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Improving the Efficiency of Cement Mortar to Immobilize Sulfate in Industrial Wastewater Using Different Nanoparticles

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Abstract: The disposal of industrial wastewater (IWW) discharged from factories is a significant topic in the environment field, and the use of cement-based materials is a useful way to treat materials with unexpected ions. In this work, IWW with abundant SO_4^{2-} collected from a factory was utilized to prepare cement mortar (IWWCM), and three kinds of nanomaterials (NMs), including nano-SiO_2 (NS), nano-$CaCO_3$ (NC), and nano-metakaolin (NMK), were used to improve the performance of IWWCM. The compressive strengths, hydration degree, hydration products, and micropore structure of the specimens were investigated. The test results showed that IWW reduced the strength of the specimens, and the use of NMs could compensate for this strength reduction. To be specific, the 28-day strength of the freshwater (FW) mixed specimen was 44.6 MPa, and the use of IWW decreased this value to 41.8 MPa. However, the strengths of the specimens with NMs were all higher than 50 MPa, indicating the advantage of NMs for the strengths of the IWWCMs. Moreover, the IWWCM showed a lower hydration degree with a poor pore structure, whereas the use of NMs in IWWCMs refined these properties, explaining the strength increase in the specimens. The results of the SO_4^{2-} content measurements also showed that the use of NMs could improve the SO_4^{2-} binding ratio, which is conducive to relieving the pressure of IWW disposal for industrial factories.

Keywords: ion binding efficiency; mechanical strength; nano modification; wastewater disposal

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1. Introduction

The disposal of industrial wastewater (IWW) has become a problem plaguing the industry due to the difficulty of treating this kind of waste. Different factories may produce different kinds of IWW; if the IWW cannot be treated properly, it will pollute the land around the factory and affect the quality of the nearby soil, which will result in many problems for the environment to a large extent [1–3]. Under these circumstances, many methods have been proposed to deal with the IWW to protect the environment, and the methods mainly include two aspects: purification treatment and resource utilization. However, during the treatment process of IWW, if the ions contained in the IWW are not toxic ions, the energy consumption of the large-scale water purification treatment of IWW may be relatively high, and the economic benefit of this treatment method is worth considering because the beneficial effect of this method may not be fully utilized. Under these circumstances, if there is a simple nontoxic IWW for large-scale resource disposal methods, it will largely alleviate the environmental and economic burdens of the factories [4–6].

Cement-based material (CBM) is a traditional and popular construction material. In the future, with the continuous development of the global economy and society, CBM will still be an important part of the construction industry [7–11]. Traditional CBM has the advantages of excellent strength, low price, a high performance–price ratio, and high ion binding efficiency, and it is now widely used in construction, road, and soil treatment areas.

However, with the continuous development of material science, the requirements for the performance of CBMs are gradually improving. As a widely used nonmetallic material, cement-based materials are constantly expanding their application scenarios. In this case, the use of nanomaterials (NMs) with high performance has gradually become a focus of reform for the material system of CBMs. The use of NMs to improve the performance improvement of materials has been proven in many research areas [12,13]. As for the CBM system, the traditional NMs include nano-silica (NS), nano-calcium carbonate (NC), and nano-metakaolin (NMK) [14–16], and the utilization of these NMs is becoming a research hotspot for improving the performance of CBMs. To be specific, NS is a typical NM possessing great pozzolanic activity, filler effect, and crystal core effect; when it is used as a reinforcing material inside CBMs, it exhibits great potential for improving the performance of the material based on the above advantages. In detail, the pozzolanic activity of NS can result in an abundant reaction between NS and CBM to create the hydration product $Ca(OH)_2$, and this reaction can not only refine the internal pore structure of the specimen but also reduce the capillary content. At the same time, the use of NS can significantly enhance the interface transition zone between the slurry and the aggregate, thus avoiding the problem of structural performance degradation [17]. Further, as a nanomaterial, NS also shows a relatively obvious crystal core effect, which can cause the generated C-S-H gel to form a more compact crystal with nanoparticles at the center [18–20]. In addition, NMK is a kind of low-cost NM, which is prepared by the calcination of the industrial mineral kaolin and is mainly composed of tetrahedral and octahedral coordinated silica and alumina. Compared with kaolin, the specific surface area of NMK is smaller, the surface of the particle is smoother, and the shape of the edges is also improved. Therefore, NMK not only has the size advantage of nanomaterials but also shows a unique pozzolanic effect and crystal core effect [21]. In the interior of concrete, NMK can not only fill the pores by itself but also react with $Ca(OH)_2$ crystals just like NS, thereby improving the hydration degree of cementing materials, enhancing the compactness of concrete, and improving the strength and toughness of concrete [22–24]. In contrast to the aforementioned two kinds of NMs, NC is an inert particle with low activity. Compared with other nanoparticles, NC also has a nucleation effect, which can promote cement hydration [25–27]. And it is also a relatively less expensive nanomaterial than NS. Based on the discussion above, it can be concluded that the use of NMs can be beneficial for the performance improvement of CBMs.

