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SYNTHESIS OF GRANULATED CARBON–MINERAL SORBENTS FROM LOCAL RAW MATERIALS

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Abstract: This study investigates the design of granulated carbon-mineral sorbents based on a carbon sorbent derived from fruit stone waste (CS), multicolored kaolin from the Angren deposit, and glauconite from the Krantau deposit. A review of the relevant literature established that firing carbon-containing granules in an oxidizing (air) atmosphere is fundamentally unsuitable because it causes carbon combustion and deterioration of the sorbent structure. Therefore, low-temperature geopolymerization was selected as the binder-forming approach to ensure the mechanical integrity of the granules while preserving the carbon phase. An experimental design matrix comprising eleven compositions (G-1 to G-11) was developed within the CS-metakaolin-activated glauconite system. For each formulation, the specific surface area, cation exchange capacity, compressive strength, abrasion resistance, equilibrium sorption time, and sorption capacities toward five heavy metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+}) were evaluated using a calculation-based predictive approach. The results indicate that the incorporation of 30 wt.% mineral components reduces the sorption capacity by only 24-25%, demonstrating that the loss of adsorption performance proceeds more slowly than the increase in mineral content. Furthermore, the selectivity sequence remained unchanged for all investigated compositions and followed the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} \approx Zn^{2+}$. Based on a multi-criteria assessment, composition G-3 (80:20:0) was identified as the optimum formulation for the treatment of wastewater containing a single heavy metal, whereas composition G-8 (70:10:20) exhibited the most favorable performance for multicomponent industrial wastewater. It should be emphasized that the numerical values presented in this study represent calculation-based model predictions and require experimental validation.

Keywords: granulated sorbent; carbon-mineral composite; Angren kaolin; Krantau glauconite; metakaolin; geopolymer binder; heavy metals; sorption capacity; sorption selectivity; multi-criteria optimization.

1. Introduction

The treatment of industrial wastewater contaminated with heavy metals remains a significant environmental challenge due to the non-biodegradable nature of these pollutants and their tendency to accumulate in food chains through bioaccumulation. Consequently, adsorption has become one of the most widely applied technologies for the removal of dissolved heavy metal ions from aqueous media because of its high efficiency, operational simplicity, and economic feasibility. However, although powdered carbonaceous sorbents possess a high specific surface area and excellent adsorption capacity, their practical application in fixed-bed adsorption columns is limited. Fine particles increase hydraulic resistance, impede fluid flow, and are readily washed out with the treated effluent. Therefore, the conversion of powdered sorbents into mechanically stable granules has become a critical prerequisite for their large-scale industrial application.

In recent years, the granulation of powdered carbonaceous sorbents using clay minerals has emerged as an active area of research. One of the most extensively investigated systems is based on activated carbon-clay granules produced by the extrusion technique. In this approach, sawdust, clay minerals, and H_2SO_4 were mixed at a volumetric ratio of 1:1:1, extruded through a die with a diameter of 4 mm, dried at 100°C, and subsequently pyrolyzed in a nitrogen atmosphere at 500°C for 2 h. The resulting granules exhibited a specific surface area of 188 m^2/g, a compressive strength of 1,1 ± 0,1 MPa, and a Pb (II) adsorption capacity of 47 mg/g. Regeneration with HCl solution (pH 1,0-1,5) achieved a desorption efficiency of 97-98%. After four consecutive adsorption–desorption cycles, the compressive strength decreased to 0,88 MPa, corresponding to an approximately 20% reduction relative to the initial value [1].

Another important contribution has been reported for biochar-kaolinite composite systems. Biomass derived from Conocarpus was modified with 10 and 20 wt.% kaolinite and subsequently pyrolyzed at 600°C. Although the incorporation of kaolinite led to the expected decrease in specific surface area, the adsorption capacity toward heavy metal ions increased significantly. The composite containing 20 wt.% kaolinite exhibited adsorption capacities of 248,3 mg/g for Pb^{2+}, 228,1 mg/g for Cu^{2+}, 63,2 mg/g for Cd^{2+}, and 45,8 mg/g for Zn^{2+} at pH 7 [2]. These findings are of fundamental importance, demonstrating that adsorption performance is governed not only by the specific surface area but also by the surface chemistry of the mineral phase and its role as a structural spacer, which enhances the accessibility of adsorption sites.

