



Adsorption abilities by heavy metals and inorganic particles and activated sludge in domestic wastewater treatment plant

Dejun Kang*¹, Hong Tang¹, Danyu Xie¹ and Pengzhen Ke*²

¹School of Municipal Engineering, Department of Civil Engineering, Fuzhou University, No 2, Xueyuan Road, University Town, Fuzhou, Fujian, P. R. China

²Hubei Environmental Monitoring Station, Wuhan, Hubei, P. R. China

ABSTRACT

In order to understand if a conventional wastewater treatment process can provide sufficient protective screen of heavy metals, a long term monitoring was conducted for the influent, effluent, and water at different stages of a domestic wastewater treatment plant. As a result, eight heavy metals such as As, Cd, Cr⁶⁺, Cu, Hg, Mn, Pb, Zn were detected. For most of the heavy metals about 40% removal could be obtained by the secondary treatment process. Of the total removal, 10 to 20% was achieved by the primary settling, while 20 to 40% was achieved by the following biological units. 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 the eight heavy metals, 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 of the activated sludge from the organic particles for model 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 unit played the main role for heavy metals adsorption.

Keywords: activated sludge, adsorption isotherm, heavy metal, inorganic particles, wastewater treatment plant

INTRODUCTION

Many industrial and metallurgical process in addition to some human activities produce rapidly increasing amounts of wastewater containing heavy metals ions in appreciable concentration. The heavy metals in environmental pollution, were mainly referring to mercury, cadmium, lead, chromium, arsenic and other metals as well as the type of significant toxicity, and also some other general toxic metals such as zinc, copper, cobalt, manganese, tin, etc^[1]. The heavy metal contamination was unlike the other types of pollution, but with the ability of concealed, bioaccumulated, long-term existed and unreversed^[2-3]. In addition, these ions are non-degradable and thus persistent, leading to both ecological and health problems. Most of the heavy metals were highly harmful even at very low concentration, which is about 0.1-0.3mg•L⁻¹^[4]. In the aquatic system the heavy metal compounds are very stable. It is not a easy thing to detoxify heavy metal compounds by the microbiology. In contrast the compounds can be biotransformed by the microbiology to other organic compounds with increasing toxicity. The concentration of heavy metals can be up to very high standards by the enrichment of the food chain of aquatic organisms. After the heavy metals are absorbed by the human body, some kinds of them can react with human physiology odd molecular substances such as protein and enzyme. After the reaction protein and enzyme will lose activity and accumulate in the organs. As the result chronic poisoning will be caused^[5].

Among the 7 heavy metals, the maximum contaminant level (MCL) of mercury has been set as 2 µg/l for drinking water in the United States (USEPA, 2009a^[6]), and 1 µg/l in World Health Organization drinking water guideline (WHO, 2004^[7]), and six heavy metals are under consideration for their health consequence in drinking water (USEPA, 2009b^[8]).

Table 1. Guideline of heavy metals

	WHO drinking water guideline (mg/L)	US EPA MCLG (mg/L)	US EPA MCL (mg/L)
As	0.01	0	0.010
Cd	0.003	0.005	0.005
Cr	0.05	0.1	0.1
Cu	2	1.3	1.3
Pb	0.01	0	0.015
Mn	0.4	-	-
Hg	0.001	0.002	0.002

Therefore, China classifies the concentrations of heavy metals as the important indicators of water pollution, so that considers the concentration as one of the important aspects of monitoring and controlling of water pollutions. In China, there were strictly limit of seven heavy metal pollutants, as total mercury, alkyl mercury, total cadmium, total chromium, hexavalent chromium, total arsenic and total lead in ‘The reuse of urban recycling water—Water quality standard for scenic environment use discharge standard of pollutants for municipal wastewater treatment plant’^[9]. It was strictly controlled of the maximum allowable emission concentration, and strictly enforced. And also, another seven metal ions were limited at the same time as selected control indicators, which were choose to implement. And also, the same 14 kinds metals were limited in national standards “urban sewage water recycling water quality Landscape”^[10]. It is an important duty to reduce the emission of heavy metals in urban wastewater treatment

