



XV BALKAN MINERAL PROCESSING CONGRESS - BMPC 2013

June 12 – 16, 2013, Sozopol, Bulgaria

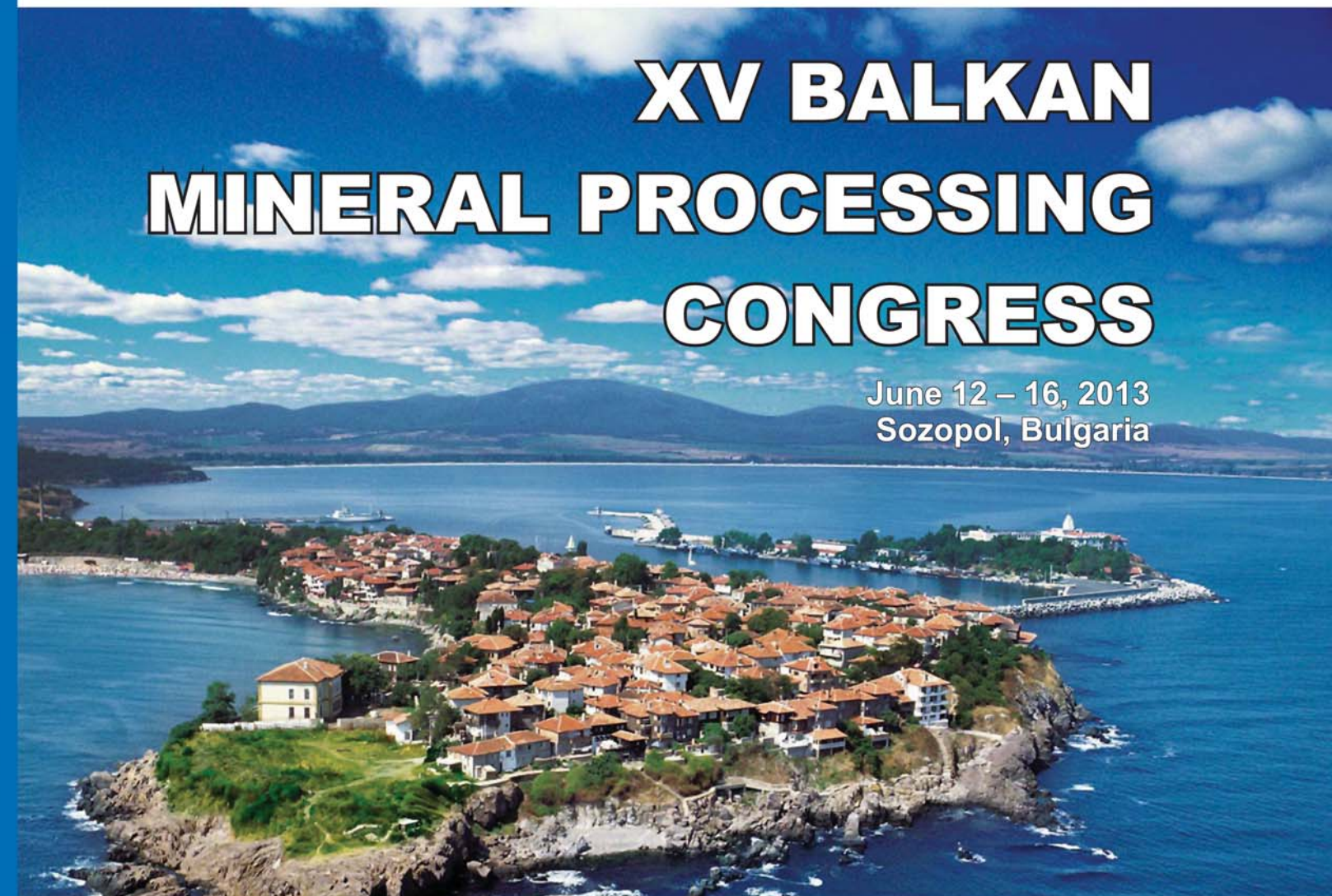


Proceedings of



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Volume I

Edited by:
**Ivan Nishkov
Irena Grigorova
Dimitar Mochev**



Publishing house "St. Ivan Rilski"



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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ADSORPTION ISOTHERMS OF REMOVING COPPER FROM AQUEOUS SOLUTIONS BY LOW COST ADSORBENT- LIGNITE

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ABSTRACT. Serbian lignite from "Kolubara" deposit was used as a low cost adsorbent for removal of copper ions (Cu^{2+}) from aqueous solutions. Lignite was subjected to the elementary and technical analysis as well as BET and FTIR analysis to provide complete characterization. Basic comparison between lignite and activated carbon was also done. Adsorption efficiency was studied as function of initial metal concentration and amount of adsorbent. Three different amounts of lignite were used (30, 45, and 60 g). Initial solutions with three different concentrations of copper (50, 200, and 330 mg/l) were prepared. Results proved that investigated lignite is very efficient sorbent material, especially in case of low copper concentration where the usual methods are either economically unrewarding or technically complicated. The effect of adsorbent amount on adsorption kinetics is visible but not crucial.