The selection of an appropriate binder system has been comprehensively investigated in industrial patents concerning the production of activated carbon granules. These studies recommend the use of 2-30 wt.% clay binder in combination with 2-12 wt.% organic binder (cellulose ether). For formulations containing 25 wt.% clay and 8 wt.% organic binder, the compressive strengths of the resulting granules reached 19,4 MPa for attapulgite, 11,4 MPa for kaolin, and 10,8 MPa for bentonite. A critical finding was that bentonite-based granules rapidly disintegrated upon contact with water, whereas granules prepared with kaolin and other non-swelling clays exhibited excellent water stability. Furthermore, these patents demonstrated that the

required mechanical strength is achieved not through high-temperature firing but by controlled drying at temperatures not exceeding 125°C under regulated humidity conditions [3-5].

A modern alternative to conventional binders is alkali-activated metakaolin (geopolymer). Owing to its amorphous aluminosilicate framework, which is structurally analogous to that of zeolites, geopolymer binders provide not only mechanical consolidation but also additional ion-exchange functionality. For zeolite 4A granules, a liquid-to-solid (L/S) ratio of 0,8 resulted in a compressive strength of 12,55 MPa and an abrasion loss of 2,42% under a pressure of 4 atm. In contrast, increasing the L/S ratio to 1,2 reduced the compressive strength to 3,38 MPa [6,7]. These findings indicate that the liquid-to-solid ratio should be minimized within the limits imposed by processing requirements in order to maximize the mechanical performance of geopolymer-bonded granules.

The most important technological conclusion drawn from the literature review is that carbon-containing granules must not be subjected to firing in an oxidizing (air) atmosphere, as activated carbon begins to oxidize and burn at temperatures above approximately 400°C. This limitation precludes the direct application of the conventional ceramic granulation route, which typically involves firing at 500-900°C, and leaves only two feasible alternatives: thermal treatment in an inert atmosphere or low-temperature geopolymerization.

Uzbekistan possesses a substantial mineral resource base suitable for the development of such carbon-mineral composites. The Angren deposit, located in the Ohangaron District of the Tashkent Region, is the country's only integrated brown coal-kaolin deposit. The kaolin resources are classified into primary kaolin, occurring beneath the coal seam, and secondary kaolin, occurring in the overburden. The latter is further subdivided into gray and variegated (multicolored) varieties. At present, only the gray kaolin is beneficiated for the production of the AKF-78 commercial grade, whereas the variegated kaolin remains largely unutilized and is continuously accumulated in waste dumps [8,9]. The mineralogical composition of the Angren kaolin is dominated by kaolinite and quartz. Its X-ray diffraction (XRD) pattern is characterized by diffraction peaks at d = 0,713, 0,436, and 0,357 nm, which are characteristic of kaolinite [8]. The crystal structure consists of a 1:1 layered aluminosilicate with no interlayer space, rendering the mineral non-swelling. Consequently, kaolin exhibits a relatively low specific surface area (7-18.4 m^2/g) and a limited cation exchange capacity ranging from 2 to 15 meq per 100 g [10, 11].

Despite its relatively low specific surface area, kaolinite-based materials exhibit a considerable adsorption capacity toward heavy metal ions. For natural kaolinite, adsorption capacities of 61,5 mg/g for Pb^{2+}, 44,7 mg/g for Cu^{2+}, and 15,5 mg/g for Zn^{2+} have been reported at pH 5 [12]. These findings indicate that the adsorption performance is governed not primarily by the specific surface area but rather by the density of reactive ≡Si–OH and ≡Al–OH functional groups located at the edge sites of the kaolinite structure. Likewise, alkali-activated metakaolin-based materials have demonstrated a Cu^{2+} adsorption capacity of 63,7 mg/g [13-15]. However, despite the extensive utilization of Angren kaolin in Uzbekistan, no published data are currently available regarding its specific surface area or cation exchange capacity in the local scientific literature. This lack of quantitative physicochemical characterization represents an important knowledge gap that the present study seeks to address.