The characteristics of NMs in improving the properties of CBMs are mainly related to the promotion of the hydration reaction and compactness of the microstructure of CBMs. For CBMs, their good binding characteristics for different kinds of ions cannot be ignored, and the hydration products generated by CBMs in the hydration process also have good binding effects on many kinds of cations and anions [28–31]. At this time, if the IWW can be used as the mixing water in the production process of CBMs, it will be able to play a role in the resource disposal of IWW. On this basis, considering the improvement effect of NMs on the performance of CBMs, if NMs can be used to enhance the hydration performance and microstructure of CBMs, the binding effect of CBMs on ions in IWW may be further improved. In this situation, the effect of NMs on the performance of IWW-mixed CBMs needs to be studied further.

Above all, the use of NMs may be good for the properties of CBMs incorporating IWW. However, the specific effect of IWW on replacing FW needs to be investigated to better understand the influence of this kind of waste on CBMs; based on this, the inclusion of NMs in the properties of IWW-mixed specimens is worth clarifying. In this work, three kinds of NMs, including NC, NS, and NMK were utilized to improve the performance of CBMs mixed with IWW, aiming to enhance the strength of the specimens and improve the SO_4^{2-} binding ratio inside the specimen. The specific effect of all the NMs on the IWW-mixed specimens was clarified based on XRD, TG-DTG, and BET analyses to better understand the role of NMs, and the SO_4^{2-} contents inside the specimens were also measured.

2. Materials and Methods

2.1. Raw Materials and Mix Proportions

Ordinary Portland cement was used; the strength grade of the cement was 42.5 MPa, sand in accordance with China ISO Standard sand was utilized as the aggregate, and the IWW collected from a factory with the SO_4^{2-} content of 5.5% and pH of 6 was used to completely replace fresh water (FW) in this research. The particle sizes of NS, NC, and NMK are 20~40 nm, 50~80 nm, and 120~160 nm, respectively. And the oxide compositions of NS, NC, and NMK are listed in Table 1. PS was used to improve the early-age fluidity for mortar, because the existence of NMs may influence the fluidity for the specimens. The detailed mix proportion for the preparation of industrial-wastewater-mixed cement mortar (IWWCM) is shown in Table 2, and FW mixed cement mortar (FWCM) was also prepared as the comparison. The abbreviations of the specimens were NS-IWWCM for IWWCM mixed with NS, NC-IWWCM for IWWCM mixed with NC, and NMK-IWWCM for IWWCM mixed with NMK, respectively.

Table 1. Oxides of nanomaterials.

Oxides	SiO_2	SO_3	TiO_2	Fe_2O_3	CaO	CuO	Al_2O_3
NS	96.64%	0.88%	0.32%	0.05%	0.1%	0.01%	0%
NC	3.02%	1.46%	95.17%	0.01%	0.21%	0%	0%
NMK	51.93%	0.11%	0.01%	0.42%	0.33%	0%	40.85%

Table 2. Mix proportion design of specimens.