Keywords: copper, lignite, initial solution concentration, adsorbent amount.

INTRODUCTION

Wastewaters that arise from many industrial activities are contaminated with different heavy metals. Copper is the most common toxic and hazardous metal, which is released into the environment in a number of different ways. Copper in the water-streams finds the way to accumulate in the environment and thus make contamination that presents harmful effect on biological systems [1-4]. The concentrations of copper as well as heavy metals must be removed or reduced from the wastewater to the level that satisfies rigid legislative standards. The World Health Organization (WHO) recommended a maximum acceptable Cu^{2+} concentration of 1.5 mg/l in drinking water [5]. Copper 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 [2,6]. Each of these methods is used only in special cases since it has some limitations in practice [7]. Major disadvantage of almost all mentioned methods is production of more new hazardous waste, mostly solid [1]. Nowadays, many researches have been involved in development of new inexpensive materials and methods for the wastewater treatment. For example, there are applying natural adsorbents such as zeolites, wood, lignite, metal oxide, fly ash, coal, and waste biomass, where the predominant mechanism is ion exchange, but also there is surface adsorption, chemisorption, complexation and adsorption-complexation [2-4,8]. It should be emphasized that removing of heavy metals from the wastewaters presented in relatively low concentration is rather difficult [7]. Lignite is considered as very attractive material for metals removal because it is widely available and inexpensive [2]. Recently, the use of lignite in wastewater treatment is becoming more and more attractive and it may be good substitution for synthetic and expensive activated carbon. Lignite has high content of exchangeable functional groups that make it suitable and effective material for the removal of heavy metals from the wastewater. In addition, lignite has high cation exchange capacity forming complexes with metal ions. It has high content of oxygen fixed in carboxyl (-COOH), alcoholic (-OH), and carbonyl groups (=C=O) representing active centers of ion exchange which can take part in ion exchange mechanism [6,9].

EXPERIMENTAL

Lignite from "Kolubara" deposit, field B, was used as an adsorbent material. It was dried first at 45°C for 24 hours, and then grounded and sieved. The lignite with the grain size of 1-2 mm was used for the adsorption experiment.

Synthetic aqueous solution of copper was prepared by dissolving the appropriate amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salt in deionized water. Three different concentrations of initial solutions were prepared: 50, 200, and 330 mg Cu^{2+} /l. Volumes of solution were constant (250 ml). Air-dried lignite as an adsorbent was used in three different amounts (30, 45, and 60 g).

The kinetic of copper adsorption 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 amount of lignite was placed into a glass vessel;

prepared solution was added to the adsorbent batch; different initial Cu^{2+} concentrations were mixed with three different adsorbent dosages. In order to quantify adsorption efficiency (percentage of adsorbed metal), suspensions were filtered and residual copper ion concentration in the filtrate was determined in predetermined time intervals by AAS. Content of copper that was leached from the lignite saturated with copper by deionized water proved literature assessment that there was no leaching from the adsorbent [2]. Changes of Cu^{2+} in treated solutions were monitored by Perkin Elmer Atomic Adsorption Spectroscopy (AAS) type AAnalyst 300.

Functional groups in lignite were examined by the FTIR method of analysis. The IR measurements were carried out by a Fourier Transform Infra Red (FT-IR) spectrophotometer based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. FTIR-ATR (Fourier transform infrared attenuated total reflection spectroscopy) spectroscopic analyses were carried out at room temperature using a Nicolet 380 spectrophotometer in the spectral range of 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} . The datasets were averaged over 64 scans.

RESULTS AND DISCUSSION

Characterization Of Lignite

Elementary and technical analyses as well as specific surface area of lignite from "Kolubara" deposit, conducted according to the standard procedure, are given in Table 1.

According to the IUPAC classification [10], 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 m^2/g . On the other side, isotherm for activated carbon is of type IV and with a hysteresis loop which is associated with mesoporous materials. The shape of hysteresis loop is of type H4 that indicates a narrow slit pores and large amount of micropores [11]. Specific surface area calculated by BET equation (S_{BET}) is 758 m^2/g . Pore size distribution of activated carbon shows that the sample is mostly microporous with certain amount of mesopores and the pores radius below 7 nm. Actually, activated carbon consists of micropores amount (S_{mic})=683 m^2/g and mesopores amount (S_{meso})=75 m^2/g .