Glauconite is an iron-rich dioctahedral 2:1 mica-group mineral characterized by a basal spacing of $d_{001} \approx 1,0$ nm. Unlike montmorillonite, it does not undergo swelling in aqueous media, a property that is of critical importance for the production of mechanically stable granulated sorbents [16, 17]. Uzbekistan possesses substantial glauconite resources, including the Changi (14 million tonnes), Mabika (21,9 + 5,5 million tonnes), Aksuv (7,4 + 3,3 million tonnes), Kofrun (34,7 million m^3), Kyzyljar (forecast resources of 128,3 million tonnes), and Krantau deposits (Republic of Karakalpakstan; approximately 9 million tonnes, P1 resource category) [18]. Experimental studies on glauconite from the Krantau deposit have demonstrated high removal efficiencies for heavy metal ions, reaching 99% for Fe, 99% for Pb, 97% for Co, 96% for Cu, 95% for Mn, 92% for Cr, 90% for Ni, 90% for Zn, and 64% for Hg. Moreover, adsorption equilibrium was established within only 30-40 min [19]. Such rapid equilibrium kinetics indicate that Krantau glauconite is a highly promising mineral component for fixed-bed adsorption systems.

Another important characteristic of glauconite is its optimum operating pH range of 7-9 [16]. In contrast, carbonaceous sorbents generally exhibit their highest adsorption efficiency under mildly acidic conditions (pH 4-6). Therefore, integrating these two phases into a single composite material is expected to broaden the overall effective pH range of the sorbent. This feature represents a significant practical advantage for the treatment of real industrial wastewater, where pH values are often highly variable.

The literature reviewed above demonstrates that no previous studies have reported the development of granulated carbon-mineral composites combining Angren kaolin and Krantau glauconite with a carbonaceous sorbent. The present study aims to address this research gap by designing a composition matrix for the carbon sorbent (CS)-metakaolin-activated glauconite system, developing a methodology for the activation of the mineral components, and identifying the optimum formulation through a calculation-based evaluation of the physicochemical and adsorption properties of the proposed composite sorbents.

2. Materials and Methods

The carbon sorbent (CS) used in this study was a powdered material produced by the pyrolysis of fruit stone waste followed by chemical activation with KOH. For the calculation-based evaluation, the sorbent was assumed to possess a specific surface area of 678 m^2/g and a cation exchange capacity (CEC) of 1,20 meq/g.

The Angren kaolin employed in this work was the variegated variety collected from waste dumps of the kaolin beneficiation plant located in the Ohangaron District, Tashkent Region, Uzbekistan. This material was selected because of its negligible cost, chemical composition suitable for metakaolin production, and the presence of 3,8-4,0 wt.% Fe_2O_3, which is expected to provide additional iron oxide-based active adsorption sites.

Commercial Angren kaolin (AKF-78 grade) was used as the reference material for comparison. Glauconite was obtained from the Krantau deposit in the Republic of Karakalpakstan in the form of glauconite-bearing sand and was used as a concentrate after beneficiation. The chemical compositions of both mineral raw materials are presented in Figure 1.

