

Removal of some heavy metals by CKD leachate

Nagwan G. Zaki^a, I.A. Khattab^{a,*}, N.M. Abd El-Monem^b

^a Chem. Eng. & Pilot Plant Department, National Research Center, Dokki, Giza, Egypt

^b Faculty of Engineering, Cairo University, Giza, Egypt

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Abstract

In this study, Cu(II), Ni(II), and Zn(II) ions were precipitated from synthetic aqueous solutions as hydroxides by using CKD leachate. Precipitation tests were carried out batch wise in agitated flasks with single-metal solutions (each solution contained 100 mg/l of one of the three metals), and a multi-metal solution that contained 50 mg/l of each of the three elements. The results showed that high removal efficiencies, approaching 100%, of these heavy metals were attained and the leachate of the solid waste CKD, therefore, can be used for removing heavy metals from aqueous solutions. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The removal of ions of heavy metals from aqueous solutions has been practiced for more than 5000 years, since Profit Moses sweetened water using wood [5]. Since Profit Moses' demonstration, scientists and engineers have developed an arsenal of separation technologies for process and environmental applications for a diversity of industries such as petrochemical, pharmaceutical, food, metal and nuclear.

Heavy metals represent special members of metals even when discharged in small quantities are hazardous to the environment and health. The specific problem associated with heavy metals in the environment is their accumulation in the food chain and their persistence in nature [2]. These aspects result in a serious hazard and threaten water supplies. Therefore, it is important to take effective precautions to avoid, water, soil and air pollution by these metals and any other pollutants. Actually, public concern over heavy metals pollution has grown constantly since the outbreak of Minamata disease caused by mercury in Japan [1]. Man's awareness of the hazards of heavy metals now covers a wide spectrum of metals such as lead, cadmium, chromium, copper, nickel and zinc. Some of these metals have a poisoning effect on human which cause severe dysfunction of the kidneys, reproductive system, liver, and brain and central nervous system [7].

To remove heavy metals effectively from metal-laden wastewater, engineers and scientists developed various physicochemical processes, e.g. adsorption [3,6–10,16,18–20], ion-exchange [4,11], microfiltration [12], chemical precipitation [5], and reverse osmosis and nanofiltration [17]. Among these processes, the most common and conventional process is the chemical precipitation. This method, however, may suffer from some drawbacks such as: cost and type of the precipitating agent, volume of the sludge produced, and the presence of some ions, such as cyanide and ammonium that may form complexes with metal ions difficult to precipitate. Nevertheless, if some of these drawbacks are eliminated and recovery of the metals is of concern the method may be appreciated.

Cement by-pass kiln dust (CKD), on the other hand, is a fine-grained, particulate material readily entrained in the combustion gasses moving through the cement kiln. It is composed primarily of variable mixtures of calcined and uncalcined feed materials, fuel combustion by-products, and some of alkali, sulphate and chloride compounds. The environmental concerns related to cement production, emission and disposal of CKD is progressively significant. The relatively high alkaline content of CKD is the main factor preventing its recycle to cement kiln. Therefore, various research works were conducted to utilize the alkaline nature of CKD and find some beneficial uses of the waste. For instance, CKD was used to activate the latent hydraulic materials such as granulated blast furnace slag [13], CKD was added with certain ratios to mortar and concrete mixtures [14], and also CKD was used in the manufacture of vitrified sewer pipes [15].

* Corresponding author. Tel.: +002 0105195273; fax: +002 02 3370931.
E-mail address: ibrahim_kattab@yahoo.com (I.A. Khattab).

In this study, CKD was washed with water, and the filtrate was used to remove Cu(II), Ni(II), and Zn(II) from single-metal and multi-metal aqueous solutions by chemical precipitation.

2. Experimental

2.1. Materials

2.1.1. Cement by-pass kiln dust

CKD was brought from Suez Cement Company. The received CKD was put in a sealed glass container which is in turn was kept in a desecrator all the time of experiments. The used CKD was weekly received from its source. It should be mentioned that no sieve analysis was done to evaluate the average particle size of the dust. The dust was used as received. The chemical composition of CKD is given in Table 1. The constituting phases of the starting sample were identified by X-ray diffraction (XRD) analysis. The main constituting phases are: calcite (CaCO_3), quartz (SiO_2), clinker phases, and anhydrite (CaSO_4).