Specimen	W/b	Binder/Sand	NM Content (%)	PS Addition (%)
FWCM	0.36	1:1	0	0.5
IWWCM	0.36	1:1	0	0.5
NS-IWWCM	0.36	1:1	1.75	1
NC-IWWCM	0.36	1:1	1.75	1
NMK-IWWCM	0.36	1:1	1.75	1

2.2. Preparation of IWWCM Specimens

The mixing process of the specimens is depicted in Figure 1. In detail, the NMs were firstly mixed with the water and polycarboxylate superplasticizer (PS) at the speed of 1500 rpm to obtain the mixed solution, and the cement and standard sand were mixed at the speed of 300 rpm for 2 min; then, the mixed solution was put into the raw materials. The mixture was further mixed at the speed of 500 rpm for 5 min. Finally, the fresh mixture was poured into the mold, and the size of the mold was 50 mm × 50 mm × 50 mm. Moreover, it needs to be emphasized that the mixing method may cause potential nonuniformity in the mechanical and seepage properties of cement-based materials. This nonuniformity issue may also exist for the application of adding other materials into the specimens, while a small amount of NMs may not induce such significant results [32,33].

2.3. Measurement Methods

In this research, the fluidity values of the newly prepared mixtures were tested, the compressive strengths of the specimens were measured, and six specimens were prepared for each batch to calculate the average values. The microstructural analysis methods including X-ray diffraction (XRD) analysis, Thermogravimetric (TG) analysis, and Brunauer–Emmett–Teller (BET) analysis were also used to study the inner microstructural performance of the IWWCM specimens with different materials, and the ion content in the IWWCM specimens was also measured to investigate the binding ratio of SO_4^{2-} inside the IWWCM. To be more specific, the compressive strengths of the specimens were tested by the universal hydraulic testing machine, and the loading rate was 2400 N/s. For XRD, TG, BET, and ion content measurement, the specimen was ground into powder to facilitate the above experiments after the termination of the hydration reaction for the specimens. In detail, an XRD test was conducted with a Bruker D8 Advance Eco Diffractometer, CuKα was used for radiation, the operation voltage and current were set to be 40 kV and 40 mA, respectively, and the scanning velocity was 4°/min. TG analysis was used with an STA449F3 produced by Netzsc Co., Ltd., Selb, Germany, the temperature rising rate was 10 °C per minute, and the range was set to be from natural room temperature to 550 °C. Finally, for BET analysis, the equipment ASAP, 2020, produced by Micromeritics Co., Ltd., Norcross, GA, USA, was used.

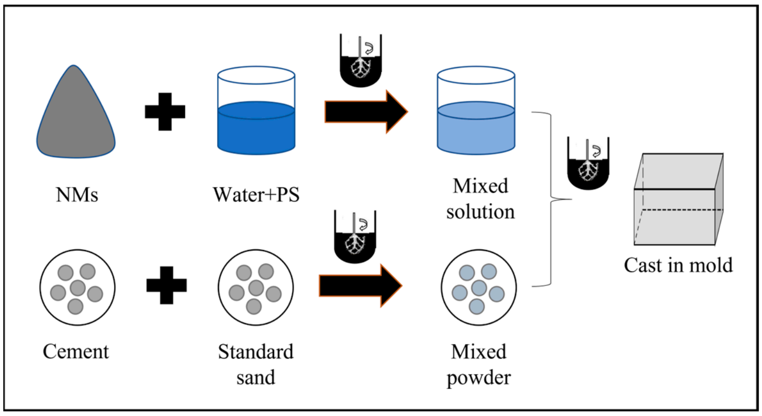

Figure 1. Mixing of the specimens.