At present, the main research focused on the determination of influent and effluent heavy metal concentrations; the effect of heavy metal influence on the microorganisms in activated sludge, the treatment and disposal methods of the heavy metal sludge, as well as the heavy metal impact on the environment and so on. Petrasek studied the total heavy metal removal efficiency^[11]; He Pei-sun studied the characteristics of municipal sewage sludge and analysis on the prospects of its reuse^[12]; Li Yin studied the bioleaching of heavy metals in sludge^[13]. There were few study of the distribution of physical forms of heavy metals and their trends of migration and transformation in urban wastewater treatment process. In abroad, they focused on the heavy metal migration from the wastewater to the sludge^[14-15]. There was still little necessary research of the heavy metal migration in the whole wastewater treatment plant at home.

A large number of experimental research and engineering practice shows that the heavy metal in urban wastewater were effectively removed during the wastewater treatment process^[11, 16-17]. There were wide range sources of heavy metals in urban wastewater, which were seriously eco-toxic. The species distribution of heavy metals in biological wastewater treatment process, removal and migration trends, influencing factors and other issues need further study. To investigate the distribution of metal ions in various processing units is the key factor to distinguish the metal migration and transformation mechanism in wastewater treatment plant^[18-19].

It has been observed that increasing pH favors the adsorption of metal ions because of less competition between H⁺ and metal ions for adsorption sites^[20].

In a wastewater treatment plant, the conventional secondary treatment process, such as the activated sludge process, is in fact a train of several treatment units including primary sedimentation, aeration, and secondary sedimentation and so on. Few studies by far have systematically investigated heavy metals fading at different stages of wastewater treatment, and there is yet 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. A series of urban wastewater in one WWTP of Xi’an, China was picked to investigate the mechanism of representative heavy metals removal by the wastewater treatment plant (WWTP). Under determine the four kinds of basic control project (Pb, Cd, Hg, As) and two kinds of the maximum allowable emissions (Cu, Zn,) heavy metals and SS concentrations of the effluent of the fine screen, primary settler, oxidation ditch and secondary sedimentation settler, it is wished to find the kinetics and partition aspects of the heavy metal transportation.

MATERIALS AND METHODS

Main equipments were floor type high-speed refrigerated centrifuge (SORVALL PC 6 Plus, U.S. Thermo Co.), electronic analytical balance (METTLER TOLEDO), pure water and ultra pure water machine (Elix, Milli-Q), ISO

condensate digestion devices, Atomic Absorption Spectrophotometer (GBC Avanta PM). Main reagents were 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ single element standard solution of Cu, Zn, Mn, Cr, Hg and As (National Research Center for Certified Reference Materials), excellent pure HNO_3 , excellent pure HCl , excellent pure H_2SO_4 . Adsorption experiments were performed using synthetic stock solutions of 1000mg/L of prepared from chemical reagents: $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2\cdot \text{H}_2\text{O}$ and $\text{Na}_3\text{AsO}_4\cdot 12\text{H}_2\text{O}$ respectively. All chemicals are of analytical grade or higher and were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.1 Sample collection and analysis

2.1.1 Sample collection

According to the process flow (Figure 1) of one urban wastewater treatment plant in the Xi'an, four sampling points were picked, which were at the end of fine screen, primary settler, oxidation ditch and secondary sedimentation settler. The WWTP treatment capacity was about $100\,000\text{m}^3\cdot\text{d}^{-1}$, with Orbal Oxidation Ditch and Reuse System. Samples were weekly collected from May 18, 2008 to July 6, 2009, from the end of four facilities and brought back to the laboratory immediately for quality analysis.

