<ICACCR 2023_Ojo, O. S., Ogungode, E. B., Alao, T. O. & Hassan, I. O.>

Second International Conference on Advances in Cement and Concrete Research, 2023

EXPERIMENTAL MEASUREMENT OF ADSORPTION OF SUPERPLASTICIZER ON CEMENT PASTE: A SYSTEMATIC REVIEW

Ojo, Olaniyi Segun,[a] Ogunbode, Ezekiel Babatunde,[b] Alao,Timothy Oyewole[b] and Hassan, Ibrahim Ogiri[c]

[a]Department of Building, Niger Delta University, Yenagoa, Bayelsa State, Nigeria
[b]Department of Building, Federal University of Technology, Minna, Niger State, Nigeria
[c]Department of Building, Federal University of Lafia, Nasarawa State, Nigeria

Abstract

Despite the deep knowledge in the cement-superplasticizer incompatibility and profound understanding of their behaviour at the organo-mineral/absorption, adsorption and precipitation phases of cement- superplasticizer. There have been questions on the experimental methods used in measuring adsorption phase of this combination. This is because past experimental methods do not take into account the absorption and precipitation phases of the combination. This information is important because it affect the rheology of cement-superplasticizer paste and invariably the performance of concrete. Therefore, this article reviews the experimental methods used in assessing adsorption of cement superplasticizer for past three decades after the discovery of the fourth generation of superplasticizer. Scopus database was used to obtain information of the past research relating to the subject matter, a quantitative assessment was done using bibliometry analyses and PRISMA (Preferred Reporting Items for Systematic Review and Meta-Analysis) for quantitative assessment. This research encouraged the use of High Performance Liquid Chromatography (HPLC) when measuring adsorption for accurate result because if right method was used, it will aid better understanding of superplasticizer behaviour and acceptability among end users.

Keywords: Cement, Superplasticizer, adsorption, rheology

1. Introduction

In the Past, before the discoveries of water reducers and high range water reducers (Superplasticizers), literatures have established the importance of water-cement ratio in improving the mechanical properties of concrete and the relevance of water in achieving a good slump and rheology of concrete [1,2]. Meanwhile, achieving a good concrete strength requires a reduced water-cement ratio and the lower the water the harder it is to turn freshly hydrated concrete. In the contrary, a good rheological concrete requires the amount of water to be increased. However, there is a limit of water that could be used, in other to avoid segregation and/or production of weak concrete. This was the case before the introduction of water reducers to concrete industry [3,4].

When water was added to cement content in concrete, it usually flocculate and reduced water-cement ratio makes the flocculation more pronounced. In other to disperse the flocculated constituents, a dispersant is needed. Apart from the economic benefit and improved mechanical properties achievable by the use of this dispersant, it also aids the production of workable and flow able concrete. Superplasticizers are usually used as dispersant [5-7].

Superplasticizers are adsorbed onto the surface of cement particles due to Van der Waal's forces of attraction between the particles of different charges[7]. This phenomenon is called 'adsorption'. These forces also created electrostatic repulsion and/or steric hindrances (depending on the type of superplasticizers used) between the forces of like charges [8]. Understanding this phenomenon broadened the knowledge of the behaviour of cement and superplasticizers and cement-superplasticizers incompatibility and as well as how it affects the behaviour and/or performance of concrete.

Several researches had been done to understudy this behaviour and different experimental measurement had been used. For instance, total organic carbon analyzer was used by [9-12] to determine the amount of carbon adsorbed by the cement. This is done by subtracting the carbon in the precipitate after adding cement from carbon in the superplasticizer without cement. Also, the behaviour of superplasticizer to different material varies for example

