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Water solution purification by phenol adsorption on solid fraction from thermal treatment of waste biomass - occurrences of unfavourable phenomenon

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ABSTRACT

Within presented work, the potential of gasification ash from the waste biomass conversion process as a sorbent for purification of the water solution was analysed and discussed. The comparison of the basic phenol removal effectiveness on the untreated materials, gasification ash and sewage sludge, gasification fuel, was done. The research aimed for comparison of the materials with and without preparation, being the washing with deionized water. The properties of the investigated materials were determined after sorption at temperature of 298 K using the sorption isotherms calculated by Freundlich equations. Moreover, the solution toxicity and leaching various chemical elements from material were analysed. It was denoted that phenol adsorption on solid fraction from the waste biomass thermo-chemical conversion process is more effective in comparison with process realized on unreacted fuel. The process intensity has been forced by the pre-treatment of the sorbent by deionized water. However, it was proved that there are many unfavourable phenomena during the process such as the increment of the solution toxicity and leaching of the chemical substances.

Keywords: Phenol; Adsorption; Solid waste fraction; Thermo-chemical process; Unfavourable phenomenon

1. Introduction

Phenol and other low-molecular weight elements are known to be toxic and inflict both severe and long-lasting effect on both humans and animals [1]. They act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations. Chemical oxidation, membrane processes and adsorption are the example of the effective methods used to eliminate low-molecular weight elements from aqueous streams and systems [2–8]. Among these processes, sorption arguably stands out with unflagging popularity. Overall efficiency of the adsorption processes is heavily dependent on the thermodynamic conditions of the process, that is, temperature and pressure, as well as the adsorbent type [9]. At the same time, one should always remember to strive for the criterion of increasing the efficiency of the process while still trying to reduce its costs. Addressing cost reduction, it can be seen that more and more interest is put on non-conventional adsorbents, that is, natural resources, bio-sorbents and waste materials, including industrial or agricultural [10–17].

Regarding sorbent materials, carbon derivatives obtained from biomass and wastes, that is, beet pulp [18] or rice husk [19] and commercial activated carbons provide excellent

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sorption properties of phenol [20]. Analyzing unconventional adsorbents such as derivatives of algae [21], olive pomace [22], red mud [23] and bagasse fly ashes from combustion process [24] despite potential low acquisition cost, the sorption effectiveness is much lower. Moreover, some of them, for example, fly ashes, are characterized by unfavourable properties such as large amounts of alkali metals [25–27].

The adsorption potential of the solid by-products from the gasification (ash) to eliminate phenol from aqueous solution is presented. Additionally, the sorption effectiveness on the untreated, granulated sewage sludge (GSS) was analysed.

The comparison of the materials with and without preparing relaying on washing with deionized water was made. The process efficiency was evaluated based on the following parameters: K_f and n, constants determined by the Freundlich equation. The presented study included also an evaluation of the unfavourable phenomena, occurring during the sorption on the unconventional adsorbents, that is, leaching of the chemicals from sorption materials (very often ones with biological activity) and the change of the solution toxicity.

2. Experimental

2.1. Adsorbents

GSS collected from Polish mechanical-biological-chemical wastewater treatment plant (with simultaneous phosphorus precipitation) formed during gasification ash was analysed. The sludge production process in this system includes: anaerobic digestion followed by dewatering and drying in a belt drier using air preheated to temperature equal to 150°C. Finally, the dried product, that is, sludge is compressed and formed into thin “pasta” (Fig. 1a). As a thermo-chemical conversion method, the hot air fixed bed gasification process of GSS was adapted. Previously adapted methodology assumed: gasification agent (air) temperature 298–523 K with the air ratio, λ, 0.12–0.27 [28]. In this study, gasification proceeded at constant thermodynamic conditions (temperature of the gasification agent was 298 K and air ratio equal to λ = 0.18. Main solid residue, gasification ash is presented in Fig. 1b.