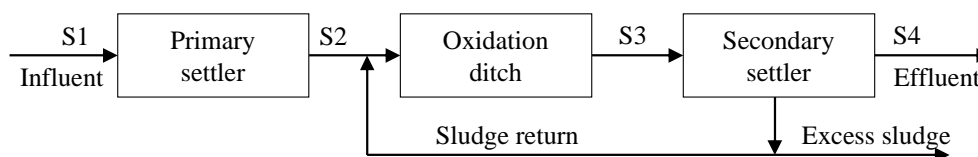


Fig. 1 Schematic flow diagram and sampling point of the WWTP

2.1.2 Sample pretreatment

The samples collected were centrifuged at 10,000 rpm for 30 minutes to separate the sludge from the supernatant. The supernatant were filtrated through $0.45\mu\text{m}$ filter membrane and the filtrates were chosen as aqueous phase. Then the aqueous phase was stored at 4°C before analysis. Then the centrifugation sediment was air dried at room temperature. It was then crushed by the agate mortar, following be sieved through 100 mesh nylon sieve.

2.1.3 Heavy metal analysis

(1) Detection method of dissolved Cu, Zn, Pb and Cd^[21-22]

The samples were adjusted to pH 1-2 with excellent pure HNO_3 . Then the supernatants obtained after centrifugations and filtrations were analyzed for the respective metal ions using an atomic absorption spectrometry. In practical, the dissolved Cu, Pb and Cd were analyzed by the graphite furnace atomic absorption spectrometry, while the dissolved Zn was analyzed by Flame atomic absorption spectrometry^[17].

(2) Detection method of dissolved Hg

Accurate 50.0 ml samples were taken to a colorimeter tube, with added 2 ml of concentrated sulfuric acid. Then an appropriate amount of 1% potassium permanganate was added, until the sample being micro-purple. The sample was analyzed by the method of hydride generation - atomic absorption spectrometry.

(3) Detection method of dissolved As^[23]

Accurate 50.0 ml sample were taken to a beaker, with added 50ml of nitric acid and 0.5 ml of perchloric acid, then to be heated until the white smoke existing above the surface. After cooling, by the order 8 ml of (1+1) hydrochloric acid, 1 ml of mixed liquor of 3% potassium iodide, 1% Ascorbic acid, 1% thiourea will be add into the nitrified liquid. Then it was diluted in a 50 ml volumetric flask by adding water. The diluted liquid was fully shaken, and after next 30min, tested by the method of hydride generation—atomic absorption spectrometry and the blank solution was prepared at the same time.

2.2 Adsorption experiment

2.2.1 Adsorbents

The quartz and kaolin were bought from Sinopharm Chemical Reagent Co., Ltd. , using as the inorganic adsorbents. Each adsorbent was air dried. Lightly grained, and following be sieved through 100 mesh nylon sieve. The particle size distribution was measured using a laser particle size analyzer (), and the specific surface area was determined by BET method using a Micromeritics Gemini analyzer(Norcrocc, USA).There size distributions were in table 2, while the specific surface area of quartz sand and kailinite were 6.38 and $15.63\text{ m}^2/\text{g}$, which depicts size distribution of quartz and kaolinite used in this investigation. The activated slydgel for the adsorption experiment was cultured in a lab-scale sequence batch reactor using synthetic wastewater for obtain sludge with identical characteristics during the experimental period. Scanning electron microscope (SEM, Hitachi S-3400N) was conducted for morphological observation of the sludge particles. It is clear that quartz was about 20 times bigger than kaolinite, and quartz has

less specific surface area.

Table 2 Characteristics of inorganic adsorbents

Adsorbents	TOC (%)	Mean particle size (μm)	Specific surface area (m^2/g)
Quartz sand	0.0065	3.674	6.38
Kaolin	0.0111	1.918	15.63

2.2.2 Typical heavy metals

For there were strictly limit of seven heavy metal pollutants, as total mercury, alkyl mercury, total cadmium, total chromium, hexavalent chromium, total arsenic and total lead in “The reuse of urban recycling water—Water quality standard for scenic environment use discharge standard of pollutants for municipal wastewater treatment plant”^[24], we choose Cu, Zn, Pb, Zn, Hg and As as six typical heavy metal ions.

2.2.3 Adsorption experiments

A lab-scale reactors was operated in a computer-controlled sequencing batch mode according to the following sequence: unreacted feed, aerated reaction, steeling, unreacted sludge withdrawal. The reactor was regulated sampled (usually once per day) at the end of the reaction phase for analytical determinations of the biomass as mixed liquor suspended solids(MLSS) and activated sludge picture were in Figure 5.