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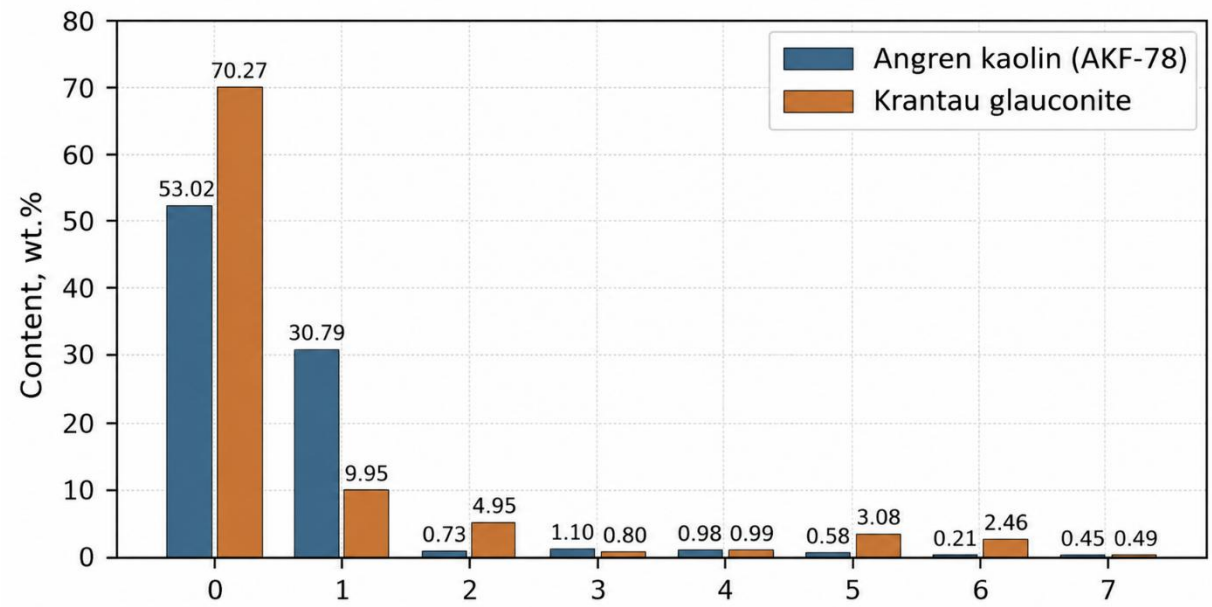


Figure 1. Chemical compositions of Angren kaolin (AKF-78) and Krantau glauconite (wt.%), according to the literature data [8,9,19]

The two minerals exhibit complementary structural and adsorption characteristics, making them suitable components of a carbon–mineral composite sorbent. Angren kaolin consists predominantly of kaolinite and quartz and possesses a 1:1 layered aluminosilicate structure with a basal spacing of d_{001} = 0,716 nm. Its optimum operating pH range is 4-6, and natural kaolinite has been reported to exhibit adsorption capacities of 61,5 mg/g for Pb^{2+} and 44,7 mg/g for Cu^{2+} [12]. In contrast, Krantau glauconite is composed mainly of glauconite and quartz and has a 2:1 mica-type structure with a basal spacing of d_{001} = 1,00 nm. The optimum operating pH range for glauconite is 7-9, while modified glauconite has been reported to exhibit Pb^{2+} adsorption capacities of 21,7-34,0 mg/g [16]. Both minerals are non-swelling in aqueous media, ensuring the dimensional stability of granulated sorbents during operation. From the standpoint of raw material availability, the reserves of Angren kaolin waste are practically unlimited, whereas the estimated reserves of the Krantau glauconite deposit are approximately 9 million tonnes.

A composition matrix consisting of eleven formulations was developed based on three components: carbon sorbent (CS), metakaolin (MK), and activated glauconite (AG). The matrix included two control samples, namely G-1 (non-granulated pure CS powder) and G-11 (a carbon-free mineral granule), together with nine experimental formulations. The compositions were systematically designed to evaluate: (i) the effect of increasing the mineral fraction (G-2 to G-4); (ii) the influence of the metakaolin-to-activated glauconite ratio (G-8, G-6, and G-9); and the behavior of the system at a highly mineralized composition limit (G-10). The complete composition matrix is presented in Figure 2.