In Table 1, the concentrations of pollutants present in the GSS and the gasification ash is presented [29]. It was denoted that main contaminants of dried sludge were PAH’s (polycyclic aromatic hydrocarbons) and heavy metals. Noteworthy, the solid gasification by-products were not discovered to contain any of the organic elements, which was detected initially in the GSS. Gasification solid fraction

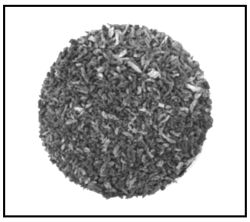
a)  b) 

Fig. 1. Investigated feedstock: samples of dried sewage sludge (a) and gasification ash (b).

Table 1
Concentration of main compounds in GSS and ash [30]

Organic compounds	Concentration, μg/kg (dry basis)	
	Sewage sludge	Ash
Sum of PAHs[1]	621.33	n.d.
Sum of pesticides[2]	1.28	n.d.
Sum of PCBs[3]	12.47	n.d.
Heavy metals	Concentration, mg/kg (dry basis)	
Zn	991.20	1,913.00
Cu	183.16	599.00
Pb	59.97	136.00
Ni	18.90	53.60
Cr	584.53	911.00
Cd	3.24	1.60
As	3.94	6.44
Hg	0.96	0.00
Se	1.70	0.01
Sum	1,847.60	3,620.65

[1]phenanthrene, anthracene, benzo(a)fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene;
[2]heptachlor, aldrin, endrin; [3]2,2′,5,5′-PCB, 2,2′,4,5,5′-PCB, 2,2′,4,4′,5,5′-PCB; n.d. - not detected.

of products contained mainly inorganic substances, with significant amount of heavy metals. Denoted presence of contaminants is a crucial information for the risk assessment associated with the use of waste derivate.

During the process, first the sorbents were pre-washed using deionized water, then dried at 60°C. Lastly, washed and dried samples were pulverized. The methodology has already been presented and discussed in previous work elsewhere [31], being the typical way for the adsorbent pretreatment in this kind of research. Furthermore, for comparison purposes, adsorbent materials without preparing were also used.

2.2. Adsorbate

The conventional phenol reagent (Merck, Warsaw, Poland) as an adsorbate was used. The solution of the adsorbate was produced by directly dissolving in water. The research was carried out at pH 7.0. It was regulated by HCl 0.1 mol/L or NaOH 0.2 mol/L. Spectrometry was adapted to determine phenol concentration with 4-aminoantipyrine at a wavelength of 510 nm.

2.3. Adsorption studies

Adsorption was carried out under static environment using Erlenmeyer flasks, with process temperature of 298 K. Investigated adsorbent material (1,000 mg/L) was added to a solution of the adsorbate (V = 100 mL, pH = 7.0) at a concentration of 60–90 mg/L.

The samples were shaken for 1 h using laboratory shaker, Labor System (Wroclaw, Poland) in a circular motion at a speed of 300 rpm. Before the marking, sample was filtered through a membrane with a pore size of 0.45 μm (Merck, Warsaw, Poland) to remove the adsorbent material. Equilibrium results were analysed using the popular Freundlich adsorption isotherm, being the base for the design of the sorption process. In previous work within this field, it was concluded [32] that the fit quality of theoretical Freundlich adsorption isotherm to experimental data is higher comparing with the Langmuir isotherm. This effect was especially significant in the studies of the phenol adsorption using ash from the GSS gasification.

The Freundlich model is given as follows [32]:

$$q_{\mathrm{eq}} = K_f \times C_{\mathrm{eq}}^{1/n} \tag{1}$$

where q_{eq} - quantity of the adsorbed substance per specified portion of the adsorbent (mg/g), C_{eq}- equilibrium strength for the solution (mg/L), K_f and n - the Freundlich constants associated with the sorption intensity.

