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ZBRINJAVANJE ZAULJENIH OTPADNIH VODA I NASTALOG MULJA U OPEKARSKOJ INDUSTRIJI

DOKTORSKI RAD

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DISPOSAL OF OILY WASTEWATER AND GENERATED SLUDGE IN THE BRICK INDUSTRY

DOCTORAL THESIS

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Sažetak

Otpadne voda onečišćena uljem predstavljaju sve veći globalni problem zbog velikih količina i visokog sadržaja onečišćenja, koji pri ispuštanju u okoliš mogu ugroziti vode, zrak i zdravlje ljudi. Njihova održiva obrada mora biti učinkovita, ekonomična i usklađena s ekološkim zahtjevima. U ovom radu prikazan je pregled najnovijih tehnologija obrade zauljenih otpadnih voda s naglaskom na elektrokemijske i napredne oksidacijske procese, te je ispitana njihova učinkovitost u ovisnosti o ključnim procesnim parametrima. Posebna pozornost posvećena je hibridnom procesu koji kombinira elektro-Fentonovu reakciju i elektrokemijsku koagulaciju s različitim vrstama elektroda (Fe, Al, NČ), a čija je primjena pokazala značajan potencijal za smanjenje organskog opterećenja izraženog preko kemijske potrošnje kisika (KPK) i ukupnih ugljikovodika u otpadnoj vodi. Tijekom provedenih ispitivanja praćene su koncentracije KPK-a, ukupnih ugljikovodika te niza elemenata u sirovoj i obrađenoj otpadnoj vodi (As, Ca, Cd, Cr, Cu, Ni, Pb, Sn, Zn) kao i u generiranom mulju (K, Ca, Fe, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb, Th). Utvrđeno je da se najveće učinkovitosti postižu pri pH – vrijednosti 7–8, kada je uklanjanje KPK-a iznosilo 96 %, a ukupnih ugljikovodika više od 93,00 %, dok je za pojedine elemente (Cd, Cu, Ni, Pb, Sn, Zn) postignuta i potpuna (100,00 %) učinkovitost uklanjanja. Primjenom predobrade mješavine sirove otpadne vode i prethodno generiranog mulja uz primarno taloženje, a potom EF/EC postupkom, učinkovitost je dodatno povećana te je ostvareno uklanjanje ukupnih ugljikovodika od 99,00 % i organskog opterećenja izraženog preko KPK-a od 98,00 %.

Pročišćavanjem ovakvih voda nastaju pročišćena tehnološka voda i elektrokemijski mulj, pa je istražena mogućnost njihove ponovne uporabe u proizvodnji opeka. Time se nastoji povezati zbrinjavanje problematičnog otpada s njegovom valorizacijom u građevinskoj industriji, u skladu s načelima kružnog gospodarstva i smanjenja emisija CO_2. U okviru istraživanja proizvedeno je 25 serija opeka: kontrolne opeke od 100 % gline te opeke s dodatkom mulja obrađenog različitim postupcima (konvencionalno i mikrovalno sušenje, kalciniranje, korištenje tekućeg mulja) u udjelima od 1 do 20 mas. %. Također su izrađene opeke korištenjem pročišćene tehnološke vode. Ispitivanja su obuhvatila fizikalna i mehanička svojstva (tlačna čvrstoća, vodoupojnost, apsorpcija vode, koeficijent zasićenja), kemijski sastav (XRF, XRD), sadržaj topivih soli, elektrovodljivost eluata, ekotoksičnost, izluživanje metala, radioaktivnost te emisije hlapljivih organskih spojeva i dimnih plinova. Dobiveni rezultati pokazali su da su opeke s manjim dodacima mulja (do 5 mas. %) usporedive s kontrolnom opekom, dok veći udjeli mogu utjecati na mehanička i fizikalna svojstva, ali ne predstavljaju rizik s aspekta radioaktivnosti i stabilnosti teških metala. Najpovoljnijom opcijom pokazala se primjena tekućeg mulja bez prethodne termičke obrade, jer omogućuje smanjenje potrošnje energije, emisija CO_2 i ukupnih troškova proizvodnje, uz zadovoljavajuća mehanička, fizikalna i ekotoksična svojstva proizvoda. Rezultati će poslužiti i za buduću klasifikaciju elektrokemijskog mulja te učinkovitije gospodarenje ovom posebnom kategorijom otpada.

Ključne riječi: ekološka svojstva, elektrokemijski generiran mulj, elektrokemijski procesi, fizikalno-kemijske karakteristike otpadne vode, glina, mehanička svojstva, modificirane opeke, napredni oksidacijski procesi, vodoupojnost opeka, zauljene otpadne vode

Abstract

Wastewater polluted with oil represents an increasing global problem due to the large volumes and high content of pollutants, which, when discharged into the environment, can endanger water, air, and human health. Their sustainable treatment must be efficient, economical, and compliant with environmental requirements. This paper presents an overview of the latest treatment technologies for oily wastewater, with an emphasis on electrochemical and advanced oxidation processes, and examines their efficiency depending on key process parameters. Special attention is given to a hybrid process combining the electro-Fenton reaction and electrochemical coagulation with different types of electrodes (Fe, Al, SS), the application of which has shown significant potential for reducing organic load expressed through chemical oxygen demand (COD) and total hydrocarbons in wastewater. During the conducted tests, the concentrations of COD, total hydrocarbons, and a series of elements in raw and treated wastewater (As, Ca, Cd, Cr, Cu, Ni, Pb, Sn, Zn) as well as in the generated sludge (K, Ca, Fe, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb, Th) were monitored. It was found that the highest efficiencies were achieved at pH values of 7–8, when COD removal reached 96% and total hydrocarbons more than 93%, while complete (100,00%) removal efficiency was achieved for some elements (Cd, Cu, Ni, Pb, Sn, Zn). Using primary sedimentation of a mixture of raw wastewater with previously generated sludge as pretreatment and followed by EF/EC treatment, the efficiency was further increased, achieving total hydrocarbon removal of 99% and organic load expressed through COD removal of 98,00%.

Treatment of such waters results in purified process water and electrochemical generated sludge, and the possibility of their reuse in brick production was investigated. The aim is to link the management of problematic waste with its valorization in the construction industry, in line with the principles of the circular economy and CO_2 emission reduction. As part of the research, 25 series of bricks were produced: control bricks made of 100% clay, and bricks with the addition of sludge treated by different methods (conventional and microwave drying, calcination, use of liquid sludge) in amounts ranging from 1 to 20 wt.%. Bricks were also produced using purified process water. Tests covered physical and mechanical properties (compressive strength, water absorption, water uptake, saturation coefficient), chemical composition (XRF, XRD), soluble salt content, leachate conductivity, ecotoxicity, metal leaching, radioactivity, as well as emissions of volatile organic compounds and flue gases. The results showed that bricks with smaller sludge additions (up to 5 wt.%) are comparable to the control brick, while higher proportions may affect mechanical and physical properties, but do not pose a risk in terms of radioactivity and heavy metal stability. The most favorable option proved to be the use of liquid sludge without prior thermal treatment, as it allows a reduction in energy consumption, CO_2 emissions, and overall production costs, while maintaining satisfactory mechanical, physical, and ecotoxicological properties of the product. The results will also contribute to the future classification of electrochemical sludge and more efficient management of this special waste category.

Keywords: oily wastewater, electrochemical processes, advanced oxidation processes, physico-chemical characteristics of wastewater, clay, electrochemically generated sludge, modified bricks, mechanical properties, brick water absorption, ecological properties.