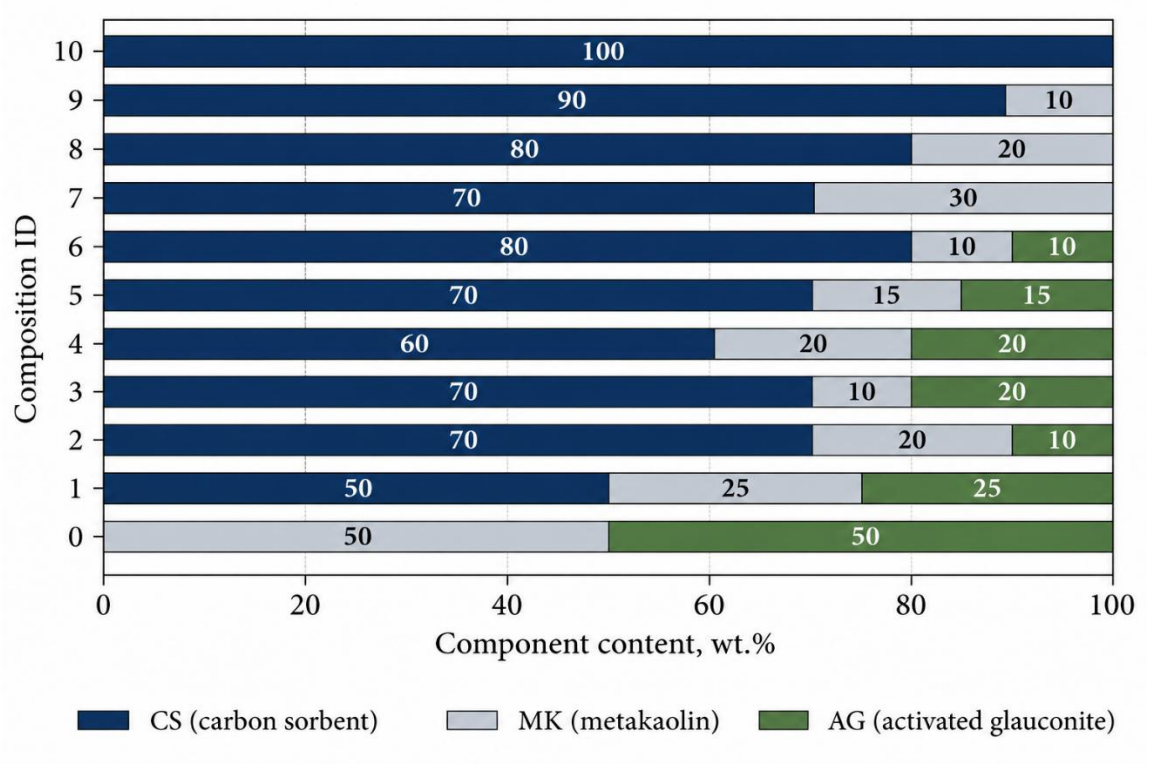


Figure 2. Composition matrix of the granulated carbon–mineral sorbent formulations (G-1–G-11), expressed as weight percentages (wt.%)

Carbon-containing granules cannot be subjected to firing in an air atmosphere because of the risk of carbon oxidation and combustion. Therefore, mechanical strength was developed through a low-temperature geopolymerization process. The binder system consisted of two components: an inorganic primary binder formed by alkali activation of metakaolin with an 8 M NaOH solution, and a temporary organic binder, carboxymethyl cellulose (CMC, 2 wt.%), which imparted the plasticity required for the extrusion process.

The granulation process was carried out according to the following sequence: dry mixing of the solid components (20 min) → wet mixing with the addition of a CMC solution and 8 M NaOH (15 min, liquid-to-solid (L/S) ratio = 0,80-0,85) → extrusion through a die with a diameter of 3 mm → cutting into granules 3,5 mm in length followed by spheronization → initial curing at 20 ± 2°C for 2 h → heat–moisture treatment at 85°C and relative humidity >95% for 24 h → final drying at 105°C for 6 h → sieving to obtain a 2-4 mm particle-size fraction → quality control.

The bulk density of the granules was estimated to be in the range of 480-560 kg/m^3. The target technical specifications for the granulated sorbents were established as follows: particle diameter, 2,0-4,0 mm; compressive strength, $\sigma \geq 1,0$ MPa; abrasion loss, $A \leq 6,0\%$; water swelling $\leq 10\%$; structural integrity after 24 h of water immersion $\geq 95\%$; specific surface area ≥ 200 m^2/g; and retention of at least 80% of the initial compressive strength after five consecutive adsorption-regeneration cycles.