Presented Eq. (1), being the empirical formula, is based on sorption on a heterogeneous surface, which can be arranged as a linear function. Such arrangement allows relatively simple calculation of the constants: K_f and n.

$$\log q_{\mathrm{eq}} = \log K_f + \frac{1}{n}\log C_{\mathrm{eq}} \tag{2}$$

2.4. Determination of the solution toxicity with the assessment of the leaching of inorganic and organic substances from adsorbents

One of the presented study goals was an assessment of the leaching organic and implied pollutants from adsorbents with simultaneous solution toxicity determination. Studies were carried out without the phenol addition to the analysed solution. Amounts of inorganic and organic elements were determined in the indirect method, using UV_{254} method.

Conductivity and general parameters of the solutions (temperature, pH) were determined using inoLab® 740 (WTW, Wrocław, Poland). The absorbance in UV_{254} was determined by the spectrophotometer Cecil 1000 by Cecil Instruments (Cambridge, United Kingdom). Toxicity of the solutions was evaluated by the bioluminescence inhibition of the marine bacteria *(Aliivibrio fischeri)*. Selected method is based on the assessment of the metabolic changes of bacteria affected by the environmental conditions, solution properties. Dependent variable are changes in the intensity of the light emitted by the microorganisms. Bioluminescence tests were conducted using MicrotoxOmni installation in the analyser Microtox 500 (Tigret Ltd., Warsaw, Poland). The system comprises both an incubator and a dedicated photometer. The principle of the assay was based on addition of a suspension of rehydrated bacteria to the solution of the sample. After 5 min of exhibition time, percentage value of bioluminescence inhibition was measured and compared against the control sample (2% Nail).

Toxicity classification of the samples was determined using the system presented by many scientists [33–35]. The methodology is connected with the amount of the effect observed in the indicator organisms. When the effect is below 25%, it was concluded that samples are non-toxic. Effect between 25% and 50% was determined as a low toxic, effect higher than 50% but lower than 75% was determined as toxic and finally effect higher than 75% was determined as highly toxic.

The indirect methods were adapted due to the complexity of structure and composition of both the GSS and the gasification ash, comprising various inorganic and organic substances. Full characterization of these elements would require both cost- and time-consuming comprehensive study.

3. Results and discussion

Performed experiments proved that both investigated adsorbents release chemicals after contact with deionized water. Conclusion was stated based on the increase of the solution conductivity (Figs. 2a and 3a) and absorbance in UV_{254} (Figs. 2b and 3b). This phenomenon was pointed both for the gasification ash and dried sewage sludge. This fragment of the research was determined with no addition of phenol to the solution. Additionally, it has been shown that the solution is characterized by different values of bioluminescence inhibition (Figs. 2c and 3c). This is due to eluting of the toxic elements with different physico-chemical properties from the tested adsorbent materials. The strength of the observed phenomena is significantly affected by both the adsorbents (ash from gasification, the GSS) and the fact if the material was initially pre-prepared or not. The intensity of the release phenomenon of the primary chemicals from adsorbents was smaller for the pre-washed ash from the gasification than for the GSS. Analyzing the GSS, the initial prewash does not significantly reduce the further release phenomenon of an organic or an inorganic substance (Figs. 3a and b). However, this phenomenon was recognized in cases of the pre-washed gasification ashes (Figs. 2a and b). What is emphasised is that initial pre-washing of the both analysed materials significantly impacts on the value of the power of the individual solution bioluminescence inhibition (Figs. 2c and 3c). Before washing process, both materials were induced toxicity of the solution. After the washing process, solutions were non-toxic. In the summary of this fragment of the work, it should be dotted that the assessment of the unfavourable phenomena connected with the use of unconventional materials to the sorption should be a significant part of the research methodology. Although it should be also noted that this problem will not apply to non-conventional adsorbents, which originally did not contain contaminants such as, for example, olive seeds [16].