3. Results and Discussion

3.1. Fluidity

The fluidity of the mixtures incorporated with different NMs is shown in Figure 2; it can be seen that the addition of NMs induced a remarkable adverse effect on the workability of the freshly prepared mixtures, in that the fluidity of the specimens showed a significant decreasing trend with the addition of 1.75% NM content. This fluidity reduction phenomenon was considered to be connected with the fairly small fineness of NMs. The small fineness of the particle would lead to a high water demand for the specimens including NMs, the internal water would be consumed at early stage, and this is a common phenomenon of the CBMs incorporated with different kinds of NMs. Further, it was also found that the fluidity of IWWCM was lower than that of FWCM. Under this circumstance, the use of PS was significant in this work to control the fluidity of the nano-modified specimens to produce accurate test results.

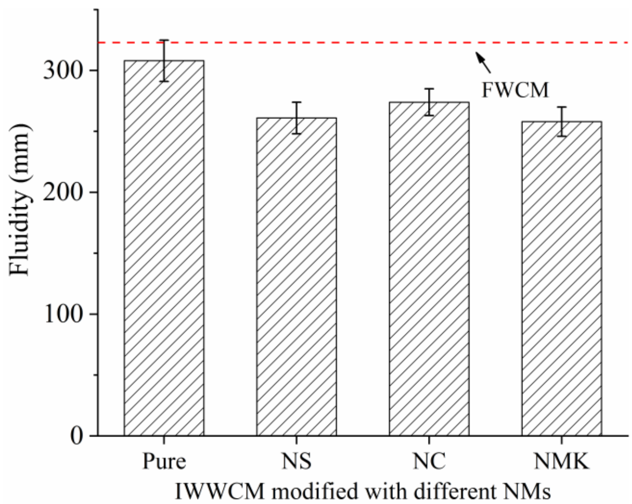

Figure 2. Fluidity of the newly prepared mixtures.

3.2. Mechanical Properties

The 28-day strengths of the IWW-mixed specimens were tested and shown in Figure 3. It can be noticed that the use of IWW as mixed water to fully replace FW in the cement mortar was harmful to the compressive strengths. To be specific, the FW-mixed specimen had a 28-day strength of 44.6 MPa, which was 7% higher than that of IWWCM with the value of 41.8 MPa. The strength test results indicated the harmful effect of excessive SO_4^{2-} inside the mixed water on the mechanical performance of the cement-based materials. In addition, it was also found that the use of NMs was helpful for the strength improvement of IWWCM. The compressive strengths of the nano-modified specimens were all higher than 50 MPa, showing a more than 10% increase compared to the FWCM specimen. This proved the advantageous effect of NMs on enlarging the mechanical strength of the IWW-mixed cement mortar. The compressive strengths of the IWWCM incorporating NS, NC, and NMK were 51.7 MPa, 54.3 Mpa, and 50.8 MPa, respectively. Compared with the pure IWWCM, the compressive strengths of the specimens were increased by 23.7%, 29.9%, and 21.5%, respectively. In addition, compared with the FWCM specimens without IWW, the strengths of the IWWCM specimens doped with NMs were also significantly improved.

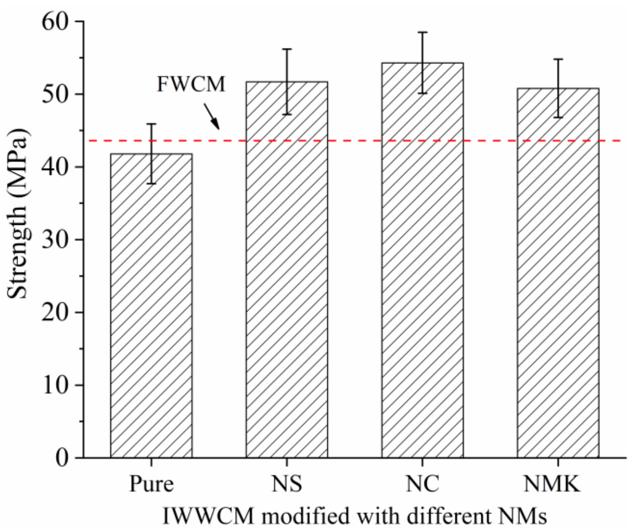

Figure 3. Compressive strengths of the specimens.