2.1.2. Synthetic solution

The sulfate compounds of Cu, Ni, and Zn were used to prepare the treated solutions. These chemicals were analar grade. A solution of 100 mg/l of each metal was prepared and its initial pH was measured. The concentration of the metal ions was checked by atomic absorption technique as well.

A multi-metal solution containing the three heavy metals was also prepared such that the concentration of each was 50 mg/l.

2.2. Equipment used

The experiments were carried out on pinch-scale glassware. The following equipment were used to asses the results obtained.

2.2.1. X-ray diffraction analyzer

A Philips X-ray diffraction analyzer (equipment model PW/1710 with Monochromator) was used. The target was copper ($\lambda = 1.542 \text{ \AA}$) at 40 kV, 30 mA, and the scanning speed was $0.02^\circ \text{ s}^{-1}$. The reflection peaks between $2\theta = 2^\circ$ and 70° , corresponding spacing (d , \AA) and relative intensities (I/I_0) were obtained.

Table 1
Composition of the used CKD

Constituents	Mass%
SiO_2	12.60
Al_2O_3	3.46
Fe_2O_3	2.65
CaO	40.65
MgO	1.83
K_2O	3.14
SO_3^{2-}	6.24
Cl^-	5.38
Free lime	14.84
Loss in ignition	9.21

2.2.2. Atomic absorption spectrophotometer

The concentration of heavy metal ions was measured by using Atomic Absorption Spectrophotometer Varian Spectra (model 220).

2.2.3. pH meter

A pH meter (type HI 8417 made by HANNA Instruments, Portugal) having a resolution of 0.01 was used to measure the pH of initial and treated solutions.

2.3. Experimental procedure

A specified mass of the CKD was taken and mixed with 250 ml of demineralized water in a glass conical flask. Agitation time of 30 min was found to be satisfactory for the soluble part of CKD to be dissolved. The mixture was filtered to separate the remaining solid from the resulted solution. The wet solid was dried in an electric oven drier at 110°C . Drying was continued until the mass of the solid remained constant. The difference between the initial mass of CKD and the mass of the dried solid was recorded as the mass of the dissolved portion. The filtrate had been kept in a glass holder after its pH was measured. Fig. 1 is a flowchart summarizing the experimental procedure.

The experimental conditions are indicated below:

- The starting weight of CKD was changed according to the order; 2.5, 5, 7.5, and 10 g. The volume of the demineralized water used for dissolution was always 250 ml.
- The volume indicated by the letter 'V' in Fig. 1 was changed from 1 to 20 ml.

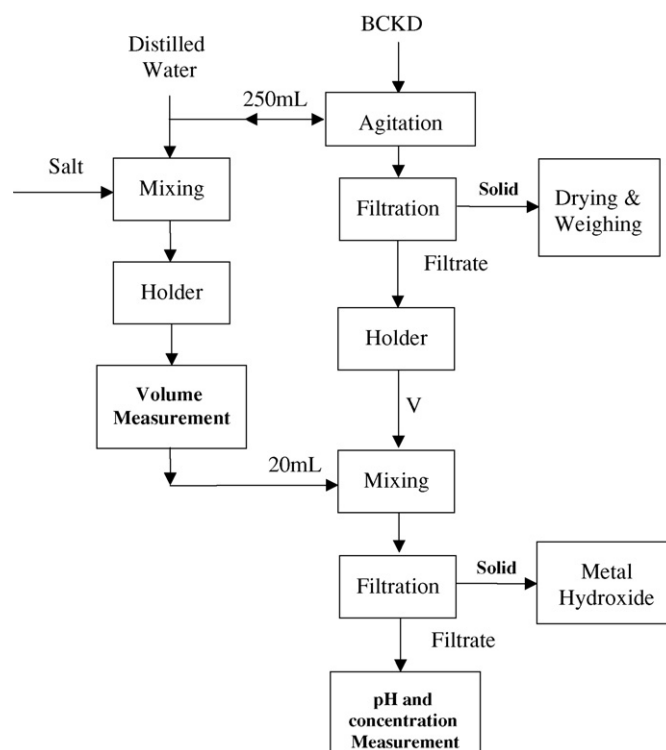


Fig. 1. Experimental procedure.

