered the WWTP with lowest content in aqueous phase, but it became the third for content in solid phase, it may be resulted from that most of Pb had already transferred into suspended solids before entering the WWTP, Pb in solid phase almost makes up the total concentration of Pb during the WWTP process. The distribution of heavy metals in solid phase could also evaluate the degree of heavy metal contamination in that area as that in aqueous phase. Besides Zn, Cr appeared at a relatively high content, which is necessary to pay attention to.

TABLE 2 : Range and mean values of metals in discharged sludge ($mg \cdot kg^{-1}$)

Metal	Mean±SD
Cd	23.2±3.4
Cu	290.6±36.8
Zn	1677.9±194.4
Pb	381.8±52.7
Hg	5.22±1.02
Cr	684.8±43.2
As	24.59±4.16

SD: standard deviation (with picking 95% confidence interval)

Metal Balance during the process of wastewater treatment

As above, heavy metals in aqueous phase were transferred into solids during the process of WWTP, so there must be a material balance. That is to say, the decrease of heavy metal concentration in

aqueous phase must be equal to the increment of that in solid phase. In order to verify the assumption, the material balance of As and Cr was conducted in this study according to Figure 6. The material balance equation for each unit can be written as

$$QC_0 - QC_e = \Delta C_s M \quad \textbf{(1)}$$

where Q is the flow ($m^3 \cdot d^{-1}$)(to simplify the calculation, we assume that the inflow of a unit was equal to its outflow); C_0 and C_e are the heavy metal concentrations of influent and effluent ($g \cdot m^{-3}$); ΔC_s is the increment of the heavy metal concentration in the solid phase, which can be calculated from the difference between the contents in solid phase before and after the processing unit; and M is the mass of spoil disposal, for example,

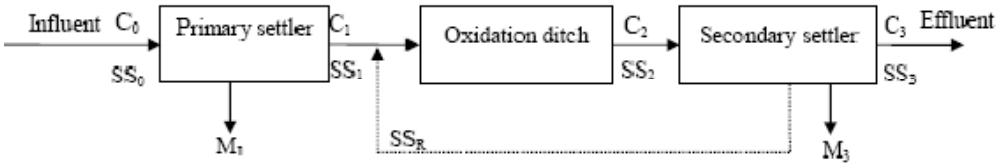

Figure 6 : Material balance along the WWTP

$M_1 = (SS_0 - SS_1)Q$.

The ΔC_s, decrease of As and Cr in aqueous phase and increment in solid phase of primary settling tank and activated sludge process were calculated with the data in Tab. 3 and the parameters obtained from long-term investigation. The results were shown in Tab. 4. It can be found from Tab. 4 that the material balance was indeed existent during the process of WWTP, since the decrease of As and Cr in aqueous phase is consistent with the increment in solid phase both for primary settling tank and activated sludge process. So the assumption above was proved to be reasonable.

Adsorption of heavy metals by inorganic particles and activated sludge

Theoretical aspects[21]

The Langmuir isotherm has been used extensively by many researchers for the sorption of heavy metal ions in clay, metal oxides, soils, etc. The Langmuir isotherm is a valid monolayer adsorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the surface. The Langmuir equation may be written as

$$q_e = \frac{q_{\max} b C_e}{1 + bC_e} \textbf{ (non-linear form)} \quad \textbf{(2)}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b} \times \frac{1}{C_e} \textbf{ (linear form)} \quad \textbf{(3)}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent ($\mu g \cdot g^{-1}$); C_e is the equilibrium concentration of solute in the bulk solution ($\mu g \cdot L^{-1}$); q_{max} is the monolayer adsorption capacity ($\mu g \cdot g^{-1}$); b is the constant related to the energy of adsorption and it is the value reciprocal of the concentration at which half the saturation of the adsorbed is attained.

Adsorption isotherms

The adsorption isotherms are of significance because they exhibit the concentration dependent equilibrium distribution towards adsorbate between the solution and the adsorbent in some condition[8].

Figure 7 shows the adsorption isotherms of As and Cr using the three types of the adsorbent mentioned above at 298K. The constants for the two ions in addition to R^2 values for each line are also shown in Figure 7. It can be seen from these figures that activated sludge gives the highest value of q_{max}, indicating that adsorbents with different particle size and specific surface area have different capacity to adsorb metal ions, the larger specific surface area is, the higher value of q_{max} is. In conclusion, the affinity of the adsorbents towards As and Cr is as follows: activated sludge > Kaolinite > Quartz.