FTIR spectra of analyzed lignite and activated carbon are shown in Figure 1. Bands were identified by comparing with the literature [12-19]. These two spectra differ significantly in the peaks and it is obvious that lignite has much more functional groups than activated carbon. Six peak areas observed in diagram are: hydroxyl group region (3100-3700 cm^{-1}), aliphatic stretching region (2931-2855 cm^{-1}), aromatic carbon (peaks at 1618 and 1606 cm^{-1}), aliphatic bending region (1509-1371 cm^{-1}), cellulose and lignin region (1300-1000 cm^{-1}), and the aromatic out-of-plane region (900-700 cm^{-1}). 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 at 3698 cm^{-1} and 3700 cm^{-1} can be assigned to the crystal water, which exists in clay minerals of the matrix lignite samples [20]. 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 1506 cm^{-1} , as well as aliphatic C-H stretching bands at 1455 cm^{-1} and 1370 cm^{-1} .

The broad band at $\sim 3406\text{ cm}^{-1}$ is attributed to -OH stretching vibrations of hydrogen bonded hydroxyl groups of absorbed 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 -CH_3 and -CH_2 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 (CH_2) and methoxyl (OCH_3). The band at $\sim 1370\text{ cm}^{-1}$ is due to symmetric aliphatic C-H bending vibrations of methyl groups (OCH_3). 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 fact, it can be concluded that driving mechanism of lignite adsorption is based on chemisorption since there are many functional groups involved in ion exchange. On the other side, the adsorption properties of activated carbon are governed by physisorption since it has high values of specific surface area as well as micro and meso porosity. It can be explained by diffusion and transport processes within meso- and micropores. Since lignite is classified as nonporous and macroporous material and its specific surface area is small, it can be assumed that all identified functional groups involved in ion exchange during the adsorption are placed at the lignite surface. Namely, when expressed in terms of per unit surface area, lignite seems to give a surprisingly good adsorption capacity compared with the activated carbon.

Tabl. 1. Basic characteristics of the lignite from Kolubara deposit, field B

Content (%)					
C	H	N+O	S	H ₂ O	Ash
65.75	5.79	27.76	1.13	46.30	11.14
Heating value (kJ/kg)					9499
BET (m ² /g)					1

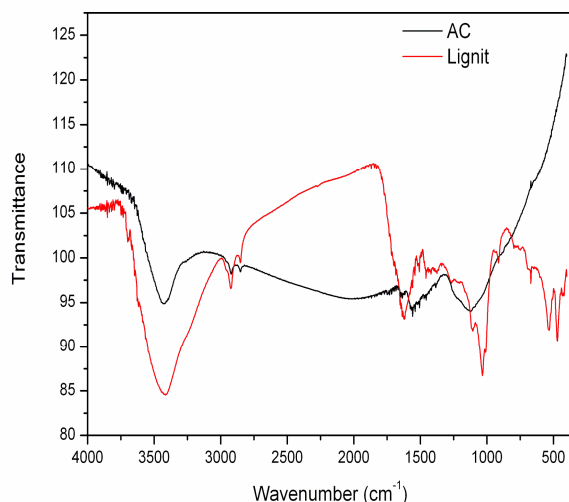


Fig. 1. FTIR spectra of lignite and activated carbon (AC)

Adsorption Experiments

Effect of adsorbent amount:

Effect of adsorbent amount on adsorption efficiency is shown in Figure 2. Increasing amount of lignite from 30 to 60 g for the same concentration of copper in solution leads to reduction of the adsorbed metal amount per mass unit of lignite. This is particularly obvious in the solution with higher copper concentration while this influence weakens in the solutions with the lowest copper concentration. It suggests that experiments should be directed to the small amounts of lignite in order to achieve better efficiency and to determine capacity of the adsorbent. On the other hand, tested masses of lignite under optimal conditions do not substantially affect the adsorption efficiency regardless the high concentration of the initial solution.