- The agitation time of CKD with water was changed in the range from 30 to 120 min at 30 min intervals. This was to investigate the effect of agitation time on the percent CKD dissolved.
- The temperature at which agitation took place was changed from room temperature ($25 \pm 3^\circ\text{C}$) to 65°C . This was to disclose the effect of temperature on the percent CKD dissolved.
- Cu, Ni, and Zn were used to represent heavy metals. Each metal was removed from its individual solution in the first part of removal experiments. In the second part of experiments, the metals were removed from a solution containing these three metals simultaneously.
- The washed CKD was analyzed by X-ray diffraction analyzer in order to know what phases has been disappeared or changed by water washing.

3. Results and discussion

3.1. Leaching of CKD

The constituting phases of the leached CKD sample were identified by XRD analysis. The results of the analysis are shown

in Fig. 2(a) is the XRD chart of the starting sample whereas Fig. 2(b) is of the leached sample. Comparing these two charts indicated that the main constituting phases were the same except that a peak of Portlandite was appeared in the XRD of the leached sample.

3.1.1. Effect of stirring time

Fig. 3(a and b) shows the effect of stirring time on the percent CKD dissolved. The initial weights of CKD were 2.5 and 7.5 g, respectively. The percent CKD dissolved is defined as:

$$\% \text{Dissolved} = \frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \times 100$$

The figures show that stirring or agitation time has no pronounce effect on the percent CKD dissolved. Also, no significant change of pH of the produced filtrate is observable. This means that dissolution of the soluble part of CKD does not need long time to take place at room temperature ($25 \pm 3^\circ\text{C}$). The alkalinity of the resulted solution is so high that it can be used for the precipitation of heavy metals from the dilute solutions containing these metals. Therefore, an agitation time of 30 min was found to be enough for the dissolution process.