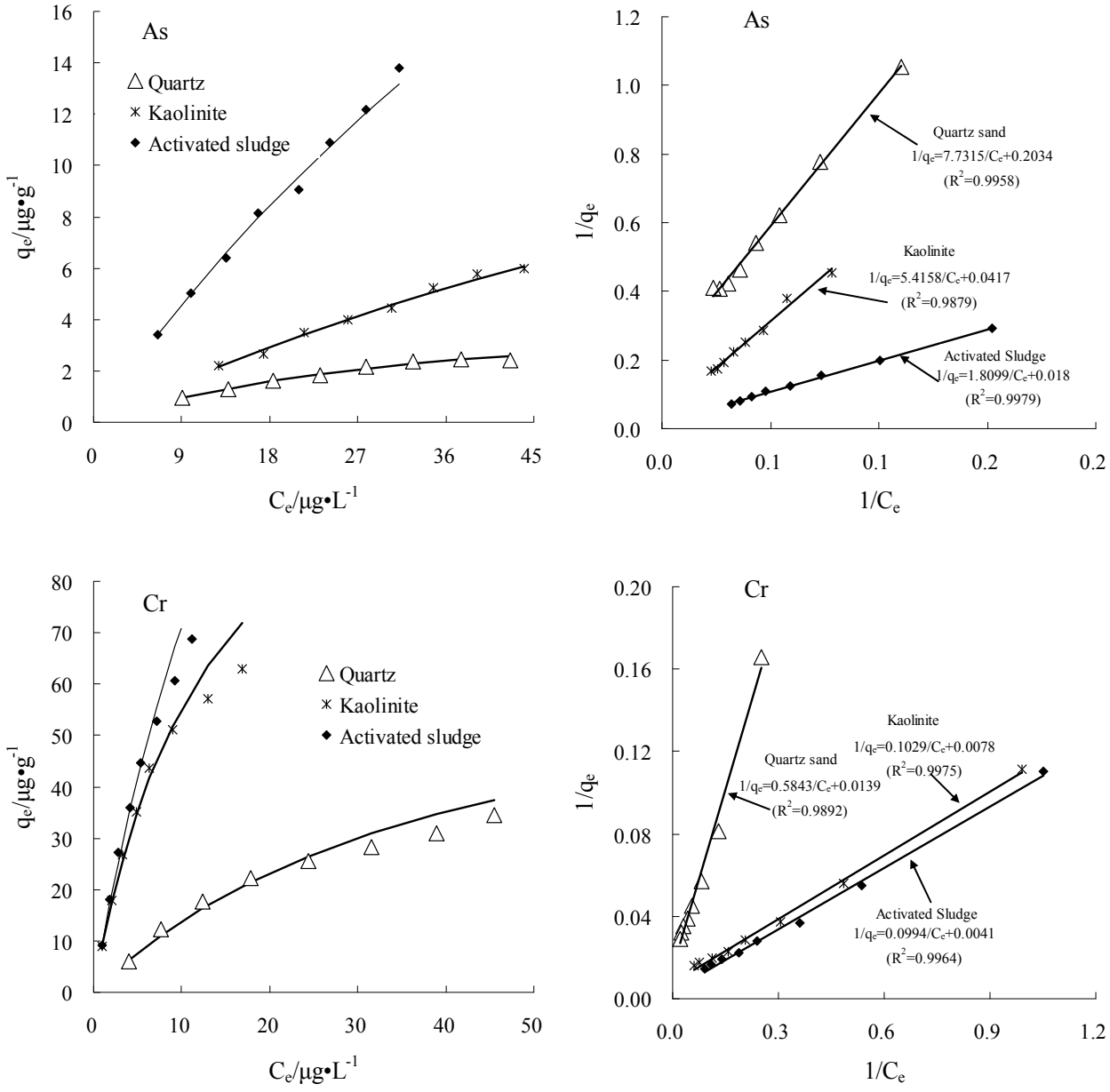

Figure 7 : Adsorption isotherms for As and Cr using the three types of adsorbent. Temperature =25°C, pH=6.0, mixing speed=160 rpm, adsorbent concentration=1000mg·L^{-1} MLSS, solution volume=100mL, contact time=24h.

Predicting the removal efficiencies of heavy metals

In order to explain how As, Cr were removed in the WWTP using the information obtained from adsorption experiment, a set of mathematic models were developed following the principle of material balance. As above, the material balance could be conducted based on Figure 6 under an assumption that

in the primary settling tank, heavy metals removal was only performed by adsorption onto inorganic particles, while in the oxidation ditch, the effect of volatilization and biodegradation were ignored. For a unit in the treatment process, the material balance can be simply written as

$$Q_0C_0 - Q_eC_e = m \quad \textbf{(4)}$$

where Q_0 and Q_e are the inflow and outflow of this unit ($m^3 \cdot d^{-1}$); C_0 and C_e are the heavy metal concentrations of influent and effluent ($g \cdot m^{-3}$); and m is the mass of heavy metals removal in this unit ($g \cdot d^{-1}$). To simplify the calculation, we assume that $Q_e \approx Q_0$ when the flow for desludging is neglected.