Batch sorption tests were carried out with 100mL of monometallic solutions to a 150mL . 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/l). The flask was then transferred to a SHA-B model constant temperature shaker with thermostat (Changzhou Guohua instrument Co., Ltd, China) and shaken under 160 oscillations per minute for 24h at 298K to ensure the sorption process to reach equilibrium. HNO_3 solution (1.0 M) was used to adjust the solution pH throughout the experiment when necessary. For the analysis of unabsorbed metal concentration, the acidification of the solution was not necessary since pH was always lower than the precipitation values for all metals. The amount of each heavy metal loaded on the sorbent is calculated by conducting a mass balance before and after the test. After shaken, the suspensions were centrifuged at 10,000 rpm for 15min (SORVALL PC 6 Plus, U.S. Thermo Co.). The initial and equilibrium concentrations of Cu(II), Zn(II), Cd(III) and Pb(II) were analyzed using absorption atomic spectroscopy (GBC Avanta PM, AAS). Hg and As were determined by Hydride Generation Atomic Absorption Spectrometry (WHG-103 Peking Hanshi Manufacturing). The amounts of metals sorbed were calculated from the difference between their concentrations in solutions before (initial concentration) and after (equilibrium concentration) sorption 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.

The supernatant was then analyzed for metal concentration by atomic absorption spectrometry. The percentage metal removal was determined based on the initial metal content in the sediment and all results are presented as percent metal removal. The sludge gathered were digested using the ISO method^[25].

The residual heavy metal concentration decreased abruptly according to time, and reached a constant after 24 h. However, the time required to reach an equilibrium state was 4–5h. Kayode found that the adsorption of Pb and Cd ions on kaolinite satisfactory fits the Freundlich isotherm. While at low concentration of metal ions, data also showed satisfactory fits to Langmuir isotherm^[26].

RESULTS AND DISCUSSION

Table 3 Range and mean values of metals in untreated wastewater ($\mu\text{g/L}$)

Metal	Mean \pm SD
Cd	0.64 \pm 0.27
Cu	12.31 \pm 2.71
Zn	59.8 \pm 8.7
Pb	0.36 \pm 0.18
Hg	0.63 \pm 0.24
As	8.12 \pm 2.97
Cr	50.60 \pm 2.97

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

3.1 Distribution of the dissolved Cu, Zn, Pb, Cd, Cr, Hg and As in domestic wastewater and characteristics of removal in WWTP

3.1.1 Detection of the six heavy metals from domestic wastewater

With about one year's consistence monitoring between May 18, 2008 and July 6, 2009 from one of the municipal wastewater treatment plant in Xi'an, Shaanxi province in China, the dissolved metal concentrations were as table 3. All data was calculated by average, and 95% Confidence Interval was picked. It can be found that zinc generally entered the treatment plant at high concentrations, with about 59.8 $\mu\text{g/L}$ in the raw water. And there was a little Cd, Pb and Hg in the four treatment stages. Along the treatment stage, all the heavy metals were progressively reduced.