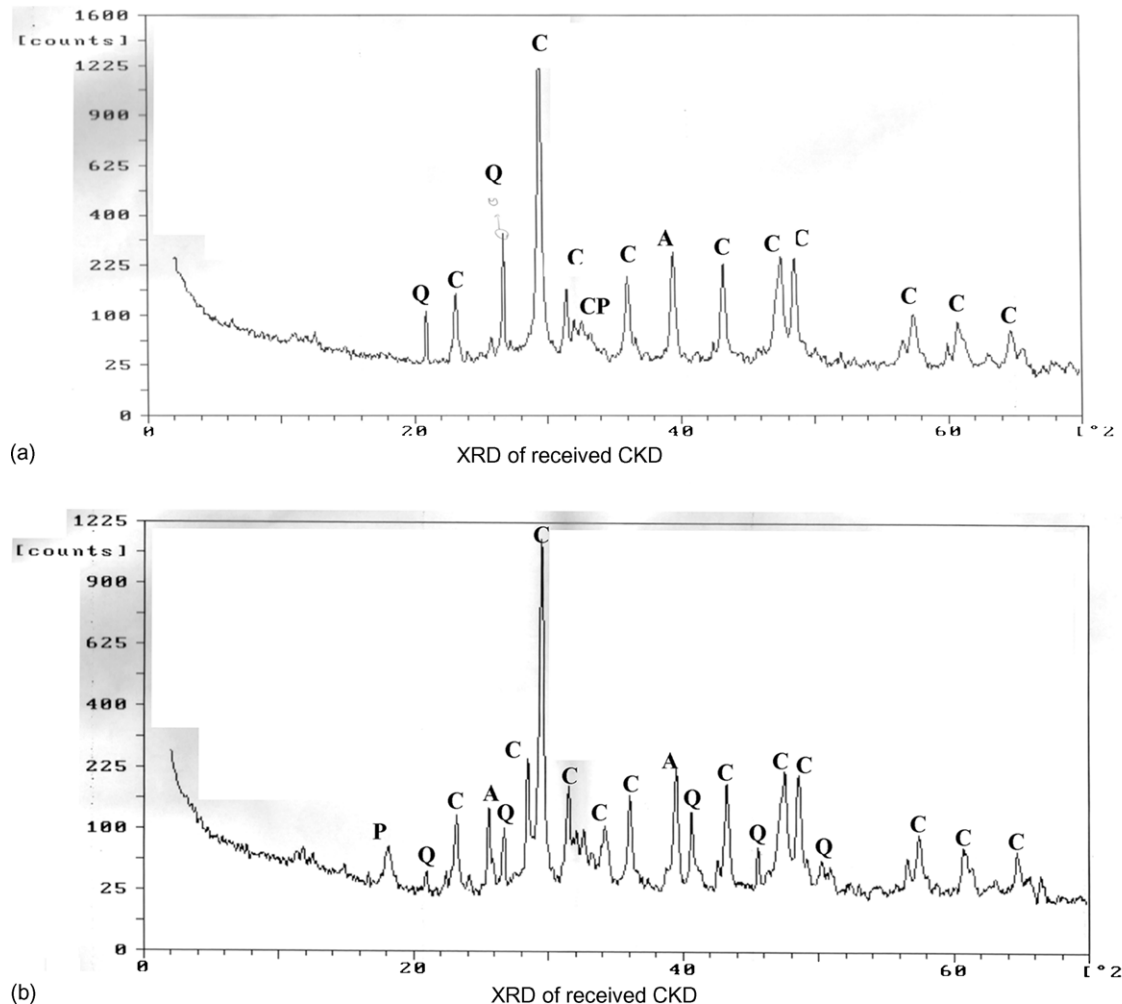


Fig. 2. XRD of CKD before and after washing. (a) XRD of received CKD and (b) XRD of washed CKD. A: anhydrite [CaSO_4]; C: calcite [CaCO_3]; CP: clinker phases; P: portlandite [$\text{Ca}(\text{OH})_2$]; Q: quartz [SiO_2].

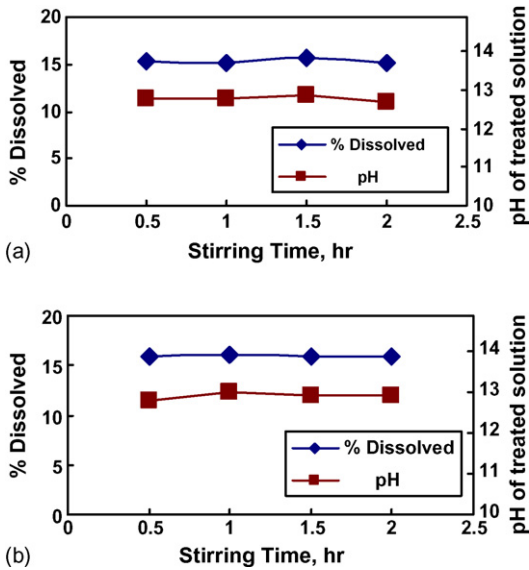


Fig. 3. Effect of stirring time on percent CKD dissolved and pH. (a) Initial mass of CKD = 2.5 g and (b) initial mass of CKD = 7.5 g.

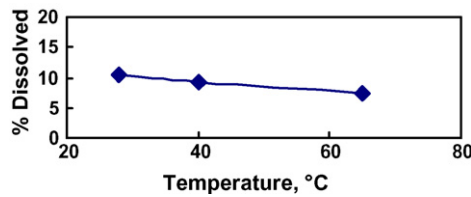


Fig. 4. Effect of temperature on percent of CKD dissolved (initial mass of CKD = 2.5 g).

3.1.2. Effect of temperature

The effect of temperature on the percent CKD dissolved is shown in Fig. 4 for a sample of the initial weight of 2.5 g. The percent dissolved decreased from about 10.6% at 28 °C to about 7.3% at 65 °C. This behavior may be attributed to the decrease of solubility of some salts, present in CKD, with increasing temperature, e.g. sulphate salts.