The obtained results regarding the solutions toxicity are hard to interpret as both the GSS and the gasification ash are polluted with inorganic and organic chemicals. To some extent, those substances have already been characterized in the previous studies within this field [31], and presented in Table 1. Elucidation of the phenomenon occurring in water environment with an un-conventional sorbent sets demand for further research. Furthermore, it is plausible that other types of contaminants are present in investigated samples. For the obtained results of the sorption (phenol concentration 60–90 mg/L), Freundlich adsorption isotherms were determined and analysed. It was the main aim for determining the constant isotherm equation coefficients (Table 2). The K_f value for the Freundlich isotherm denotes adsorption capacity, while the n value describes strength of the adsorption. The lowest K_f value was denoted

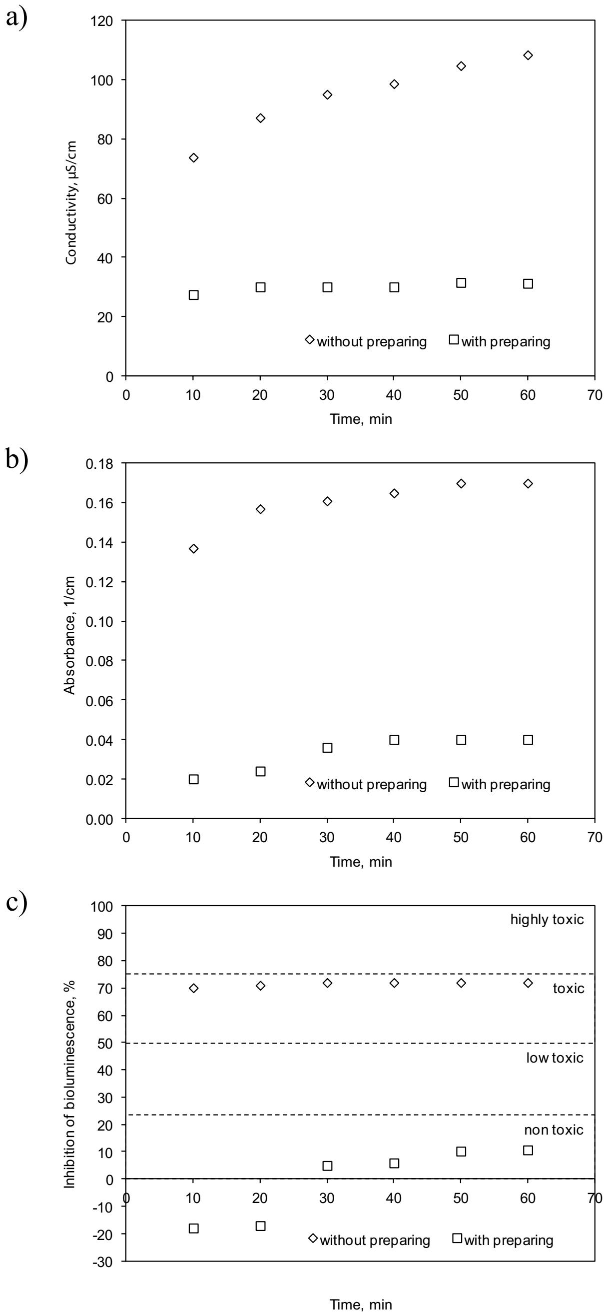


Fig. 2. Impact of the sample preparation on the solution conductivity (a), total organic carbon TOC (b) and the inhibition of the bioluminescence (c) in a solution of deionized water containing tested ash (no phenol addition).

