



XV BALKAN MINERAL PROCESSING CONGRESS - BMPC 2013

June 12 – 16, 2013, Sozopol, Bulgaria

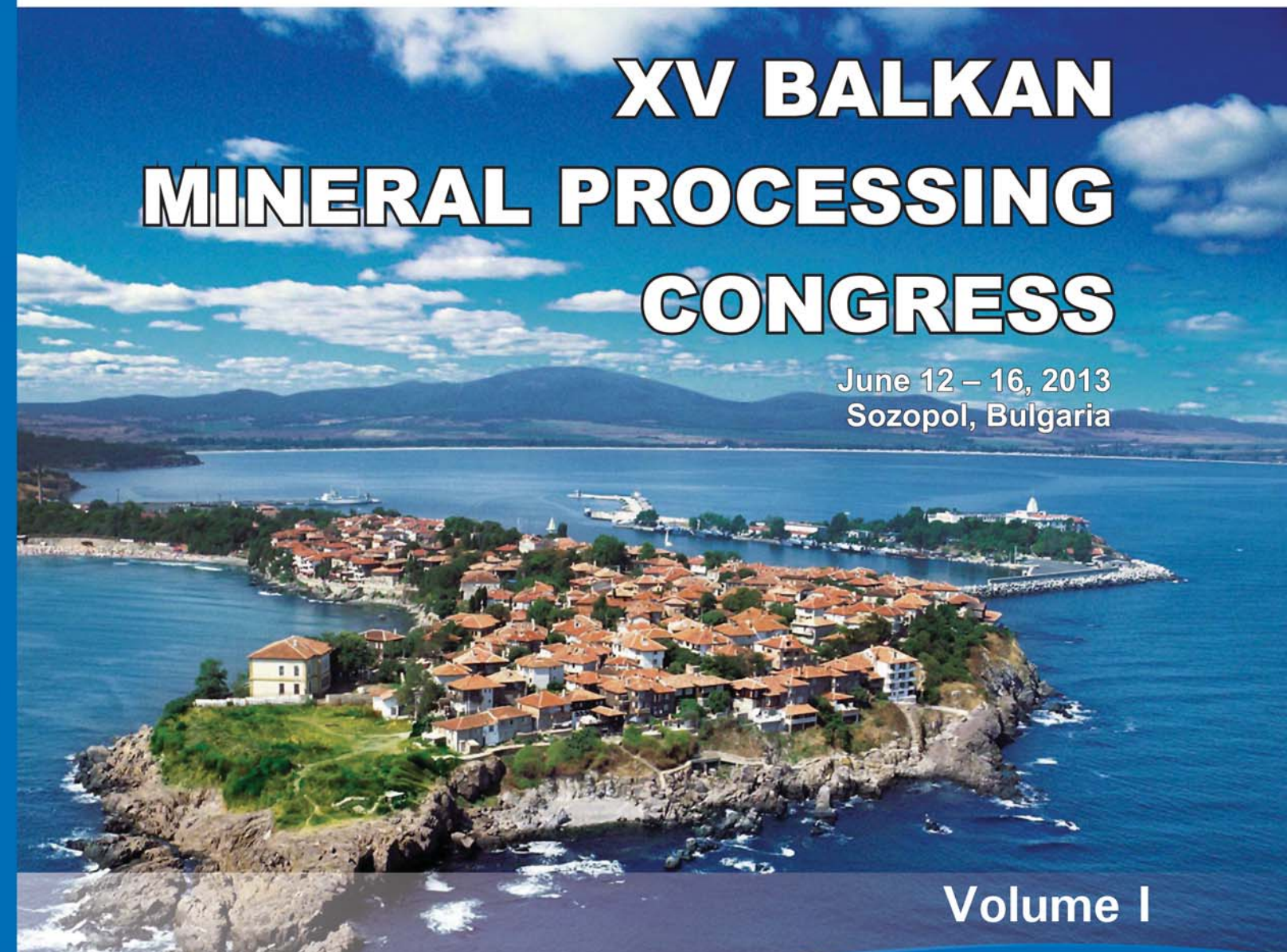


Proceedings of



XV BALKAN MINERAL PROCESSING CONGRESS

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Volume I

Edited by:
Ivan Nishkov
Irena Grigorova
Dimitar Mochev



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Department of Mineral Processing and Recycling
University of Mining and Geology "St. Ivan Rilski"

Volume I

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CHAIRMAN'S FOREWORD



Dear Colleagues,

In 2013 forty years complete since the first Balkan Mineral Processing Conference has been held in Varna, Bulgaria, 1973.