3.1.3. Effect of initial weight of CKD

Fig. 5 shows the effect of the initial weight of CKD on the percent dissolved and the pH of the filtrate. The stirring time was 30 min at the same stirring rate. As the weight was increased, a slight increase was observed in both the percent dissolved and pH of the filtrate. It might be of importance to state that when the washed CKD samples were tested for any combined water, by

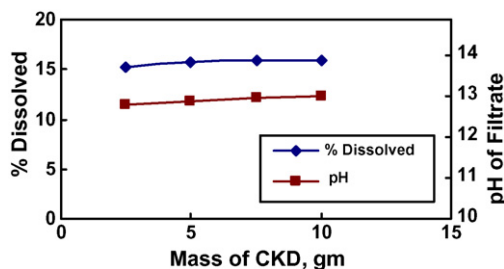


Fig. 5. Percent CKD dissolved and pH of filtrate vs. mass of CKD (stirring time = 0.5 h).

heating the samples in an electric oven for 180 min at 200 °C, no loss in weight was detected. This means that the loss in weight of CKD is due to the dissolution of some constituents of CKD.

3.2. Removal of Cu, Ni, and Zn from single-metal solutions

3.2.1. Removal of Cu

The removal of Cu from wastewaters has been under investigations by many researchers. Typical discharge standards in the UK are 28 µg/l [12]. In order to achieve this limit efficiently, a

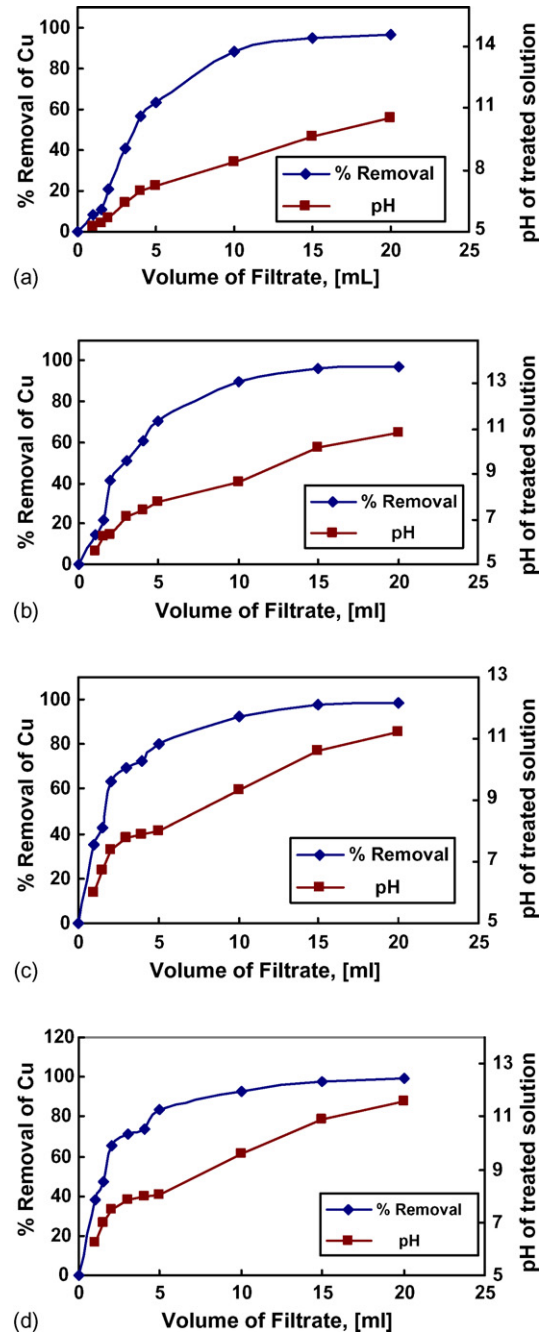


Fig. 6. Removal of Cu(II) from 100 mg/l CuSO₄ solution. (a) Mass of CKD = 2.5 g, (b) mass of CKD = 5 g, (c) mass of CKD = 7.5 g and (d) mass of CKD = 10 g.

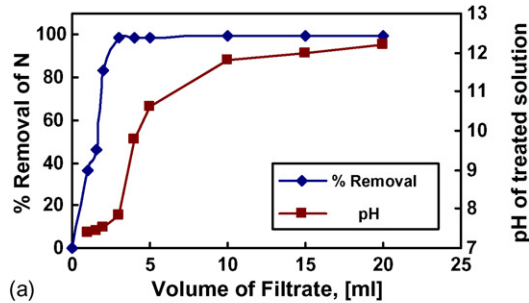
proper method should be used. Chemical precipitation of Cu^{2+} , as CuS or $\text{Cu}(\text{OH})_2$, may be a suitable method for achieving this target.