Polynaphthalene Superplasticizer adsorbed better in blended cement plus soda lime waste glass powder than polycarboxylate ether superplasticizer [9]. UV Spectrophotometer was used by [9, 13-15] where the superplasticizer only was first measured by UV spectrophometer and peaks obtained, the obtained peak were compared with peaks obtained after addition of cement. Competitive adsorption of sodium tripolyphosphate and superplasticizer (Superplasticizer used are Lignosulphate, Polynaphthalene and polycarboxylate) on cement was determined using UV Spectrophotometer [15]. The results showed that lignosulphate/Polynaphthalene plus sodium tripolyphosphate on cement led to improved fluidity and fluidity retention [15]. Dynamic light scattering was used by [16-19], it studies diffusion behaviour of macromolecules, superplasticizer adsorbed on cement particles are diffused and different wave length determined. High Performance Liquid Chromatography/ Gel Permeation Chromatography/ Mass Spectrometry-Gas Chromatography was used by [7,20,21]. This method was proposed by [7]. It work based on the principle of separation and identification of monomers from polymer, different peaks signify the level of saturation. The highest peak is the saturation point (adsorption stage), the peak before the highest peak is absorption stage while the peak after is the precipitation stage. These adsorption stage, absorption stage and precipitation stage gave complete information on adsorption behaviour. The higher the saturation peak the better the adsorption and the more compatible the cement with the superplasticizer.

Review Methodology

In systematic review, literatures play a role of facilitators by attempting to answer some salient questions and identify the research gap and areas where further researches are required or propose a new method [22]. In this review, an attempt is made to evaluate the amount of literatures available on adsorption of superplasticizer on cement and assess the experimental methods used so far to evaluate adsorption.

In other to achieve the aim of the review, a literature review was done from the year 1990 to 2023 this was after the discovery of the last generation of superplasticizer in the late 1980s [23]. PRISMA (Preferred Reporting Items for Systematic Review and Meta-Analysis) [24] was used to evaluate the qualitative review while bibliometric analysis was use for quatitative review, According to [8], four methods had been used to experimentally assess the adsorption of superplasticizer on cement. They are; Total organic Carbon analyzer, UV spectrophotometer, Chromatography (High Performance Liquid Chromatography, Gel permeation Chromatography and Mass spectrometry-Gas Chromatography), and more recently Dynamic light scattering methods. These methods were critically assessed. There are four stages of PRISMA, they are; identifications, screening, eligibility and inclusion as listed in the figure 1. The information obtained will be our basis for qualitative review where inference was made.

2.1 Literature Search

Literatures published were extracted from the scopus database on the key areas of the topic (this include all published materials in all journals in scopus database) and screened until the volume is reduced for easy references. As at 11/8/2023, the keyword "Adsorption" AND "Superplasticizer" were searched on the scopus database, 655 documents were in the scopus database relating to the search criteria without filter. When the search was filter to the year 1990-2023, 643 documents popped up, beginning from the year 1992. The language was filter to English, 526 documents were in the database, the filter was trimmed to only articles (eliminating reviews, books and conference papers) and 387 documents were in the scopus database.

It is believed some of the journals were not relevant to the subject; therefore the search criteria were redrafted to include each method. The search criteria became the initial search and the experimental methods, for example "Superplasticizer" AND "Adsorption" AND "Total Organic Carbon" AND "UV Spectrophotometer" OR "UV spectrophotometry" AND "High Performance Liquid Chromatography" OR "Gel Permeation Chromatography" OR "Mass Spectrometry Gas Chromatography" AND "Dynamic light Scattering" OR "Evaporative light Scattering".

2.2 Identification

Typing all the above search criteria at once will give no document. This is understandable because the scopus database is a computer database using artificial intelligent, it was looking for information on documents having all the