It has been a tradition to organize each anniversary Balkan Mineral Processing Congress in Bulgaria: I BMPC - Varna, 1973; V BMPC – Varna, 1989, X BMPC - Varna, 2003, XV – Sozopol, 2013.

In the period from 1973 to 2013 altogether 15 Balkan Mineral Processing Congresses (Conferences) have been organized. The first one took place in Bulgaria (Varna), 1973 and the last one in Bulgaria (Sozopol), 2013.

BMPC Chronology is as follow: I (Conference) - 1973 - Varna, Bulgaria; II (Conference) 1977 Baia Mare, Romania; III (Conference) - 1980 Belgrade, Serbia; IV (Conference) - 1984 Istanbul, Turkey; V (Conference) - 1989 Varna, Bulgaria; VI (Conference) - 1995 Ohrid, Macedonia; VII (Conference) - 1997 Vatra Dornei, Romania; VII (Conference) - 1999 Belgrade, Serbia; IX (Congress) - 2001 Istanbul, Turkey; X (Congress) - 2003 Varna, Bulgaria; XI (Congress) - 2005 Dures, Albania; XII (Congress) - 2007 Delphi, Greece; XIII (Congress) - 2009 Bucharest, Romania; XIV (Congress) - 2011 Tuzla, Bosnia and Herzegovina; XV (Congress) - 2013 Sozopol, Bulgaria.

The XV Balkan Mineral Processing Congress "The Wave of Changes in Processing and Recycling", Sozopol, Bulgaria, June 12 - 16, 2013 is organized by University of Mining and Geology "St. Ivan Rilski" and Municipality of Sozopol. We are proud that Bulgaria is hosting the XV Anniversary Balkan Mineral Processing Congress - 2013.

The town of Sozopol is a cultural center of national importance and the most ancient town on the Bulgarian Black Sea coast. Archeological explorations prove more than a six thousand cultural tradition. Ancient Sozopol takes first place in "Wonders of Bulgaria 2011" ranking.

The XV Balkan Mineral Processing Congress is the most important scientific event in Europe in the field of mineral processing and recycling industry in 2013 which is traditionally attended by participants from North and South America, Canada, Australia, China, India, Russia, Brazil and many others countries.

The Balkan Mineral Processing Congresses have played an important role in the history of Mineral Processing. The BMPC brings together practitioners in mineral processing industry in all forms to exchange recent research achievements. Our mission is to share scientific data, knowledge and experience, to exchange recent innovations and developments in order to further global progress in mineral processing and recycling.

Because of the 40 years Anniversary of the BMPC, Balkan Mineral Processing Technical Exhibition is concurrent with the Balkan Mineral Processing Congress. The technical exhibition is held parallel to the Congress. The companies active in the mineral processing from Germany, Italy, Finland, Bulgaria, Turkey, Australia and others countries have an opportunity of exhibiting their products and services to an international audience of congress delegates.

We are honored and pleased to welcome all academic and research professionals, scientists, experts, production company representatives, engineering and supplier companies from the mineral processing industry and recycling to celebrate 40 years of Balkan Mineral Processing Congress in Sozopol town, Bulgaria.

BMPC 2013 program includes plenary, technical and poster sessions, satellite symposia and thematic seminars for dialogue and cooperation in responding to future challenges related to raw materials, technical and art exhibitions, corporate and product presentations.

XV Balkan Mineral Processing Congress provides the opportunity for sharing scientific data, knowledge and experience, to exchange recent innovations and developments in order to further global progress in mineral processing and recycling. Balkan Mineral Processing Congress is the best opportunity to learn about the latest mineral processing and recycling technologies.

We hope that the proceedings from XV BMPC will constitute a contribution to the global mineral processing progress.

A handwritten signature in blue ink, appearing to be 'Ivan Nishkov', written in a cursive style.