Fig. 6(a) shows the change of the percent removal of copper ions from aqueous solution containing 100 mg/l of $\text{Cu}(\text{II})$ with the volume of CKD leachate. The leachate was produced from washing 2.5 g of CKD. The volume of the Cu -laden solution was hold constant at 20 ml, while the volume of the leachate was changed in the range from 1.5 to 20 ml. The percentage removal of the metal increased and the pH of remaining solution increased as well. The precipitation of Cu as copper hydroxide started at a pH slightly less than 5.5. This is in agreement with

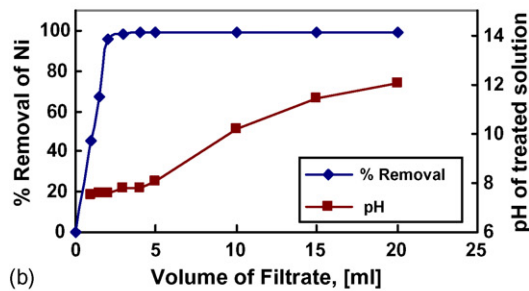
the theoretical solubility diagram presented elsewhere [21]. At higher pH values the percentage removal is higher; it is about 97% and the pH of solution after treatment had a pH of 10.

The same behavior is shown in Fig. 6(b–d) except that the percent removal is increased, for the same volume of leachate added to the same volume of the copper solution, as the initial mass of CKD increased. This is a result of the slight increase of pH of the leachate as the initial mass of CKD was increased.

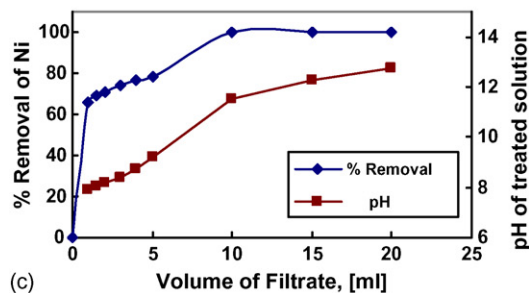
The inspection Fig. 6 indicates that about 99% of the initial load of Cu^{2+} can be removed by adding a proper volume of



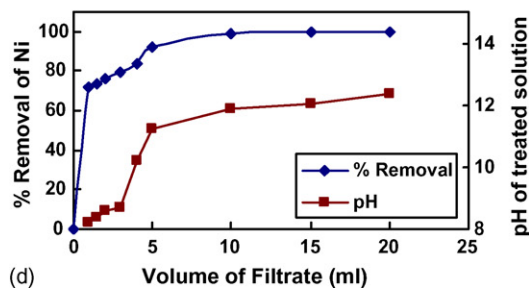
(a)



(b)



(c)

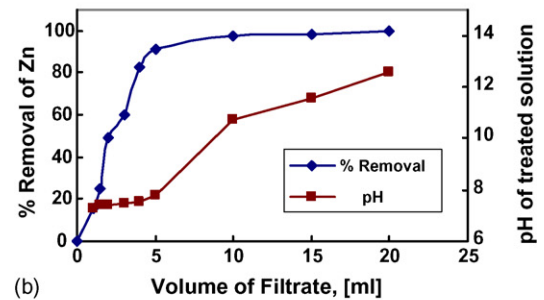


(d)

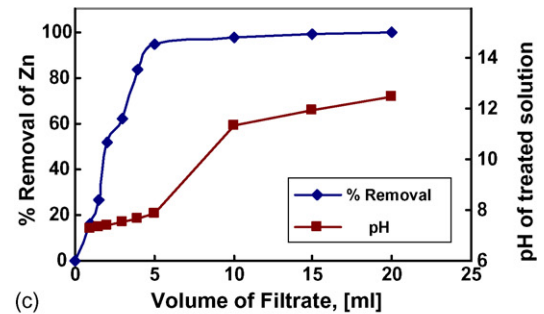
Fig. 7. Removal of $\text{Ni}(\text{II})$ from 100 mg/l NiSO_4 solution. (a) Mass of CKD=2.5 g, (b) mass of CKD=5 g, (c) mass of CKD=7.5 g and (d) mass of CKD=10 g.