3. Results

The calculated results indicate that increasing the mineral content gives rise to three competing trends: a reduction in specific surface area and cation exchange capacity, accompanied by an improvement in mechanical strength and a decrease in the time required to reach adsorption equilibrium (Figures 3-5).

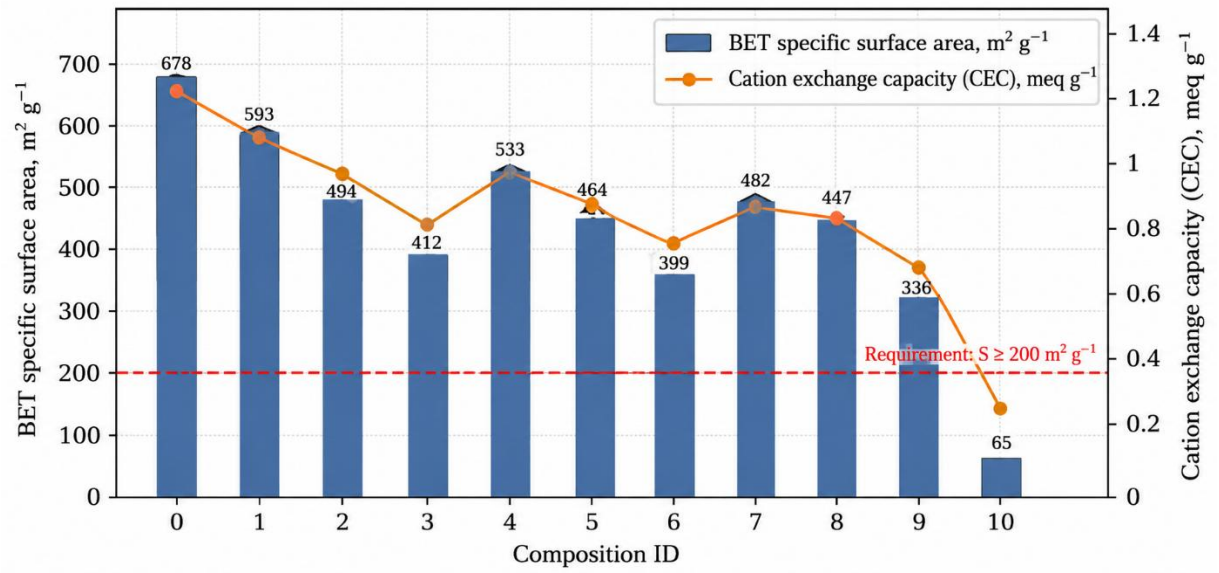


Figure 3. Predicted values of the BET specific surface area and cation exchange capacity (CEC) of the granulated sorbents.