3.1.2 Occurrence of heavy metals in WWTP

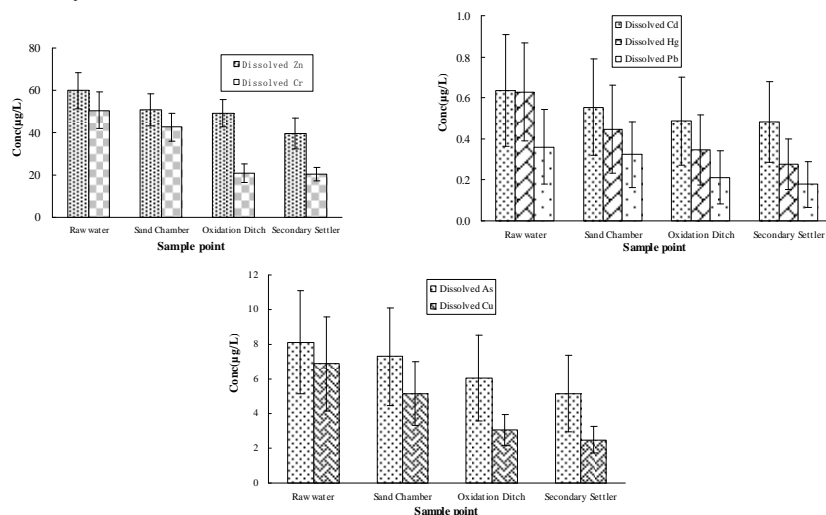


Fig. 2. Average distribution of the dissolved Cu, Zn, Pb, Cd, Hg and As in the different stages

As can be seen from Figure 2: The contents of six kinds of heavy metals were in order of $\text{Zn} > \text{Cu} > \text{As} > \text{Cd} > \text{Hg} > \text{Pb}$, but the values of metal content were very low with trace ($\mu\text{g}\cdot\text{L}^{-1}$), indicating that urban sewage polluted by metal ions was not very serious. The contents of six kinds of heavy metals were decreased gradually in the sewage treatment process, indicating that four wastewater treatment facilities in urban wastewater treatment plant (WWTP) own a certain capacity for removing metal ions.

3.1.4 The distribution of Cu, Zn, Mn, Cr, Hg and As in the solid phase

Table 4 Range and mean values of metals in discharged sludge (mg/kg)

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

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

The process of municipal wastewater treatment plant could remove As, Hg and Cu in aqueous phase, the removal efficiency of which was general, among which primary settler and secondary sedimentation settler played a major role in the removal of Zn, indicating that the removal of Zn depends mainly on physical precipitation. 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.

It can be found that different heavy metals were removed differently in such WWTP, and the primary settler also had a little ability to remove heavy metals, while it has less ability than oxidation ditch and secondary settling tank. And the primary settler were designed to remove suspended solid with diameter less than 0.1mm, while oxidation ditch

was designed to remove organic matter like COD and BOD, $\text{NH}_4\text{-N}$ and T-P, and in secondary settling tank slight matter were further removed. Through simulate experiment, quartz and kaolin were chosen as different diameter and different specific surface area inorganic adsorbent, and stabilized activated sludge were chosen as organic adsorbent.

3.2 Adsorption of typical heavy metals by inorganic particles and activated sludge

3.2.1 Theory of Langmuir adsorption isotherms^[27]

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 absorption 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

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

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b} \times \frac{1}{C_e} \quad (\text{linear form}) \quad (2)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent($\mu\text{g/g}$), C_e , the equilibrium concentration of solute in the bulk solution ($\mu\text{g/L}$), q_{\max} , the monolayer adsorption capacity($\mu\text{g/g}$) and b is the constant related to the energy of adsorption. It is the value reciprocal of the concentration at which half the saturation of the adsorbed is attained.

3.2.2 Adsorption isotherms

The significance of the adsorption isotherms is that they present the concentration dependent equilibrium distribution towards adsorbate between the solution and the adsorbent at certain conditions.

3.3 Effect of adsorbent characteristics and adsorption parameters

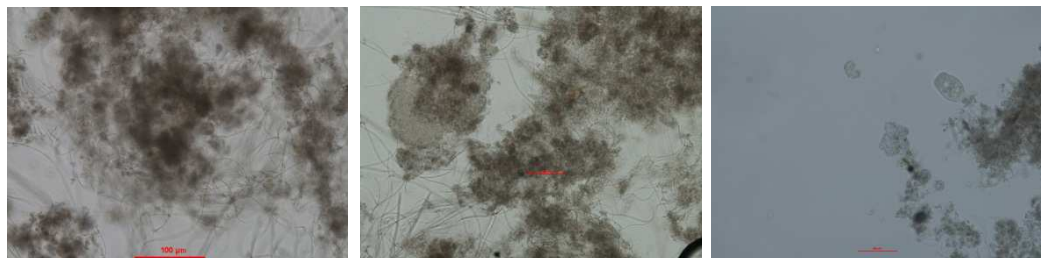


Fig. 5. Image of the activated sludge

Heavy metal removal in the primary settler

items	Cu	Zn	As	Cr
$\Delta C_{s1}(\text{mg/kg})$	13.8	6.1	1.49	100.2
Decrease in water phase of primary settler (kg/d)	0.097	0.051	0.010	0.671
Increase in solid phase of the primary settler(kg/d)	0.093	0.041	0.010	0.676