The mechanical strength results showed that the use of NMs could not only compensate for the strength degradation induced by the inclusion of harmful ions but also significantly improve the mechanical performance of the cement mortar mixed with IWW, showing the potential for the performance improvement on the specimen using IWW. However, the specific mechanism of this effect still needs to be studied, and further experiments are also needed to verify the mechanism of the use of NMs on enhancing the performance of cement mortar mixed with IWW and to determine whether the addition of NMs can improve the ion binding efficiency inside the specimen mixed with IWW.

3.3. SO_4^{2-} Content Measurement

In this study, the existence of excessive free SO_4^{2-} inside IWW was proved to be harmful to the fluidity and mechanical strength of the specimens as shown in Sections 3.1 and 3.2. This adverse effect of SO_4^{2-} on the properties of cement mortar was also confirmed by some of the previous literature [34–36]. The specific effect of sulfate on the performance of cement-based materials is illustrated as below: the SO_4^{2-} inside the specimen causes the formation of some additional substances, including gypsum, thaumasite, etc., and the addition of SO_4^{2-} also results in the change in the chemical composition of ettringite. It should be noted that these substances have expansion properties, and the generation of too many expansion substances induces adverse effects on the performance of the cement-based materials [37,38], because these materials can cause inevitable cracks inside the matrix, which will continue to extend with the continuous extension of service time and even cause large cracks with significant adverse effects on the concrete structure [39,40]. In order to avoid this situation, when using IWW containing a large amount of SO_4^{2-} as mixing water, it is necessary to reduce the content of free SO_4^{2-} in the matrix as much as possible.

In this work, the SO_4^{2-} binding efficiency of the specimen was measured, and the experimental results are shown in Figure 4. It can be seen that the SO_4^{2-} binding efficiency exhibited the same law as the compressive strength for IWWCM. To be specific, the SO_4^{2-} content of the IWW-mixed plain cement mortar was limited, with a value of 25.7%. However, the use of NMs significantly improved the SO_4^{2-} binding efficiency of the specimens. In detail, the SO_4^{2-} binding efficiency of the specimens mixed with NS, NC, and NMK were 33.6%, 35.8%, and 37.2%, respectively. Compared with plain cement mortar, the ion adsorption efficiency was increased by 30.7%, 39.3%, and 44.7%, respectively. This improvement effect indicated the beneficial effect of NMs on the SO_4^{2-} binding efficiency of cement mortar and proved that the beneficial effect of NMs on the performance of cement-based materials with IWW mixing water depends not only on the enhancement effect on the hydration degree and microstructure of the specimens but also on the reduction of the free SO_4^{2-} content inside the specimens.

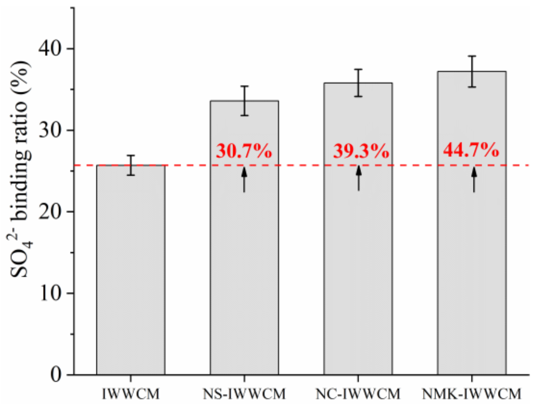

Figure 4. SO_4^{2-} binding ratios of IWWCM specimens incorporated with different NMs.

3.4. XRD Analysis

XRD analysis is a typical test method for the identification of the phase composition inside cement-based materials, and this method was used in this work to analyze the generation of hydration products in the specimens incorporating different kinds of NMs. As shown in Figure 5, it can be found that the main phase composition inside the specimens was consistent, and this indicated that the inclusion of IWW or NMs may not induce additional products at this curing environment. However, it needs to be emphasized that the XRD analysis was semi-quantitatively used in this work to reflect the hydration situation of the specimens with different mixed situation; further analysis is crucial for further verification of the effect of the incorporation of nanomaterials.