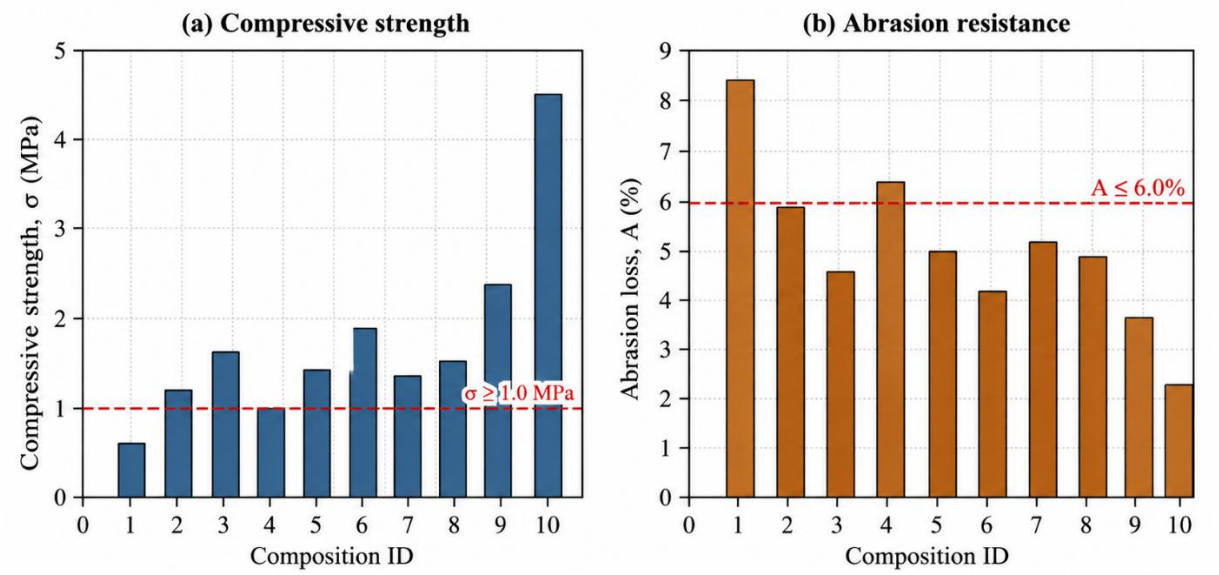


Figure 4. Predicted compressive strength and abrasion resistance of the granulated sorbents. The dashed lines represent the limits specified by the technical requirements

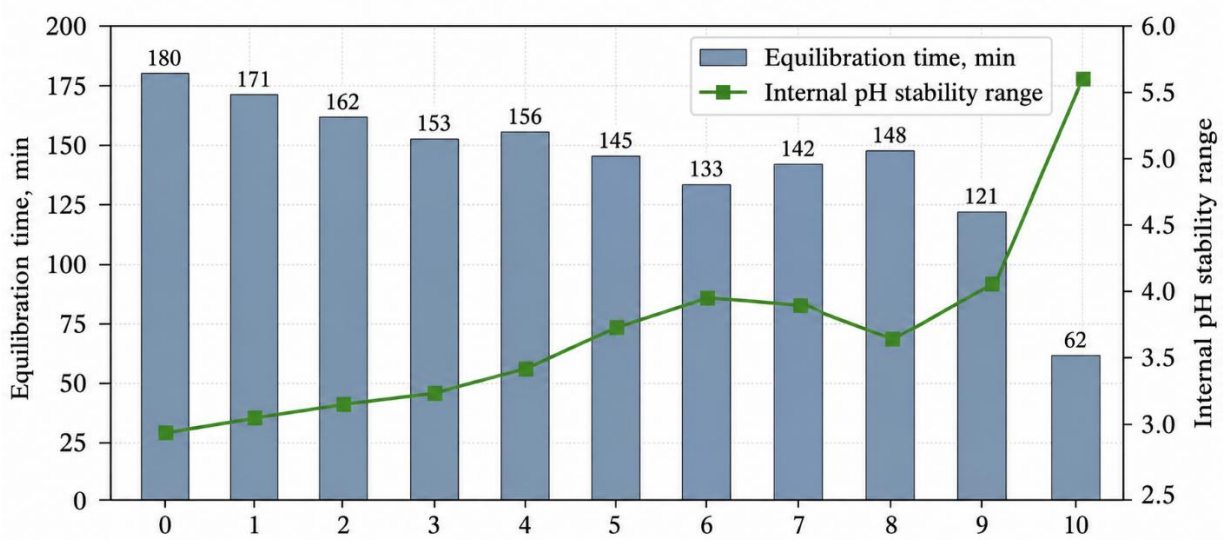


Figure 5. Predicted adsorption equilibrium time and effective operating pH range of the granulated sorbents.

The technical requirements for compressive strength ($\sigma \geq 1,0$ MPa) and abrasion loss ($A \leq 6,0\%$) were satisfied by formulations G-3, G-4, G-6, G-7, G-8, G-9, and G-10. In contrast, formulations G-2 ($\sigma = 0,68$ MPa) and G-5 ($A = 6,4\%$) did not exhibit sufficient mechanical stability, indicating that a mineral content of 10 wt.% is inadequate to ensure effective reinforcement of the granules. This observation is consistent with previous reports, in which the minimum clay binder content required for industrial applications was established at 15-20 wt.% [3, 4]. In Figure 4, the formulations that fail to satisfy the specified technical requirements are highlighted using a distinct color.