Prof. Dr. Ivan Nishkov
Chairman of XV BMPC Organizing Committee

Sozopol, Bulgaria, May 11, 2013

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KINETICS OF COPPER ADSORPTION FROM WASTEWATER BY LIGNITE

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ABSTRACT. Kolubara lignite was used as a natural and low cost adsorption material for removal of copper (Cu^{2+}) from the aqueous solutions. As a method, batch adsorption procedure was applied. Results show that domestic lignite is good adsorbent material since about 90 % of copper cations were removed in 5 minutes of contact time from the solutions of low copper concentration (50 mg/l) regardless the adsorbent amount, while the same effect of adsorption was achieved in 60 minutes in case of solutions with high concentrations of copper (330 mg/l). Optimum removal of copper ions was achieved at $\text{pH} = 5.0$. The study proved that tested lignite is very efficient adsorbent material. This behavior can be explained by FTIR spectrum despite a small specific surface area of lignite. Many bands are attributed to the functional groups involved in chemisorption and ionic exchange, basic mechanisms of copper adsorption.

Keywords: copper, lignite, contact time, pH.

INTRODUCTION

Copper is known as one of the most common toxic and hazardous metal which is often used in electrical, mining, and electronic industries, iron, steel and non-ferrous production, electroplating, metal finishing, printing and photographic procedures. Copper, as well as the other heavy metals, is released into the environment in a number of different ways and it finds the way to get into the water-streams and thus make environmental contamination that presents threat to humans, animals, and plants. This can cause serious and complex problem [1-4]. Concentrations of copper as well as heavy metals from the wastewater and water-streams have to be reduced in order to satisfy rigid legislative standards. They can be removed by various technologies, most often expensive or inefficient and technically complicated especially because of limited low residual concentrations required by the EPA (Environmental Protection Agency) [2-4]. The conventional techniques for heavy metals removing from aqueous solutions include oxidation, reduction, chemical precipitation, filtration, ion exchange, adsorption, membrane techniques, electrolytic or liquid extraction, reverse osmosis, biological process [2,5]. Each of these methods is used only in special cases since it has some limitations in practice [6]. Namely, the major disadvantage of almost all mentioned methods is production of new hazardous waste, mostly solid, at the end of the treatment [1].

Nowadays, many researches have been involved in development of new inexpensive materials and methods for the treatment of wastewater containing heavy metals, for example natural adsorbents such as zeolites, wood, lignite, metal oxides, fly ash, coal, and waste biomass [7-9]. Predominant mechanism in this process is ion exchange, but also there is surface adsorption, chemisorption, complexation and adsorption-complexation [2-4,10]. In spite of relatively small adsorption capacity of lower quality coals, compared with expensive synthetic materials used for ionic exchange, lignite is considered as a very attractive material for metals removal since it is widely available and inexpensive [2]. It should be emphasized that removing heavy metals from the wastewaters presented in relatively low concentration is rather difficult [6]. Recently, the use of lignite in wastewater treatment has become more and more attractive since it can be good substitution for synthetic and expensive activated carbon. Lignite possesses all necessary characteristics that make it a very efficient material for the removal of copper and other heavy metals from the wastewater [2,6,11,12].

The primary aim of this study was to determine adsorption parameters of low cost Kolubara lignite during the removal of copper from the synthetic aqueous solutions. It was found that tested lignite is an excellent adsorbent for copper, especially in case of aqueous solution with small copper concentration.

EXPERIMENTAL

Material

Lignite from Kolubara deposit, field B, used as a fuel in power plant Nikola Tesla, was applied in experiments as an adsorbent material. First, it was dried at 45°C for 24 hours, and then grounded and sieved. Fractions from 1-2 mm were used for the adsorption experiment, while fine fractions, under 1 mm, were used for elementary analyses. Adsorption and desorption isotherms of N_2 were measured on lignite sample, at -196°C , using the gravimetric McBain method. The specific surface area (S_{BET}), pore size distribution was estimated by applying BJH method [13] to desorption branch of isotherms and mesopore surface and micropore volume were estimated by using the high resolution α_s plot method [14-16].

Micropore surface (S_{mic}) was calculated by subtracting S_{meso} from S_{BET} .

Method

The kinetics of copper adsorption on lignite was conducted by batch technique at ambient temperature in aqueous solutions under continuous stirring conditions. The procedure was as follows: weighted amount of lignite was placed into a glass vessel with cover. Prepared copper solution was added and then agitated. In order to quantify adsorption efficiency (percent of adsorbed metal), suspension was filtered and residual copper ion concentration in the filtrate was determined by Perkin Elmer Atomic Adsorption Spectroscopy (AAS) type AAnalyst 300.