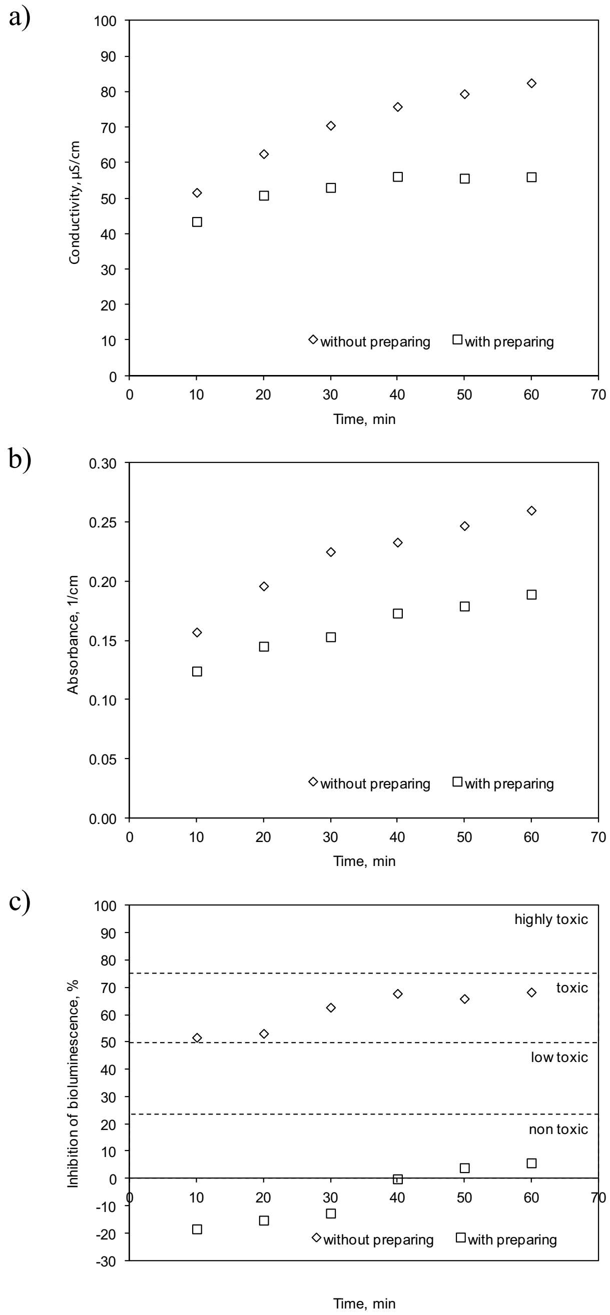


Fig. 3. Impact of the sample preparation on the conductivity of the solution (a), total organic carbon TOC (b) and the bioluminescence inhibition (c) in a solution of deionized water containing tested GSS (no phenol addition).

for GSS without preparation, and the highest for deionized water pre-washed ash. Nevertheless, it can be said that the sorption strength for ash is much lower in comparison with GSS. However, initial preparation of the adsorbents had an impact on the value of this parameter. The results were also referred to earlier own research in this area [19]. The capacity of sorption of the GSS gasification from another treatment system (without chemical precipitation of phosphorus) was investigated.

The analysed ash was made using the same methodology as used in the presented paper. It was determined that the constant K_f in this case was slightly lower (42.218 mg/g) than the ash tested at present work (48.865 mg/g). On this basis, it can be summed up that the system type, which produced gasified GSS may affect on its adsorption properties.

Among these properties, a specific surface area of the adsorbent should be mentioned [12]. In the case of the

Table 2
Impact of preparation process on sorption Freundlich parameters for phenol adsorption onto GSS and gasification ash

	GSS		Ash	
	Without preparing	With preparing	Without preparing	With preparing
K_f (mg/g)	8.724	13.236	29.995	48.865
$1/n$	0.839	0.988	0.532	0.592
R^2	0.955	0.960	0.971	0.953

gasification ash, this parameter will depend upon the gasification temperature.

4. Conclusion

The following conclusions can be stated based on the obtained results:

- For both investigated adsorbents, GSS and gasification ash, environment of deionized water resulted in release of the inorganic and organic substances. Under these conditions the growth of the solution toxicity was denoted as well. The intensity of this phenomenon was lower in the case of gasification ash than for the GSS, which was affected by the initial fitting of the material through the washing in deionized water.
- Analysis of the coefficients of the isotherms showed, that GSS without preparation presents the lowest sorption capacity (determined based on the K_f) and the pre-prepared ash from gasification showed the highest sorption capacity. However, comparing the adsorption strength, it can be realised that this parameter for ash is much lower in comparison to GSS. However, in that case, initial formulation of the adsorbent material had an impact on this parameter.
- Taking into consideration both unfavourable phenomena and adsorption capacity of the analysed unconventional adsorbent it can be concluded, that its effective usage is connected with the fact if the material was initially pre-prepared or not.
- The comparative results showed that gasification ash, as a representative of biomass thermal-conversion by-product, presented higher potential as an unconventional adsorbent when compared with GSS.