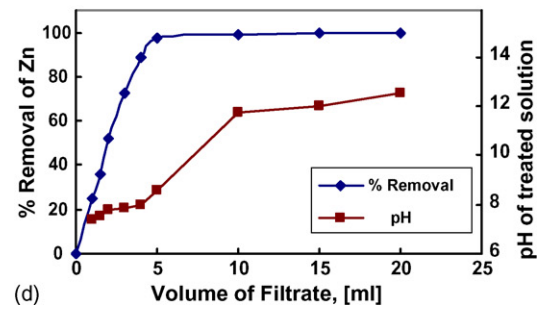
(a)



(b)



(c)



(d)

Fig. 8. Removal of $\text{Zn}(\text{II})$ from 100 mg/l ZnSO_4 solution. (a) Mass of CKD=2.5 g, (b) mass of CKD=5 g, (c) mass of CKD=7.5 g and (d) mass of CKD=10 g.

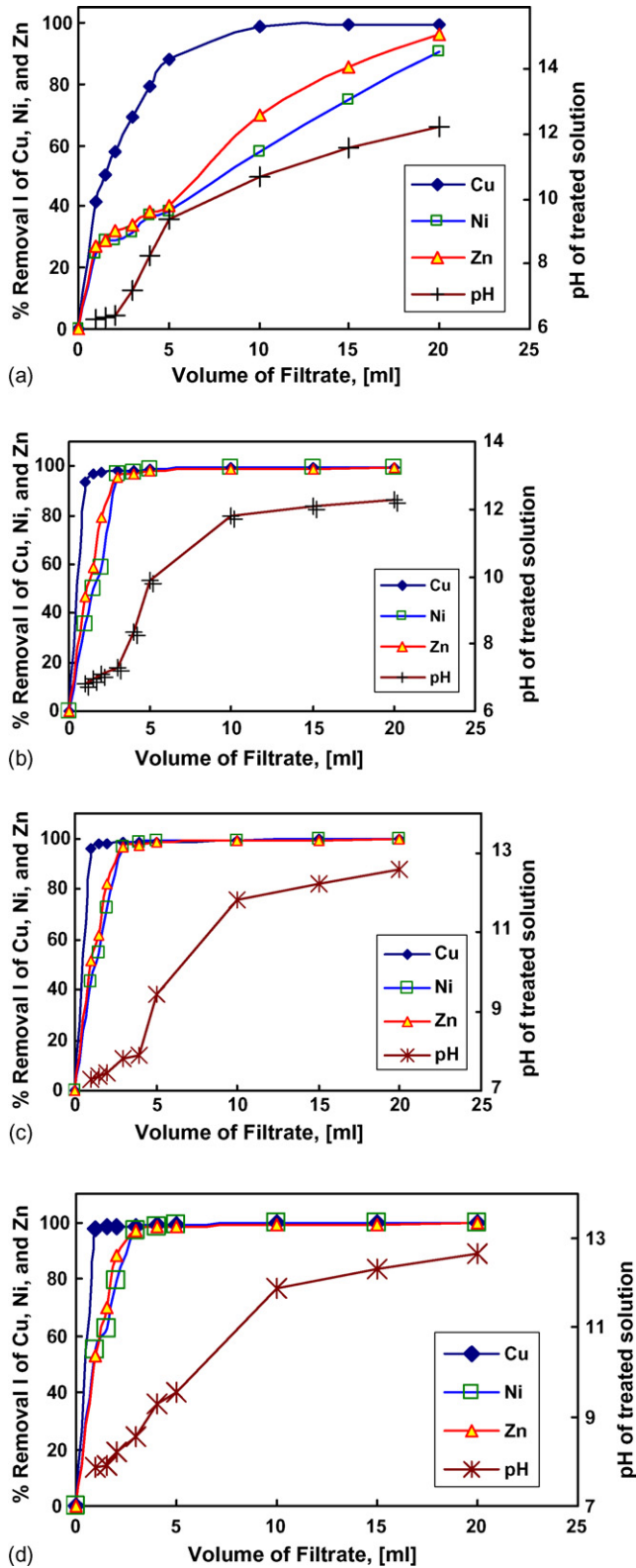


Fig. 9. Removal of metals from 150 mg/l multi-metal solution. (a) Mass of CKD = 2.5 g, (b) mass of CKD = 5 g, (c) mass of CKD = 7.5 g and (d) mass of CKD = 10 g.