3.5. TG Analysis

The test results of Thermogravimetry (TG) and differential Thermogravimetry (DTG) analysis are, respectively, shown in Figure 6. Generally, TG analysis is considered to be able to quantifiably judge the content of hydration products inside the cement-based materials, including Ettringite, calcium hydroxide, and so on, through the weight loss of the substances at the corresponding heat decomposition peaks. In this work, the test was conducted within the temperature range of 25~550 °C, due to the ability of NMs to react with water or hydration products inside the specimen; the total weight losses of the specimens within the same temperature range were also used as an indicator to evaluate the hydration degree of the specimen. As shown in Figure 6, the use of IWW may lead to the adverse influence on the hydration performance of the specimen, in that the IWW-mixed specimen without any treatment exhibited the lowest total weight loss, which could further prove that the use of IWW was harmful for the hydration reaction inside the specimen, and this result matched the compressive strength and XRD test results. In addition, the use of NMs was beneficial for the hydration performance of IWWCM; the total weight loss values of the NS-IWWCM, NC-IWWCM, and NMK-IWWCM specimens were 13.1%, 12.7%, and 14%, respectively. This improved total weight loss proved the advantage of NMs in stimulating the hydration reactivity of the specimens [41–43]. Moreover, the DTG results shown in Figure 6 also verified the higher hydration degree in the NM-mixed specimens, in that the peaks of the heat were much higher in the specimens modified with NMs. The higher hydration degree was not only good for the strength development of the specimens but could also promote the ion adsorption efficiency of the cement-based materials' incorporation of excessive ions.

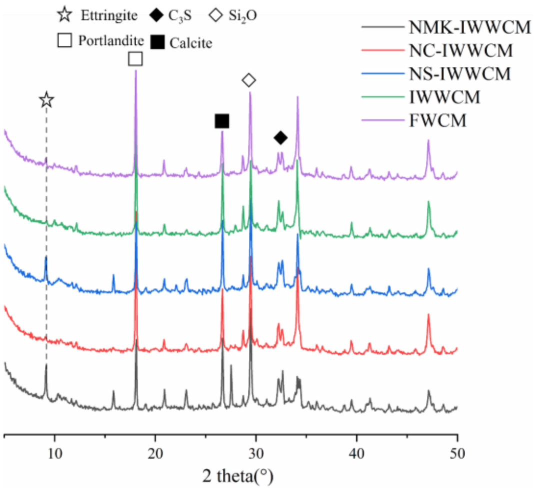

Figure 5. XRD test results of IWWCM specimens with different NMs.

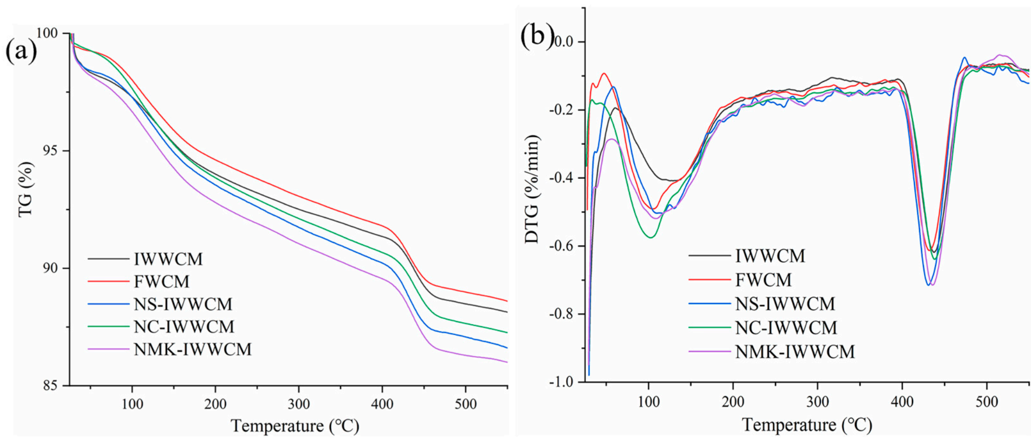

Figure 6. TG and DTG analysis results of the IWWCM specimens with different NMs (**a**) TG and (**b**) DTG.