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References

[1] K. Zoschke, C. Engel, H. Börnick, E. Worch, Adsorption of geosmin and 2-methylisoborneol onto powdered activated carbon at non-equilibrium conditions. Influence of NOM and process modeling, Water Res., 45 (2011) 4544–4550.
[2] O. Autin, J. Hart, P. Jarvis, J. MacAdam, S.A. Parsons, B. Jefferson, The impact of background organic matter and alkalinity on the degradation of the pesticide metaldehyde by two advanced oxidation processes: UV/H_2O_2 and UV/TiO_2, Water Res., 47 (2013) 2041–2049.
[3] T. Botelho, M. Costa, M. Wilk, A. Magdziarz, Evaluation of the combustion characteristics of raw and torrefied grape pomace in a thermogravimetric analyzer and in a drop tube furnace, Fuel, 212 (2018) 95–100.
[4] K.G. Linden, E.J. Rosenfeldt, S.W. Kullman, UV/H_2O_2 degradation of endocrine-disrupting chemicals in water evaluated via toxicity assays, Water Sci. Technol., 55 (2007) 313–319.
[5] M. Wilk, A. Magdziarz, K. Jayaraman, M. Szymańska-Chargot, I. Gökalp, Hydrothermal carbonization characteristics of sewage sludge and lignocellulosic biomass. A comparative study, Biomass Bioenergy, 120 (2019) 166–175.
[6] S. Miralles-Cuevas, I. Oller, A. Ruiz Aguirre, J.A. Sánchez Pérez, S. Malato Rodríguez, Removal of pharmaceuticals at microg L-1 by combined nanofiltration and mild solar photo-Fenton, Chem. Eng. J., 239 (2014) 68–74.
[7] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment - a literature review, Water Res., 38 (2004) 2795–2809.
[8] A. Magdziarz, M. Wilk, R. Straka, Combustion process of torrefied wood biomass - a kinetic study, J. Therm. Anal. Calorim., 127 (2017) 1339–1349.
[9] S. Werle, K.Q. Tran, A. Magdziarz, S. Sobek, M. Pogrzeba, T. Lovas, Energy crops for sustainable phytoremediation – fuel characterization, Energy Procedia, 158 (2019) 862–872.
[10] Z. Aksu, D. Akpinar, Modelling of simultaneous biosorption of phenol and nickel(II) onto dried aerobic activated sludge, Sep. Purif. Technol., 21 (2000) 87–99.
[11] T.T. Trinh, S. Werle, K.Q. Tran, A. Magdziarz, S. Sobek, M. Pogrzeba, Energy crops for sustainable phytoremediation – thermal decomposition kinetics, Energy Procedia, 158 (2019) 873–878.
[12] S. Aredes, B. Klein, M. Pawlik, The removal of arsenic from water using natural iron oxide minerals, J. Clean. Prod., 29–30 (2012) 208–213.
[13] S. Sobek, S. Werle, Kinetic modelling of waste wood devolatilization during pyrolysis based on thermogravimetric data and solar pyrolysis reactor performance, Fuel, 261 (2020) 116459
[14] K.V. Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, *Dyes Pigm.*, 74 (2007) 595–597.
[15] S. Sobek, S. Werle, Gasification of sewage sludge within a circular economy perspective: a Polish case study, Environ. Sci. Pollut. Res., 26 (2019) 35422–35432.
[16] M.A. Martín-Lara, G. Blázquez, M.C. Trujillo, A. Pérez, M. Calero, New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone, J. Clean. Prod., 81 (2014) 120–129.
[17] K. Zhou, Q. Zhang, B. Wang, J. Liu, P. Wen, Z. Gui, Y. Hu, The integrated utilization of typical clays in removal of organic dyes and polymer nanocomposites, J. Clean. Prod., 81 (2014) 281–289.
[18] G. Dursun, H. Cicek, A.Y. Dursun, Adsorption of phenol from aqueous solution by using carbonized beet pulp, J. Hazard. Mater., 125 (2005) 175–182.
[19] M. Ajmal, A.R.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, B. Özkaya, Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, Bioresour. Technol., 2 (2003) 147–149.