As the heavy metals are removed by their adsorption onto particles, the mass of heavy metals removal can be evaluated as

$$m = M_pK_pC_e \quad \textbf{(5)}$$

where M_p is the mass of solid particles in processing unit ($g \cdot d^{-1}$); K_p is the partition coefficient of heavy metals in it ($m^3 \cdot g^{-1}$). Substituting Eq. (5) into Eq. (4) will yield

$$Q_0C_0 - Q_eC_e = M_pK_pC_e \quad \textbf{(6)}$$

and the removal of heavy metals in this unit can be calculated as

$$R = \frac{C_0 - C_e}{C_0} = \frac{M_pK_p}{M_pK_p + Q_0} \quad \textbf{(7)}$$

And the adsorption follows the Langmuir adsorption model,

$$R_{cal} = \frac{M_pK_p}{M_pK_p + Q_0} = \frac{M_p\frac{q_{\max}b}{1+bC_e}}{M_p\frac{q_{\max}b}{1+bC_e} + Q_0} = \frac{M_pq_{\max}b}{M_pq_{\max}b + Q_0(1+bC_e)} \quad \textbf{(8)}$$

and $C_e = C_0(1 - R_{cal})$

$$\textbf{so } R_{cal} = \frac{M_pq_{\max}b}{M_pq_{\max}b + Q_0(1+bC_e)} = \frac{M_pq_{\max}b}{M_pq_{\max}b + Q_0[1+bC_0(1-R_{cal})]} \quad \textbf{(9)}$$

and the value of R_{cal} is between zero and 1, so we should only choose :

$$R_{cal} = \frac{\frac{M_pq_{\max}b + Q_0 + bC_0Q_0}{bC_0Q_0} - \sqrt{(\frac{M_pq_{\max}b + Q_0 + bC_0Q_0}{bC_0Q_0})^2 - \frac{4M_pq_{\max}b}{bC_0Q_0}}}{2} \quad \textbf{(10)}$$

The predicted removal efficiencies of As and Cr in the primary settling tank (by quartz and kaolinite) and activated sludge process (by quartz, kaolinite and activated sludge) were calculated

respectively with Eq. (10). The actual removal efficiencies were also calculated with the data in Tab. 3. The results were shown in Tab. 5. It can be found from Tab. 5 that the removal of As and Cr in the primary settling tank was supposed to be performed by their adsorption onto inorganic particles, since the predicted removal efficiencies were consistent with the actual ones achieved by kaolinite. The calculated K_p–R relation can reasonably reflect the practical condition in the WWTP, and the different level of removal for these metals is due to the difference in their equilibrium partitioning coefficient K_p. When it came to activated sludge process, the predicted removal efficiency of As obtained by activated sludge was consistent with the actual one, indicating that the removal of As during the activated sludge process was mainly depended on the adsorption onto activated sludge. But for Cr, the actual removal efficiency is larger than that calculated by kaolinite, but smaller than that calculated by activated sludge, which may manifest that the removal of Cr was conducted by the combined effects of kaolinite and activated sludge. Taken together, the models developed in this study fit well to the actual removal efficiencies of heavy metals in a WWTP, which provides a realistic method of predicting the contents of heavy metals in a WWTP's effluent when the influent concentration is known.

CONCLUSIONS

The present study tried to investigate the characteristics of heavy metal removal by conventional wastewater treatment process under the assumption that adsorption onto particle surface may be the main mechanism. Quartz, kaolinite and activated sludge were used to simulate the different suspended solids in the WWTP. A series of heavy metal (As, Cr) adsorption by quartz, kaolinite and activated sludge were conducted to investigate the different adsorption ability for heavy metals. The activated sludge has the largest adsorption ability to heavy metals indicating that activated sludge can be easily used as a cheap bioadsorbent for heavy metals. The main finding from the adsorption experiment was that the inorganic particles and activated sludge displayed Langmuir adsorption characteristics. Finally, a set of mathematic models were developed using the information obtained from adsorption experiment, which proved to be very realistic, and could be used to predict the contents of heavy metals in a WWTP's effluent. This continuous process will be subjected of further investigations in our labs.

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