search criteria. Therefore the search criteria were narrowed down to initials search plus each experimental method, that was when some documents were retrieved. For instance, the search criteria are now: "Superplasticizer" AND "Adsorption" AND "Total Organic Carbon"; Superplasticizer" AND "Adsorption" AND "UV Spectrophotometer" OR "UV spectrophotometry"; Superplasticizer" AND "Adsorption" AND "High Performance Liquid Chromatography" OR "Gel Permeation Chromatography" OR "Mass Spectrometry Gas Chromatography"; Superplasticizer" AND "Adsorption" AND "Dynamic light Scattering" OR "Evaporative light Scattering". The total documents received were 270 documents.
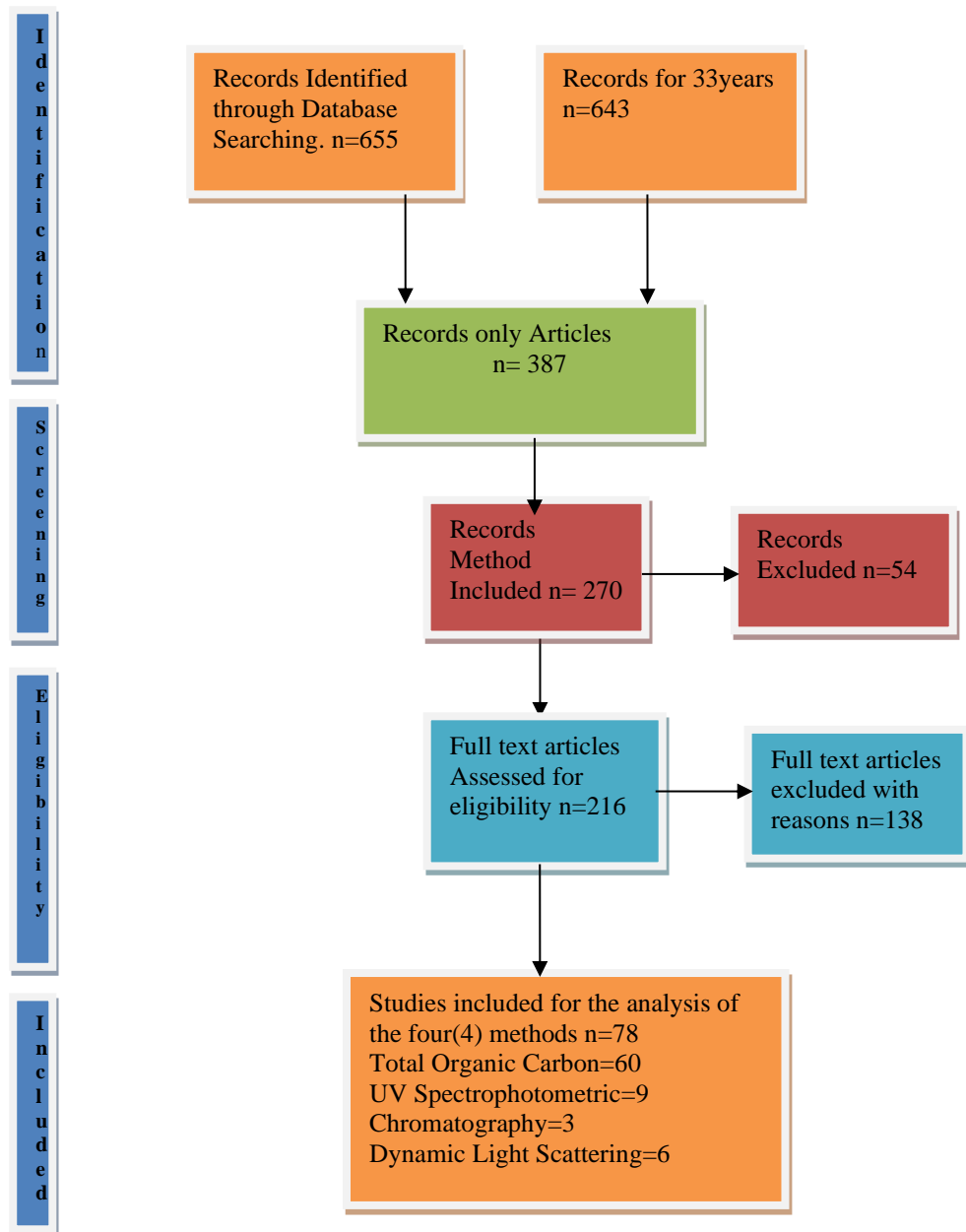

Figure 1: PRISMA 2009 flow Diagram [22]

2.3 Screening

A thorough screening was done on the retrieved documents to enhance the quality of this literature review with the aid of scopus database. The years were screened to 1990-2023 (that is 33 years spanning four (4) decades). There are many languages in the scopus database, these were removed and limited to only English Language. A further limit was done to remove reviews, conferences, books etc. leaving only articles. This led to removal of 45 documents.