[20] L.J. Kennedy, J.J. Vijaya, K. Kayalvizhi, G. Sekaran, Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage process, Chem. Eng. J., 132 (2007) 279–287.
[21] R. Aravindhan, J.R. Rao, B.U. Nair, Application of a chemically modified green macro algae as a biosorbent for phenol removal, J. Environ. Manage., 90 (2009) 1877–1883.
[22] A.S. Stasinakis, I. Elia, A.V. Petalas, C.P. Halvadakis, Removal of total phenols from olive-mill wastewater using an agricultural by-product olive pomace, J. Hazard. Mater., 160 (2008) 408–413.
[23] A. Tor, Y. Cengeloglu, M.E. Aydin, M. Ersoz, Removal of phenol from aqueous phase by using neutralized red mud, J. Colloid Interface Sci., 300 (2006) 498–503.
[24] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics, Colloids Surf., A, , 272 (2008) 89–104.
[25] X. Yao, H. Zhou, K. Xu, Q. Xu, L. Li, Investigation on the fusion characterization and melting kinetics of ashes from co-firing of anthracite and pine sawdust, Renew. Energy, 145 (2020) 835–846.
[26] X. Yao, H. Zhou, K. Xu, Q. Xu, L. Li, Evaluation of the fusion and agglomeration properties of ashes from combustion of biomass, coal and their mixtures and the effects of K_2CO_3 additives. Fuel, 255 (2019) 115829.
[27] X. Yao, H. Zhou, K. Xu, S. Chen, J. Ge, Q. Xu, Systematic study on ash transformation behaviour and thermal kinetic characteristics during co-firing of biomass with high ratios of bituminous coal, Renew. Energy, 147 (2020) 1453–1468.
[28] S. Werle, M. Dudziak, Gaseous fuels production from dried sewage sludge via air gasification, Waste Manage. Res., 32 (2014) 601–607.
[29] S. Werle, M. Dudziak, Analysis of organic and inorganic contaminants in dried sewage sludge and by-products of dried sewage sludge gasification, Energies, 7 (2014) 462–476
[30] S. Werle, M. Dudziak, In: M.N.V. Prasad, P.J. de Campos Vavas, S. Venkata Mohan, Industrial and Municipal Sludge, Butterworth-Heinemann, Oxford, 2019, pp. 575–594.
[31] U. Thawornchaisit, K. Pakulanon, Application of dried sewage sludge as phenol biosorbent, Bioresour. Technol., 98 (2007) 140–144.
[32] M. Dudziak, S. Werle, Studies on the adsorption of phenol on dried sewage sludge and solid gasification by-products, Desal. Wat. Treat., 57 (2016) 1067–1074.
[33] Q.S. Liu, T. Zheng, P. Wang, J.P. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibres, Chem. Eng. J., 157 (2010) 348–356.
[34] S. Werle, M. Dudziak, Evaluation of toxicity of sewage sludge and gasification waste-products, Przemysł Chemiczny, 92 (2013) 1350–1353 (in Polish).
[35] B. Cwalina, A. Wiącek-Rosińska, Acute toxicity tests based on bacterial bioluminescence in evaluation of environment contamination and remediation effects, Archiwum Ochrony Środowiska, 9 (2003) 107–114 (in Polish).