Synthetic aqueous solution of copper was prepared by dissolving of appropriate amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt in deionised water. Volume of the solutions was constant (250 ml), as well as stirring conditions. Effect of three different concentrations of initial solutions on adsorption was investigated: 50, 200, and 330 mg Cu^{2+} /l. Volumes of the solution were constant (250 ml). Also, three different amounts of air dried lignite were used as a sorbent (30, 45, and 60 g) and their effect on adsorption was followed during the experiment. All experiments were monitored depending on contact time up to one hour.

The kinetic sorption of copper on lignite was conducted by batch technique at ambient temperature in aqueous solutions under continuous stirring with 200 rpm. The procedure was described as follows: weighted amounts of sorbent material was placed into a glass vessel with a cover; prepared solution was added to the sorbent batch; different initial Cu (II) ion concentrations were mixed with three different adsorbent dosage. In order to quantify sorption efficiency, suspensions were filtered and residual copper ion concentration in the filtrates was determined at predetermined time intervals after the sorption by AAS. Content of copper in solutions that was leached with deionized water from the treated lignite saturated with copper proved literatural assesment that there was no leaching from the sorbent [2].

The lignite saturated with copper was treated with deionized water. The analysis of the obtained solution proved literature assessment that there was no leaching from the adsorbent [2].

The effects of experimental parameters such as initial copper concentration and adsorbent dosage on copper sorption efficiency were investigated.

Changes of Cu^{2+} in treated solutions was monitored by Perkin Elmer Atomic Adsorption Spectroscopy (AAS) type AAnalyst 300.

RESULTS AND DISCUSSION

Adsorbent Properties

According to the IUPAC classification [17], nitrogen adsorption-desorption isotherm for lignite, as the amount of N_2 adsorbed as function of relative pressure at -196°C , is of type I which is associated with nonporous and macroporous materials. Specific surface area calculated by BET equation (S_{BET}) is $1 \text{ m}^2/\text{g}$.

FTIR spectra of analyzed lignite is shown in Figure 1. Bands were identify by comparison to the literature [18-25]. It is obvious that lignite has numerous functional groups that can be involved in adsorption process.

Six peak areas observed in diagram of Figure 1 are: hydroxyl group region ($3100\text{-}3700 \text{ cm}^{-1}$), aliphatic stretching region ($2931\text{-}2855 \text{ cm}^{-1}$), aromatic carbon (peaks at 1618 and 1606 cm^{-1}), aliphatic bending region ($1509\text{-}1371 \text{ cm}^{-1}$), cellulose and lignin region (1300-

1000 cm^{-1}), and the aromatic out-of-plane region 900-700 cm^{-1}) were measured. Additionally, intense vibrations at 3698 cm^{-1} , 3620 cm^{-1} , 531 cm^{-1} and 469 cm^{-1} are attributed to clay and silicate minerals. The small peaks in the range of 3698 cm^{-1} and 3700 cm^{-1} can be assigned to the crystal water which exists in clay minerals of the matrix lignite samples [26].

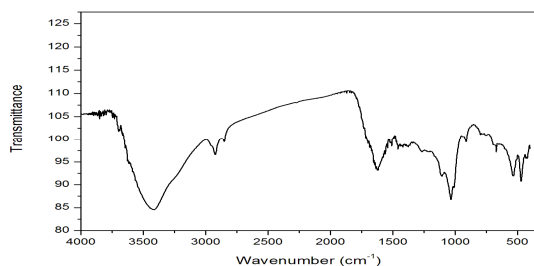


Fig. 1. FTIR spectrum of lignite

Lignite spectra show typical infrared characteristics of the organic compound, coal, including aliphatic C-H stretching bands at 2924 cm^{-1} and 2856 cm^{-1} , C=C or C=O aromatic ring stretching vibrations at 1610 cm^{-1} and at 1506 cm^{-1} , as well as aliphatic C-H stretching bands at 1455 cm^{-1} , 1370 cm^{-1} .

The broad band at $\sim 3406 \text{ cm}^{-1}$ is attributed to -OH stretching vibrations of hydrogen bonded hydroxyl groups of adsorbed water either of clay minerals or phenol groups.

The bands at $\sim 2931 \text{ cm}^{-1}$ and $\sim 2855 \text{ cm}^{-1}$ are attributed to aliphatic CH vibration of -CH₃ and -CH₂ stretching vibrations, respectively.