2.4 Eligibility

Two hundred and sixteen (216) documents retrieved required further trimming. Some of these documents have no importance to the subject matter. The aim of this systematic review is to assess information on the experimental methods used in assessing adsorption of superplasticizer on cement; however, some of these methods could be used to assess other characteristics other than adsorption, therefore some of these methods could be in the articles but were not used to assess adsorption. In addition, some documents appeared in duplicate which were removed. The documents retrieved were imported to excel and further screening was done to assess the eligibility criteria. This led to removal of 138 documents.

2.5 Inclusion

Seventy Eight (78) documents were included in this literature review for further analysis. These Seventy Eight (78) documents included are break down in the table 1.

Table 1: Documents Included for analysis

Methods	Documents Included
Total Organic Carbon	60
UV Spectrophotometry	9
Chromatography	3
Dynamic Light Scattering	6

2. Results and Discussion

There are many articles related to the subject and all the four methods have been used at least in three articles. The method usually used before the years bench mark is UV spectrophotometer. It was observed that some journals used UV spectrophotometer to assess the adsorption.

3.1 Year Base

The retrieved documents were breakdown into year; this is to enable easy identification of the number of published articles per year. This article has shown that 2018 and 2022 were the years that have high number of publications with eight (8) articles on the experimental methods where total organic analyzer were used (figure 2). UV spectrophotometer was used thrice in 2018 the highest number of time it was used to measure adsorption. Dynamic light scattering has always been used for other things but until recently it was used as a means of measuring adsorption. Chromatography method was actually proposed by Flatt et. al. (1998) and only two articles have used this method thereafter.
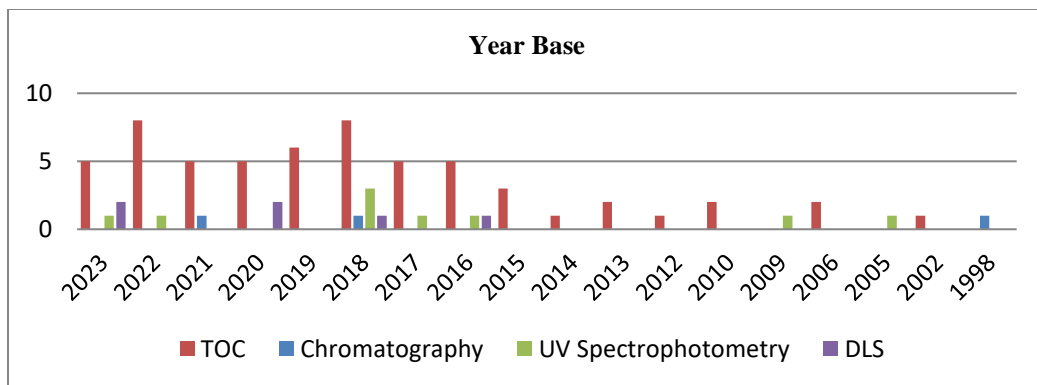
Figure 2: number of articles published per year