Heavy metal removal in the activated sludge process

items	Cu	Zn	As	Cr
$\Delta C_{s2}(\text{mg/kg})$	33.8	167.2	3.68	86.1
Decrease in water phase of the activated sludge process (kg/d)	0.731	3.678	0.079	1.871
Increase in solid phase of the activated sludge process (kg/d)	0.736	3.639	0.080	1.874

3.5 Modeling of typical heavy metal removal in WWTP

In order to explain how Cu, Zn, As and Cr were removed in the WWTP using the information obtained from adsorption experiment, a set of mathematic models were developed following the principle of mass balance. In a WWYP, particles that can perform heavy metals adsorption may include two categories, i.e. inorganic particles and

activated sludge particles. Therefore, a series of adsorption experiments were conducted using quartz sand and kaolinite as representative inorganic adsorbent, and lab-cultured activated sludge as organic adsorbent for adsorbing six typical heavy metals. Therefore, the mass balance could be calculated based on Fig. 8 under an assumption that in the primary settler, heavy metals removal was only performed by adsorption on to inorganic particles, while in the oxidation ditch, in addition to adsorption, while the effect of volatilization and biodegradation can be ignored.

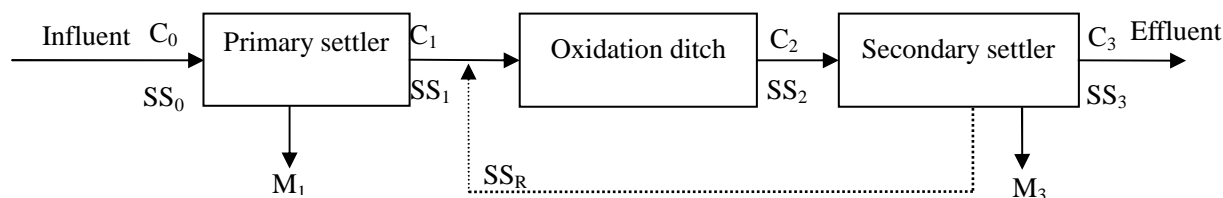


Fig. 8. Mass balance along the WWTP

For the primary settler, the mass balance can be simply written as

$$Q_0 C_0 - Q_1 C_1 = m_1 \quad (3)$$

where Q_0 and Q_1 are the inflow and outflow of the primary settler (m^3/d), C_0 and C_1 are the heavy metal concentrations of influent and effluent of the primary settler (g/m^3), and m_1 is the mass rate of heavy metals removal in the primary settler (g/d). For simplifying the calculation, we can assume that $Q_1 \approx Q_0$ when the flow for desludging is neglected.

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

$$m_1 = M_{p1} K_{p1} C_1 \quad (4)$$

where M_{p1} is the mass of solid particles in the primary settler (g/d), K_{p1} is the partition coefficient of heavy metals in the primary settler (m^3/g). Substituting Eq. (4) into Eq. (3) will yield

$$Q_0 C_0 - Q_1 C_1 = M_{p1} K_{p1} C_1 \quad (5)$$

and the removal of heavy metals in the primary settler R_1 can be calculated as

$$R_1 = \frac{C_0 - C_1}{C_0} = \frac{M_{p1} K_{p1}}{M_{p1} K_{p1} + Q_0} \quad (6)$$

where $Q_1 \approx Q_0$ is considered.

In the activated sludge process, the mass balance can be written as

$$Q_1 C_1 - Q_3 C_3 = M_3 \quad (7)$$

where Q_1 and Q_3 are the inflow of the oxidation ditch and effluent (m^3/d), C_1 and C_3 are the heavy metals concentrations of influent of the oxidation ditch and effluent (g/m^3), M_3 was the mass rates of heavy metals removal by adsorption. It can also be assumed that $Q_3 \approx Q_1 \approx Q_0$ when the desludging flow is neglected.