3.6. Micropore Structure Analysis

In this work, the micropore structure of the IWWCM was measured by the BET test, and the results are shown in Figure 7. For cement-based materials, the distribution of micropores within the size of 100 nm is considered to be related to the hydration reaction reactivity of the specimen and can reflect the densification of the nanoscale microstructure of the specimens. It can be seen from Figure 7 that the use of NMs could effectively modify the distribution of the micropore structure inside the IWWCM specimens such that the pore distribution curves of the nano-modified specimens were much lower than that of pure IWWCM. Considering that the distribution of micropores smaller than 100 nm is connected with the hydration degree of the specimen, the micropore structure test result could also verify the improved hydration reaction of the IWWCM modified with NMs. Moreover, two high peaks were found in the micropore distribution curve of the IWWCM specimen, the highest peak appeared at the pore diameter around 42 nm, and this was the largest pore diameter for the high peaks shown in all the curves [11,44–46]. For the specimens modified with NMs, the highest peaks mainly appeared within 10 nm, and this test result also showed the beneficial effect of NMs on the hydration reaction activity of the IWWCM specimens. The test result also proved the beneficial effect of NMs on the micropore structure of the IWWCM specimens.

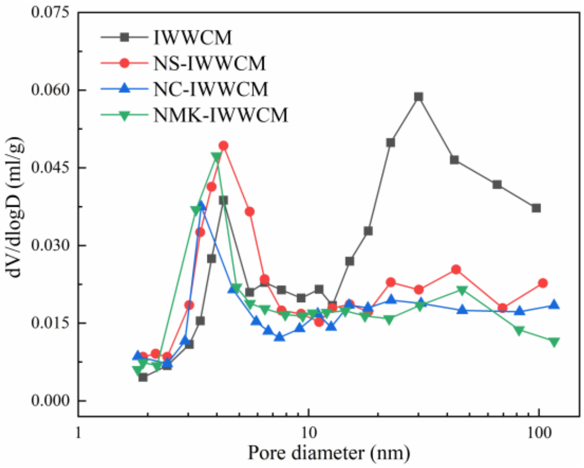

Figure 7. BET pore structure analysis of IWWCM specimens with different NMs.

3.7. Specific Surface Area Measurement

The specific surface area (SSA) values of the specimens were measured by Nitrogen adsorption analysis as shown in Figure 8, and the SSA values were tested by the BET and Langmuir methods, respectively. As shown in Figure 8, the use of NMs could lead to an increase in the SSA values of the internal microstructure of cement mortar. To be specific, in terms of BET-SSA, the values of the IWWCM, NS-IWWCM, NC-IWWCM, and NMK-IWWCM specimens were 2.97 m^2/g, 3.35 m^2/g, 4.16 m^2/g, and 5.72 m^2/g, respectively. The SSA values of Langmuir showed the same development rule. The SSA values of Langmuir for IWWCM, NS-IWWCM, NC-IWWCM, and NMK-IWWCM were 4.08 m^2/g, 4.72 m^2/g, 5.83 m^2/g, and 6.41 m^2/g, respectively. It was found that the SSA values of the IWWCM doped with NMs increased significantly compared with that of the specimen with no NMs. This SSA-increasing phenomenon indicated the specific effect of NMs on changing the internal microstructure of IWWCM. It should be clarified that the increase in the SSA showed that the complexity of the internal microstructure for cement mortar was improved, and this was beneficial for the binding of excessive SO_4^{2-} inside the specimen, as the complicated microstructure could adsorb the ions inside the specimen. Moreover, previous sections verified the effect of NMs on improving the hydration reaction of cement mortar, which would also improve the ion adsorption efficiency. Based on the discussion above, it can be summarized that the addition of NMs could both improve the hydration reaction and the micropore structure of cement-based materials; considering the hydration effect inside the specimen, NMs are promising for the performance improvement of the cement-based materials mixed with IWW collected from industrial factories.