3.2 Cited By

The number of times each journal is cited were shown in figure 3, a journal by Zhang et. al., published in the year 2015 has the highest number of citations with 236 citations. This article showed that total organic carbon analyzer was used to measure adsorption.
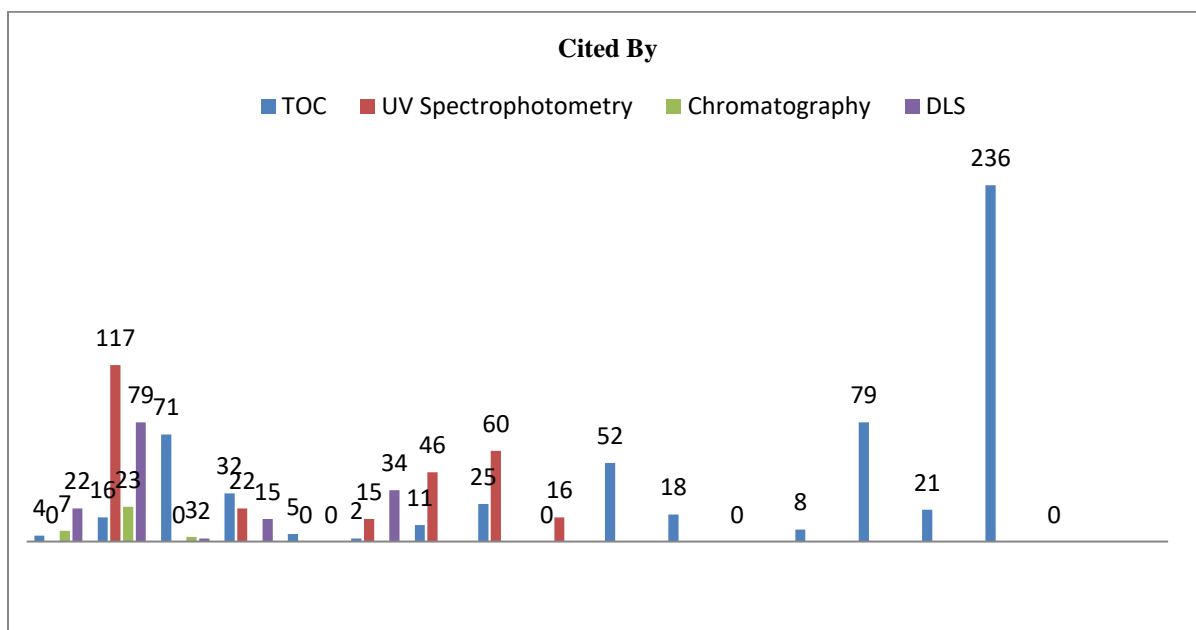

Figure 3: number of citations per article

One hundred and seventeen (117) articles cite [25] where UV spectrophotometer was used for adsorption measurement. The next highest citation per method was by [26] where dynamic light scattering method of measuring adsorption was used. The article by [7] received the highest citations for chromatography method.

3.3Subject Base

The most common area of specialization where articles are published more is in the 'Materials' field, followed by "Engineering". Figure 4-7 show the pie graph of the subjects that had undertook any of the method of measurement adsorption in analyzing the function of superplasticizer.
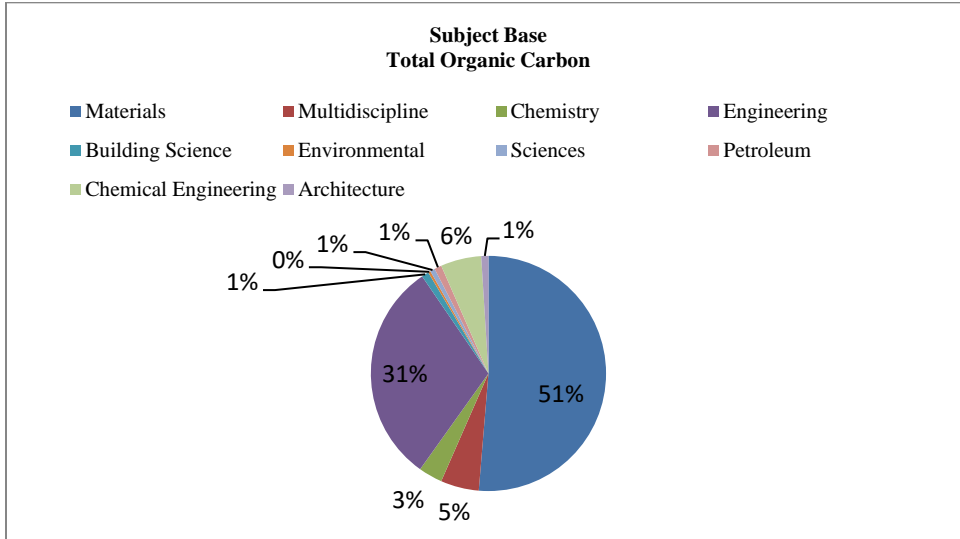
Subject Base
Total Organic Carbon

■ Materials   ■ Multidiscipline   ■ Chemistry   ■ Engineering
■ Building Science   ■ Environmental   ■ Sciences   ■ Petroleum
■ Chemical Engineering   ■ Architecture