The strong band at $\sim 1606 \text{ cm}^{-1}$ is attributed either to C=O or C=C aromatic ring stretching vibrations.

The band at $\sim 1505 \text{ cm}^{-1}$ is due to C=O stretching vibrations.

The band at $\sim 1454 \text{ cm}^{-1}$ is attributed to symmetric aliphatic C-H vibrations of methylene (CH₂) and methoxyl (OCH₃).

The band at $\sim 1370 \text{ cm}^{-1}$ is due to symmetric aliphatic C-H bending vibrations of methyl groups (OCH₃).

The band at $\sim 1265 \text{ cm}^{-1}$ is attributed to C-O stretching vibrations.

The peak at $\sim 1033 \text{ cm}^{-1}$ is due to C-O-H bonds in cellulose as well as to C-O stretching vibrations of aliphatic ethers (R-O-R') and alcohols (R-OH).

Adsorption is a process of mass transfer of adsorbate in solution to the adsorbent surface driven by physical and/or chemical forces. For adsorbate, its adsorption capacity and mechanisms are closely associated with the adsorbent surface characteristics. Based on that, it can be assumed that driving mechanism of adsorbate with numerous functional groups is based on chemisorption since they involved in ion exchange. On the other side, the adsorption properties of adsorbate with high values of specific surface area as well as micro and meso porosity are govern by physisorption. It can be explained by diffusion and transport processes of mass within meso- and micropores. Since lignite is classified as nonporous and macroporous materials and specific surface area is quite small, it can be assumed that functional groups are involved in ion exchange during the adsorption.

Adsorption Kinetics

Influence of pH solution on copper removal:

Carboxyl and hydroxyl groups are the main exchangeable functional groups that take part in the adsorption of metal ions onto lignite derived adsorbents. With increasing of pH solution, these functionalities dissociate, i.e., become deprotonated and negatively charged. During the adsorption, H⁺ and other exchangeable cations (e.g. Na⁺, Ca²⁺, and Mg²⁺) are substituted with metal cations and released from the adsorbent to the solution [11].

Generally, very important parameter that should be controlled during the adsorption process is pH of the initial aqueous solution. Lignite mass of 30 g and contact time of 30 minutes used in this part of study were fixed.

The metal cations in the aqueous solution convert to different hydrolysis products. At low to high pH values, copper ions exist as Cu²⁺, Cu(OH)⁺, and as neutral compound Cu(OH)₂. The dominant species of copper in the pH range from 3-5 are Cu²⁺ and Cu(OH)⁺ ions, while the copper occurs as insoluble Cu(OH)_{2(s)} above pH 6.3. Experiments were performed with the pH values in the range of 2 – 6, since Cu(OH)₂ started to precipitate above pH of 6. Increase of pH from 2 to 5 leads to the rise of adsorption efficiency from 20 to 94 %, respectively [4-6].

Figure 2 shows influence of pH value on sorption efficiency of lignite.

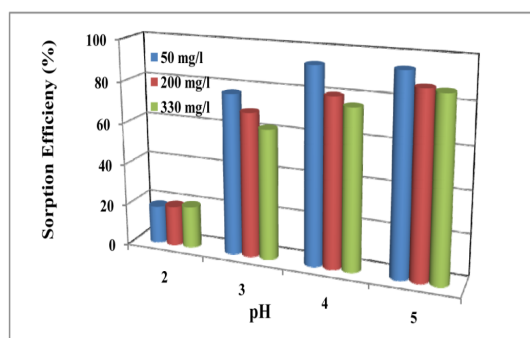
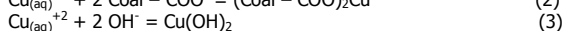
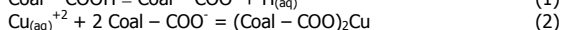
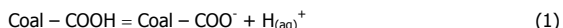


Fig. 2. Influence of pH on copper adsorption efficiency; 30 g of lignite and 30 min of contact time

Based on the results presented in Fig. 2, it is obvious that the percentage of adsorbed copper ions suddenly increases with rising of pH reaching the highest value at pH of 4-5. It can be explained by observation that the increase of pH value induces replacement of hydrogen ions from the surface of the lignite with the copper ions resulting in improvement of the adsorption efficiency extent.