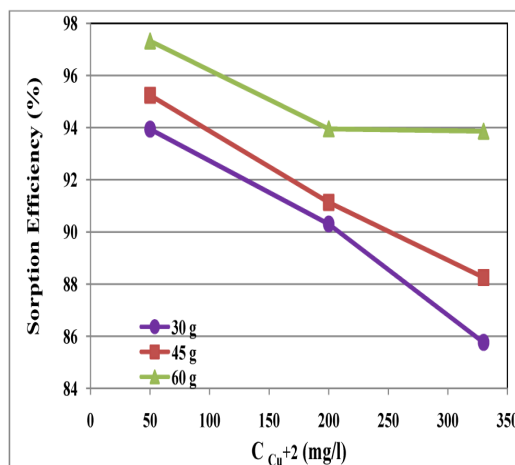


Fig. 2. Effect of adsorbent mass on sorption efficiency (conditions: pH= 5, contact time= 30 min)

Effect of initial solution concentration on copper removal and adsorption isotherm:

Effect of the initial solution concentration (50, 200, and 330 mg Cu²⁺/l) on the copper removal was observed and the obtained results are shown in Figure 3. Different amounts of the adsorbent were used (30, 45, and 60 g). It is obvious that for all lignite amounts, the adsorption of Cu²⁺ and, therefore, adsorption efficiency decreases with the increase of the initial solution concentration.

It was found that the equilibrium time was around 30 minutes, so the results of the initial solution concentration influence on copper removal are shown for that period. Effect of the initial solution concentration on copper adsorption was investigated for the following conditions: V = 250 ml, pH = 5, t = 20 °C.

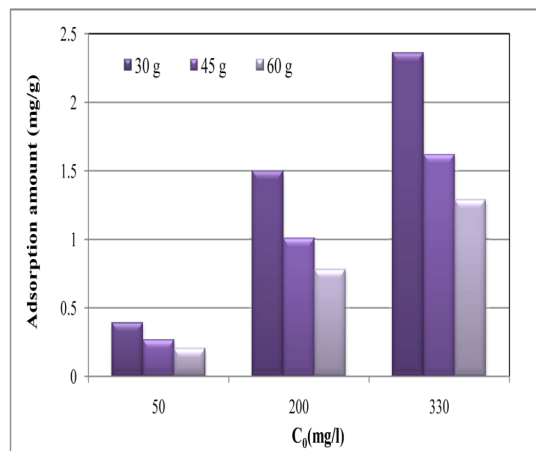


Fig. 3. Adsorption of copper ions on lignite for different initial solution concentrations

For all used initial solutions, the amount of adsorbed Cu²⁺ ions decreases with the increase of the concentration. This is especially emphasized in case of the adsorbent mass of 30 g, where the adsorption efficiency decreases from 94 % to 86 % for the initial concentrations of 50 mg/l and 330 mg/l, respectively. Based on the results presented in Figure 3, it is obvious that lignite is an effective adsorbent material for copper removal from the aqueous solutions, especially in case of low solution concentration; the adsorption efficiency is 94 - 97 % from the initial solution with concentration of 50 mg Cu²⁺/l.

In the solution with low concentration (regardless the adsorbent mass), the ratio of surface active sites (functional groups) on lignite to the total copper ions in solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. Since the driving force that presents concentration gradient is stronger in case of high concentrations, adsorbed amount of Cu²⁺ per unit of adsorbent mass will be higher.

It is obvious that the influence of lignite mass on adsorption efficiency is visible but not crucial particularly in the cases of low concentrations. The influence of adsorbent mass increases with

concentration rising; this is evident in case of initial solution concentration of 330 mg Cu²⁺/l.

Isotherm of copper adsorption by lignite is shown in Figure 5. Initial experimental conditions were: lignite amount of 30 g, pH = 5.0 and contact time of 30 minutes.

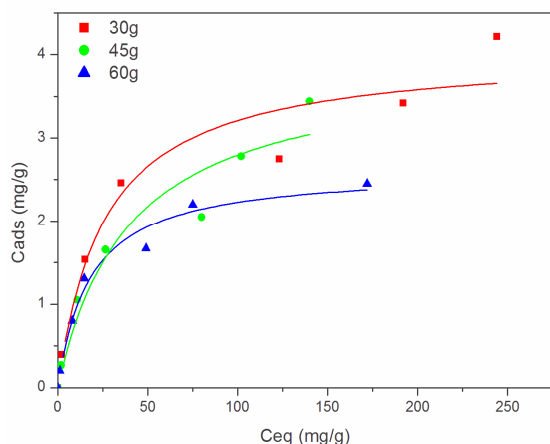


Fig. 4. Isotherms of copper adsorption by lignite using Langmuir model

Adsorption isotherm used for describing results of copper adsorption on lignite as an adsorbent is presented using the equation of Langmuir, Figure 4. Results for copper adsorption fit excellent to a Langmuirian type isotherm expressed by the following equation [2,4]:

$$q = \frac{q_{max} b C_e}{1 + b C_e} \quad (1)$$

where *q* is the amount of metal ion absorbed per unit mass of lignite (mg/g), *C_e* is the equilibrium copper concentration (mg/l), *q_{max}* is the maximum adsorption capacity (mg/g), *b* is constant related to adsorption intensity (l/mg) [2,4].