1%   0%   1%   1%   6%   1%
51%
31%
3%   5%

Figure 4: Subject base by TOC

Subject Base
UV Spectrophotometry

■ Materials   ■ Engineering   ■ Environment
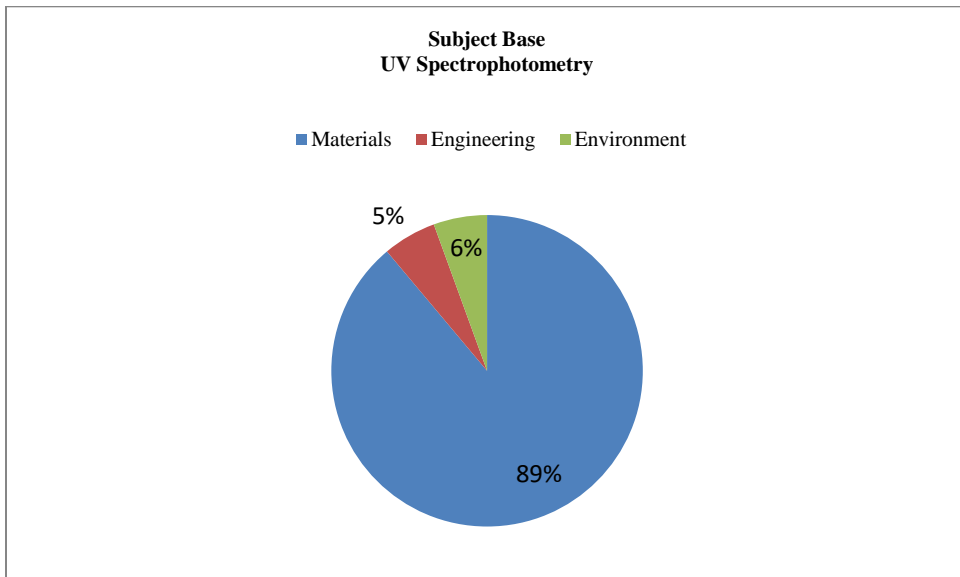
5%   6%
89%

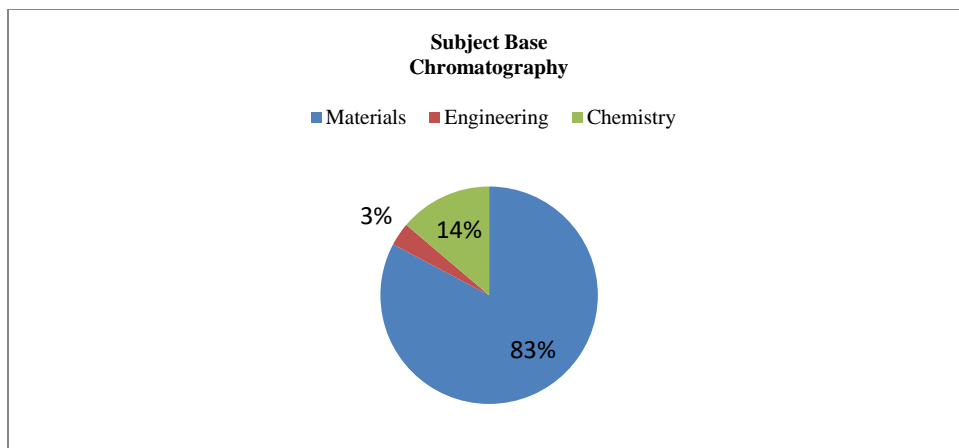Figure 5: Subject base by UV Spectrophotometer