the leachate to a certain volume of the Cu-laden wastewater. The total time needed to accomplish the metal removal is the time of agitation, which was 10 min in this work, the time of agglomeration and the time of filtration. The total time will not certainly be more than 3 h which is the time needed to reach 99% removal of Cu^{2+} by adsorption as in the works of Lee et al. [7], Yu et al. [10] and Jang et al. [20]. Moreover, if there is no other heavy metals in the treated wastewater the precipitated $\text{Cu}(\text{OH})_2$ can be used to recover Cu in a nearly high quality form.

3.2.2. Removal of Ni

The removal of nickel from waste streams has also been a subject of research by many investigators. Typical discharge standard in the UK is $200 \mu\text{g/l}$ [12]. Fig. 7 shows how the percentage removal of Ni^{2+} is increased by increasing the volume of the added leachate. The removal of Ni^{2+} started at a pH value slightly above 7 which is in agreement with the theoretical solubility diagram presented elsewhere [21].

In the work of Yavuz et al. [18] a time of more than 6 h was needed to remove about 72.3% of the original load of Ni^{2+} by adsorption on kaolinite at room temperature. As shown in Fig. 7(a–d), a percent removal of 99% can be reached in a much shorter time when a proper volume of a solution of high alkalinity such as the leachate of CKD is added.

3.2.3. Removal of Zn

Zinc is not considered detrimental to human health, but it will impart an undesirable taste to drinking water [8]. Removal of zinc has also been investigated by many investigators in the last decade. They applied adsorption as the removal technique, e.g. the works of Gharaibeh et al. [8], Sekhar et al. [19], and Jang et al. [20]. To reach high percentage removal of zinc they needed long time (not less than 60 min).

Fig. 8(a–d) illustrate that zinc can be removed efficiently from solutions containing it by the leachate of CKD. The removal of Zn^{2+} started at a pH of 7 and almost complete removal was attained at a pH of about 11.

3.3. Removal of Cu, Ni, and Zn from a multi-metal solution

Industrial wastewaters often contain a mixture of metal ions. Therefore, it is important to investigate the precipitation behavior of Cu, Ni and Zn from an aqueous solution containing the ions of the three metals. A multi-metal solution was treated with CKD leachate. The obtained results are shown in Fig. 9(a–d). The trend is the same as for a solution containing a single-metal, i.e. the percent removal of a metal increases with the increase of the added volume of the leachate.

It is worth noting that the removal of Cu^{2+} is easier at lower pH values than the removal of both Ni^{2+} and Zn^{2+} . This result was also observed in the works of Bayhan et al. [12] and Meunier et al. [16] regardless they applied adsorption technique.

4. Conclusions

1. On washing CKD with water a portion of its weight is dissolved. The percentage dissolved ranges from about 11.5 to

- 15% of the original weight and is independent of stirring time and the original weight of CKD; while it slightly decreases with increasing the temperature during the washing process.
- The leachate of CKD is highly alkaline (pH > 12). The pH of the leachate slightly increases with increasing the original weight of CKD.
 - Due to its high alkalinity, the leachate of CKD has high potential to be used for removing heavy metals, as hydroxides, from the solutions containing them.
 - The parameters affecting the removal of heavy metals by hydroxide precipitation method are the pH and the concentration of the dissolved heavy metal ion of the solution to be treated.
 - For a waste solution containing 100 mg/l of Cu^{2+} ions the removal starts at a value of pH > 5.5.
 - For a waste solution containing 100 mg/l Ni^{2+} ions the removal starts at a value of pH > 7.
 - For a waste solution containing 100 mg/l Zn^{2+} ions the removal starts at a value of pH > 7.3.
 - Copper may selectively be removed from a multi-metal solution containing Cu, Ni, and Zn ions as hydroxide at a value of pH < 7. However, the selective removal of Ni or Zn should be done by other chemical precipitation method.
 - When a solid material is added to a waste solution to remove heavy metals by adsorption, the pH of the solution should be specified otherwise a portion of the dissolved heavy metal is going to precipitate as hydroxide.

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