The mass rate of heavy metals removal by adsorption is similar to Eq. (4) as

$$M_3 = M_{p2} K_{p2} C_3 \quad (8)$$

where M_{p2} is the mass of waste activated sludge (g/d), K_{p2} is the partition coefficient of heavy metals in the activated process (m^3/g). The mass balance relationship becomes

$$Q_1 C_1 - Q_3 C_3 = M_{p2} K_{p2} C_3 \quad (9)$$

The removal of heavy metal in the oxidation ditch, R_2 , can then be calculated as

$$R_2 = \frac{C_1 - C_3}{C_1} = \frac{M_{p2}K_{p2}}{M_{p2}K_{p2} + Q_0} \quad (10)$$

where $Q_3 \approx Q_1 \approx Q_0$ is considered.

It can use the material balance for a unit in the treatment process,

$$Q_0C_0 - Q_3C_3 = m_2$$

$$m_2 = M_p K_p C_3$$

And it can get: $Q_0C_0 - Q_3C_3 = M_p K_p C_3$

And the adsorption follows the Langmuir adsorption model, then it could be

$$R_{cal} = \frac{\frac{M_p q_{max} b + Q_0 + bC_0 Q_0}{bC_0 Q_0} - \sqrt{\left(\frac{M_p q_{max} b + Q_0 + bC_0 Q_0}{bC_0 Q_0}\right)^2 - \frac{4M_p q_{max} b}{bC_0 Q_0}}}{2}$$

And in the activated sludge process,

Removal Efficiency	Cu	Zn	As	Cr
$R_{real} = \frac{C_1 - C_3}{C_1}$	0.776	0.736	0.118	0.520
R_{cal} R_{Quartz}	0.016	0.021	0.027	0.196
R_{cal} R_{Kaolin}	0.284	0.031	0.043	0.485
R_{cal} $R_{Activated\ sludge}$	0.702	0.727	0.118	0.605

It can be seen from the above table that if heavy metals removal in the primary settler is supposed to be performed by their adsorption onto inorganic particles, the calculated $K_{p1}-R_1$ relation can reasonably reflect the practical condition in the WWTP, and the different level of removal for Cu, Zn, Hg, As, Pb and Cd is due to the difference in their equilibrium partitioning coefficient K_{p1} .

CONCLUSION

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 wastewater treatment plant. A series of heavy metal (Pb, Zn, Cu, Cd, Hg, As) adsorption by quartz, kaolinite and activated sludge were conducted to investigate the different adsorption ability to heavy metals. From Langmuir plots it was observed that the quartz had the maximum adsorption capacity order: As(11.507 μ g/g)>Zn(10.277 μ g/g)>Hg(6.757 μ g/g)>Pb(2.393 μ g/g)>Cd(1.112 μ g/g)>Cu(1.017 μ g/g), but for kaolinite: Zn(93.458 μ g/g)>Pb(45.45 μ g/g)> Cu(26.810 μ g/g)>As(23.981 μ g/g)>Hg(9.124 μ g/g)>Cd(1.511 μ g/g). The activated sludge has the largest adsorption ability to Zn79.36 μ g/g. And it was found that as metal ion concentration increases, the equilibrium pH of the metal ion in solution decreased from the initial pH value on all of the three adsorbents. The main finding from the adsorption experiment was that the inorganic particles and activated sludge displayed Langmuir adsorption characteristics. As the difference surface structures And Activated sludge can be easily used as a cheap bioadsorbent for heavy metal ions such as Cu^{2+} , Hg^{2+} , As, Cd^{2+} . Langmuir models was found to fit the experimental adsorption data of the heavy metal onto the quartz, kaolinite and activated sludge. The average pH in the oxidation ditch and secondary settler were 7.73 and 7.80, which caused the heavy metal further removed in the secondary settler. This continuous process will be subjected of further investigations in our labs.

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