The Langmuir model is probably the best-known and most widely applied adsorption isotherm, since it shows good agreement with a wide variety of experimental data. It should be emphasized that Langmuir isotherm can be applied to the adsorption on completely homogenous surface with negligible interaction between adsorbed molecules. Regardless the basic assumption that this model cannot be applied for heterogeneous adsorbent surface, it was quite successful in predicting the experimental saturation capacity of the applied adsorbent [6].

Comparative adsorption isotherms of activated carbon and lignite are shown in Figure 5. It is evident that lignite shows better adsorption properties than activated carbon.

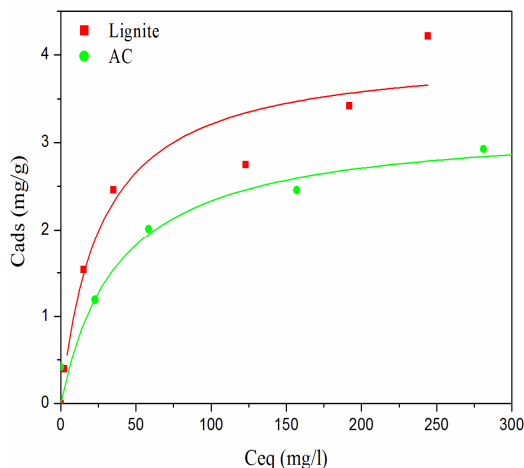


Fig. 5. Comparative isotherms of copper adsorption by activated carbon and lignite

As seen on diagrams presenting FTIR spectra (Figure 1), lignite has more specific adsorption bands than activated carbon. On the other side, specific surface area of activated carbon is higher as well as number of micro and meso pores. It can be concluded that the influence of oxygen functional groups is dominant for explaining adsorption behavior of lignite. Also, results of FTIR functionality analysis suggest that chemical adsorption plays important role for high adsorption efficiency of lignite.

Experimental data of the presented work were excellently fitted to the Langmuir equation since the regression analysis gave high correlation coefficients *R*² > 0.9, as shown in Table 2. The maximum adsorption capacities calculated by the Langmuir equation were 4.045, 3.908 and 2.625 mg/g for lignite masses of 30, 45 and 60 g, respectively (Table 2).

Tabl. 2. Langmuir parameters for copper adsorption on lignite

	<i>R</i> ²	<i>q_m</i> (mg/g)	<i>K</i> (l/mg)
Lignite- 30g	0.9228	4.045	0.038
Lignite- 45g	0.9191	3.908	0.025
Lignite- 60g	0.9740	2.625	0.056
Activated carbon	0.9497	3.229	0.026

The shape of all the isotherms is of "L1" type according to Giles classification for isotherms [4,21] which indicated that the curves do not reach any plateau (the adsorbent does not show clearly a limited adsorption capacity) [4,22]. „L" or Langmuir isotherm type is usually associated with ionic substrates, like metal cations, adsorption with weak competition from the solvent molecules [21,23]

The obtained adsorption capacities are not in accordance with those that are usually reported in the literature because of high masses of the used adsorbent. These results indicate that the saturation of lignite by copper ions was not achieved regardless the initial concentration of solution. It is obvious that the increasing amounts of lignite from 30 g to 60 g for the same initial solution concentration lead to decrease of the adsorption capacity value. Numerous free, available, and active sites on the adsorbent surface prove the assumption that much smaller lignite amount than 30 g can give good results in means of removing copper from the aqueous solution.

CONCLUSION

The most important conclusions from this research are summarized as follows:

- Serbian lignite from "Kolubara" deposit can be used as an adsorbent in its raw form.
- Lignite is highly effective, inexpensive and naturally available adsorbent for Cu²⁺ removal from aqueous solutions.
- Optimal parameters presented in this paper were: *C*₀ = 50 mg Cu²⁺/l and the adsorbent amount of 30 g.
- 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 significantly lower compared with the activated carbon, it can be assumed that the adsorption capacity of the lignite was augmented by chemisorption.

Isothermal tests show that the adsorption data agree well with Langmuir model. The obtained maximum adsorption capacities were 4.045, 3.908 and 2.625 mg/g for lignite masses of 30, 45 and 60 g, respectively.

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