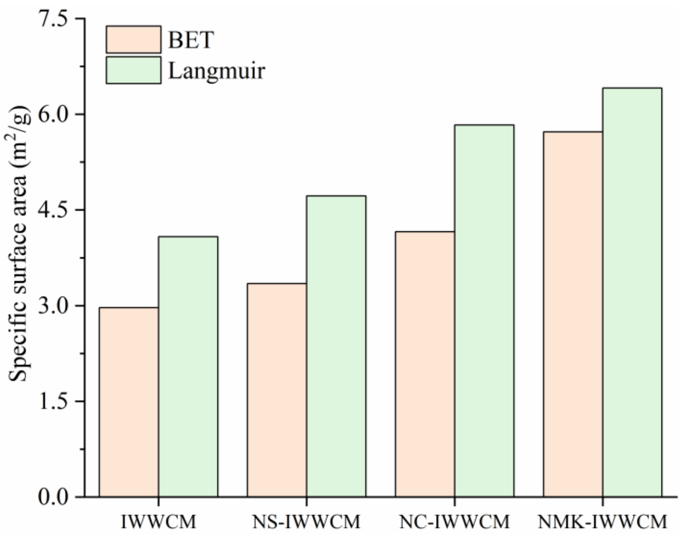

Figure 8. Specific surface area values of the specimens with different NMs.

4. Conclusions

In this study, FW was fully replaced by IWW to prepare cement mortar, aiming to realize the large-scale resource disposal of untreated IWW discharged from industrial factories. To improve the performance of cement mortar, IWWCM specimens were treated with three different NMs, including NS, NC, and NMK, and the properties of the specimens with different material systems were tested and compared in detail. For the compressive strength, the complete replacement of FW by IWW showed a significant negative effect on the strength of the specimens. The 28-day compressive strength of IWWCM-mixed specimen was 6.3% lower than that of the FWCM specimen. However, the use of NMs could refine this adverse effect induced by the inclusion of IWW, and the compressive strengths of the IWWCM specimens were, respectively, increased by 23.7%, 29.9%, and 21.5% with the use of NS, NC, and NMK. Moreover, NMs could not only improve the mechanical strength of the IWWCM specimens but also increased the adsorption efficiency of SO_4^{2-} in the IWWCM specimens. To be precise, compared with the IWWCM specimens with no NMs, the SO_4^{2-} binding ratios of the IWWCM specimens doped with NS, NC, and NMK increased by 30.7%, 39.3%, and 44.7%, respectively. The improvement mechanism of NMs on the mechanical strength and the SO_4^{2-} adsorption efficiency of the IWWCM specimens was studied from the perspective of the microscopic properties of the IWWCM specimens, including XRD, TG and BET analyses. It was revealed that NMs could improve the internal hydration reactivity and hydration degree of the specimen, along with the microscopic pore structure, leading to the high performance of the IWWCM specimens.

5. Limitations and Future Aspects

This work presents the utilization of NMs to improve the performance of cement-based materials mixed with IWW containing SO_4^{2-}; the results revealed the beneficial effect of NMs on improving the compressive strengths and ion adsorption efficiency with the higher hydration degree and refined pore structure. However, some issues still need to be further clarified in future work. The high-efficiency distribution of NMs is an important issue, although NMs exhibited an advantage in enhancing the properties of the specimens in this work, the distribution situation of NMs was not regarded as a core question, and if NMs can be highly dispersed in the specimens, the enhancing effect of NMs on the performance of the specimens can be further enlarged. Moreover, the IWW used in this work a contained high amount of SO_4^{2-}, and the IWW in many other places possesses many other harmful ions; hence, the specific effect of NMs on IWW including multiple ions needs to be further verified.

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