Hydrogen ions induce metal complexation because they have great affinity for many complexing and ion exchange sites. At very low pH (< 2.0) functional groups (hydroxyl, carboxyl, phenol, methoxyl, etc.) of the coals are protonated. Equilibrium reaction of metal adsorption can be considered as follows [6]:



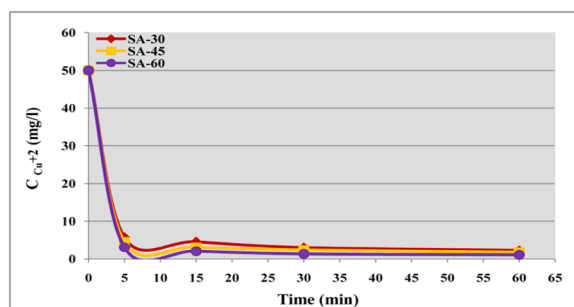
Due to high concentration of H⁺ ions for the pH lower than 2, equilibrium of the reaction (1) will be shifted to the left side according the equilibrium law. Since sites of ion exchange on the lignite are mainly protonated, less available groups for ion exchange become available. As expected, the efficiency generally increases with increasing pH, while the effect of pH is indistinctive or even reverse. The increase of the adsorption efficiency is the most explicit for pH values between 2 and 4, probably reflecting progressive deprotonation of carboxylic groups. Namely, in mentioned pH range, the carboxyl groups (-COOH) from the lignite can lose H⁺ and be appreciably deprotonated. That will shift the reaction (2) to the right, while the increase of the solution pH increases copper ion removal. In this pH range, process of ion exchange is the major mechanism for the removal of copper ions from the aqueous solution. As already mentioned, hydrolysis reaction (3) happened at pH ≥ 6 and copper hydroxide precipitation was occurred [6,27,28]. It is obvious that optimum pH for Cu²⁺ adsorption by lignite is 5.0, so the adsorption experiments regarding influence of the adsorbent amount, initial concentration and contact time were performed with pH value of 5.

Influence of contact time on the copper removal:

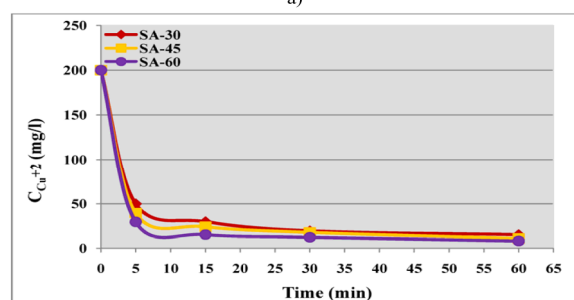
In order to achieve the equilibrium state with maximally reduced adsorption time, tests were carried out with greater amounts of coal thus providing large number of available active adsorption sites on free adsorbent surface.

Namely, possible use of small amounts of coal that can provide good adsorption efficiency but for more reasonable time was a goal of this testing. The efficiency of copper adsorption from aqueous solutions with three different initial concentrations (50, 200, and 330 mg Cu²⁺/l) on three different amounts of lignite (30, 45, and 60 g) was observed depending on contact time up to 60 minutes, as shown in Figure 3. Based on the change in metal concentration in the aqueous solution before and after achieving equilibrium adsorption, the adsorption efficiency was calculated. Copper removal from the aqueous solutions in the first 5 minutes has a significant practical value. In all cases, the majority of copper ions was removed at the beginning of the adsorption process, during the first 5 minutes of contact time. Besides, it is obvious that the adsorption occurred in 3 stages. The first stage lasted for five minutes. In this period, there was decrease in Cu²⁺ ions concentration of 65 - 92 % depending on the solution concentration and the adsorbent amount. The adsorption of Cu²⁺ in this stage happened so quickly. During the second stage within the next 15 minutes removing of Cu²⁺ was more than 90 % for all solution concentrations and adsorbent amounts while the adsorption happened much slowly. It is very important to determine the equilibrium time for each type of lignite used as an adsorbent material. Equilibrium time, that is the contact time characterized by unchanging Cu²⁺ concentration in the solution, was achieved after 30