Based on the expected phase composition, the granulated sorbents should exhibit the following characteristic X-ray diffraction (XRD) reflections: amorphous carbon-a broad halo at $2\theta = 20$-$26°$ corresponding to the (002) plane and a second broad halo at 42-45° assigned to the (100) plane; quartz-sharp reflections at $2\theta = 26,64°$ (101) and 20,86° (100); glauconite-characteristic reflections at $2\theta = 8,84°$ (001, d = 1,00 nm), 17,7° (002), and 61,3° (060, d = 0,151 nm); and metakaolin-a broad amorphous halo within the 2θ range of 20-30°. The absence of the kaolinite reflections at $2\theta = 12,34°$ (001, d = 0,716 nm) and 24,87° (002) is considered evidence of complete calcination, whereas the persistence of these peaks indicates insufficient calcination temperature and/or residence time.

The components differ considerably in terms of their point of zero charge (PZC): 5,5-6,0 for the carbon sorbent (CS), 3,5-4,5 for metakaolin, and 6,3-8,0 for activated glauconite. Based on an additive estimation, the PZC of the granulated composites is expected to lie within the range of 5,2-6,2. This range ensures that, under the intended operating conditions (pH 5-6), the sorbent surface remains nearly neutral or slightly negatively charged, thereby promoting the adsorption of metal cations while remaining below the onset of metal hydroxide precipitation (approximately pH 6,0 for $Cu(OH)_2$ and pH 6,5 for $Pb(OH)_2$).

The optimal composition was selected using a multi-criteria evaluation method for two different scenarios. For wastewater containing a single metal component (Cu^{2+} as the dominant ion),

the optimal composition was identified as G-3 (UCS:MK:FG = 80:20:0). In contrast, for real industrial wastewater with a multicomponent composition, the optimal formulation was G-8 (UCS:MK:FG = 70:10:20). The difference in the results obtained for these two cases leads to an important methodological conclusion: the optimization of sorbent composition is target-dependent, and there is no single universally "best" composition suitable for all applications.

The calculated physicochemical and sorption characteristics of the G-8 granules demonstrated their high potential as an effective sorbent material. The specific surface area (S_{BET}) reached 482 m^2/g, while the cation exchange capacity (CEC) was 0.94 mmol-eq/g. The granules exhibited sufficient mechanical stability, with a compressive strength of 1,38 MPa and an attrition loss of only 5,2%. The equilibrium adsorption time was 142 min. The maximum sorption capacities toward heavy metal ions were determined as 119,3 mg/g for Cu^{2+}, 128,5 mg/g for Pb^{2+}, 97,0 mg/g for Cd^{2+}, 88.0 mg/g for Zn^{2+}, and 89,5 mg/g for Ni^{2+}, respectively.

4. Conclusion

1. It was established that firing carbon-containing granules in an air atmosphere is an unacceptable process condition and represents a fundamental technological limitation. Therefore, the required mechanical strength was achieved through a low-temperature geopolymerization regime, consisting of curing at 85°C for 24 h (relative humidity >95%), followed by drying at 105°C for 6 h.

2. It was demonstrated that the introduction of 30% mineral components resulted in only a 24-25% decrease in sorption capacity. The selectivity sequence remained unchanged as $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} \approx Zn^{2+}$. The obtained results indicate that the total mineral fraction has a greater influence on sorption capacity than the individual ratio of mineral components within the composite structure.

3. Based on the multi-criteria evaluation, the G-3 composition (80:20:0) was identified as optimal for single-metal-containing wastewater, whereas the G-8 composition (70:10:20) was found to be the most suitable for real multicomponent industrial wastewater. These findings confirm that optimization of sorbent composition is highly dependent on the intended application objective, and no universal formulation can provide maximum efficiency under all treatment conditions.

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