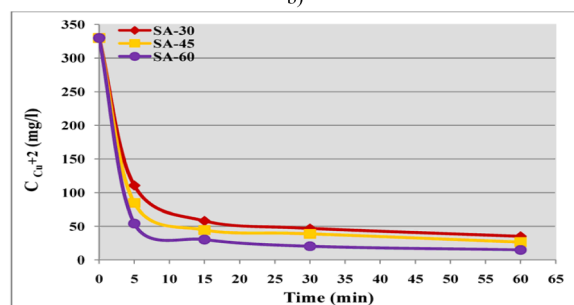
minutes for all used concentrations of solutions and amounts of adsorbent; this period is denoted as the third stage of the adsorption. Sufficient contact time for both adsorbents is 30 minutes, since they achieve equilibrium for the mentioned time.



a)



b)



c)

Fig. 3. Influence of contact time on copper adsorption for three different masses of lignite as adsorbent: a) 30 g; b) 45 g; c) 60 g at pH = 5;

High adsorption rate at the beginning of the adsorption process is due to the numerous readily available active adsorbing sites on the adsorbent surface; that is the large uncovered surface area of lignite which was provided by high amount of lignite while the copper ions can interact easily [6]. Additionally, the driving force for the adsorption is the difference between concentration of copper in the solution and solid/liquid interface which has the highest value at the beginning of the process, resulting in fast adsorption. Lower slopes of the curves confirm that the second stage was a bit lower due to lower diffusion velocity of copper ions within the pores of the lignite structure. It can be observed that the best adsorption efficiency (> 90 %) was achieved in the case of initial solution with the lowest copper ions concentration (50 mg Cu²⁺/l) for all adsorbent amounts. In addition, the smallest difference in adsorption efficiency of three initial solutions concentration was observed by using 60 g of lignite.

Sorption efficiency of lignite and activated carbon in case of low initial concentration depending on contact time is presented in Figure 4. It is obvious that activated carbon shows better adsorption efficiency than lignite for longer contact time, but these differences are insignificant. Namely, it should be emphasized that used lignite is low cost raw material and plentiful in Serbia while activated carbon is more expensive due to pretreatment.

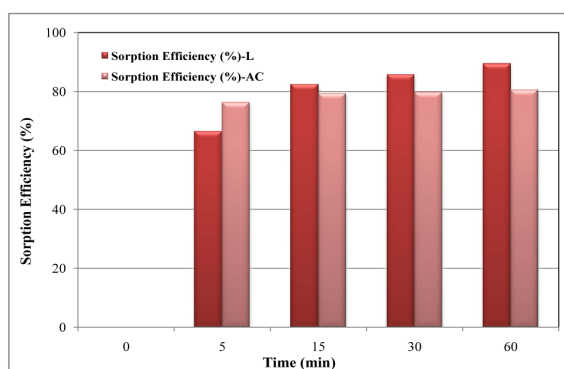


Fig. 4. Influence of contact time on copper adsorption for lignite; pH=5.5

CONCLUSION

Because of plentiful amounts of lignite in Serbia and rationalization of the adsorption process, the idea of this research was to avoid pre-treatment and use adsorbent in its raw form suitable for application in thermal power plant. This research shown that lignite from Kolubara deposit is highly effective, inexpensive and naturally available adsorbent for Cu²⁺ removal from aqueous solutions because of the environmental protection. In order to support explanation of lignite adsorption efficiency, FTIR analysis and determination of specific surface area were done.

The effects of pH and contact time on adsorption process of Cu²⁺ on lignite were followed. In a metal-lignite system, interaction process happened in the interval of pH = 2,0-5,0. The maximum adsorption is achieved if the pH solution is around 5,0. It was found that the rate of adsorption is very high at the beginning of the process in case of low copper concentration in the initial solution. In the first 5 minutes, it reaches 90 % due to higher amount of the adsorbent than it is usual. Sufficient contact time for both adsorbents is 30 minutes, since they achieve equilibrium for the mentioned time. Optimal parameters presented in this paper were: pH = 5,0 and τ = 30 min. The calculated adsorption capacities are not in accordance with literature available values because high adsorbent masses were used. As the surface area of the lignite was quite small, it can be assumed that the adsorption capacity of the lignite was augmented by chemisorption.

It can be concluded that in order to achieve better efficiency and economy, further investigation should be directed to the usage of much smaller amounts of lignite that can provide complete saturation by copper ions to the maximum utilization of adsorbent in wastewater treatment. Most important advantages of lignite as a potential industrial adsorbent compared to activated carbon are that no pre-treatment is required, its low cost, high adsorption capacity, and plentiful resources.

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