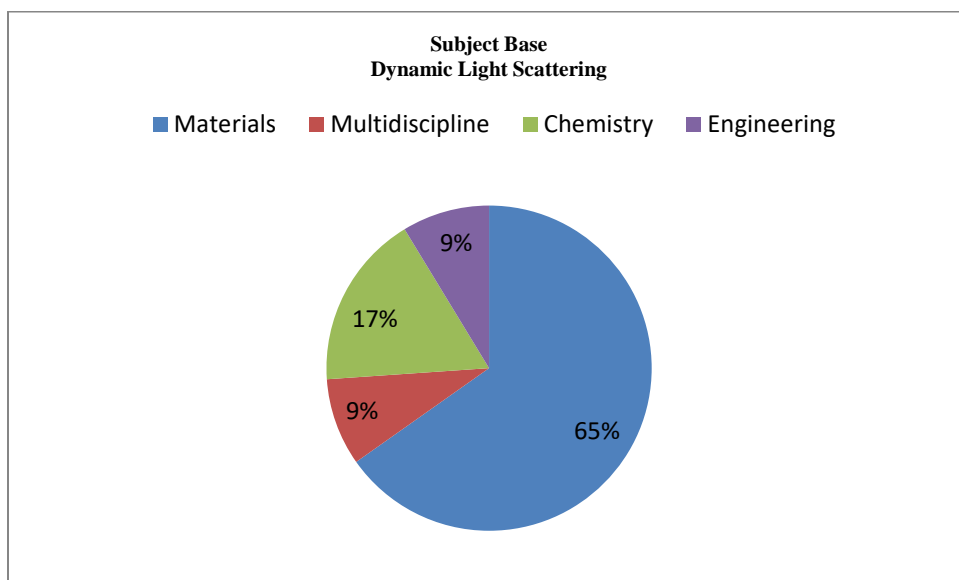Figure 6: Subject base by Chromatograhy

Figure 7: Subject base by dynamic light scattering

3.4 Journal Source

The source of journals per document was identified in figure 8. The results showed that 'Construction and building materials' journal received or housed many of the articles written on adsorption.
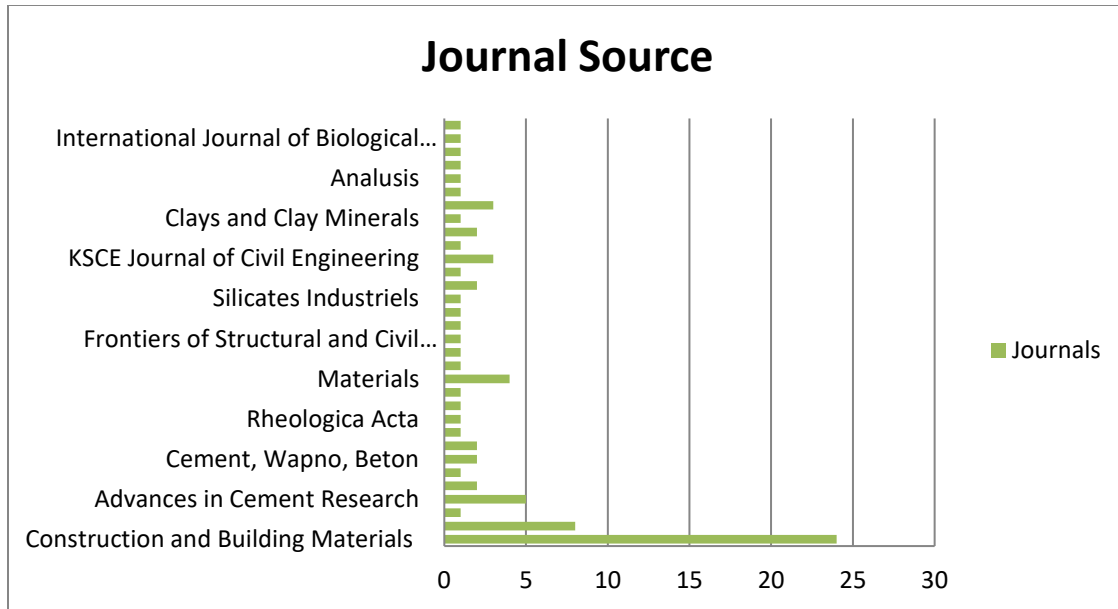
Figure 8: Journal source for the articles assessed

3.5Discussion

The review of literature above has shown that total organic carbon analyzer was used mostly by the researchers; it is followed by UV spectrophotometer and Dynamic light scattering respectively. It is worthy to note that it only total organic carbon analyzer among the experimental methods that is solely for measurement of adsorption of superplasticizer in cement chemistry, other methods could be used for others things for instance UV spectrophotometer could be used to measure zeta potentials [15], Dynamic light scattering could be used for determining the characteristics of superplasticizer [15]and High performance liquid chromatography or Gel permeation chromatography or mass spectrometry gas chromatography[27] could be used measure the poly disparity index by determining the molecular weight and molecular number.
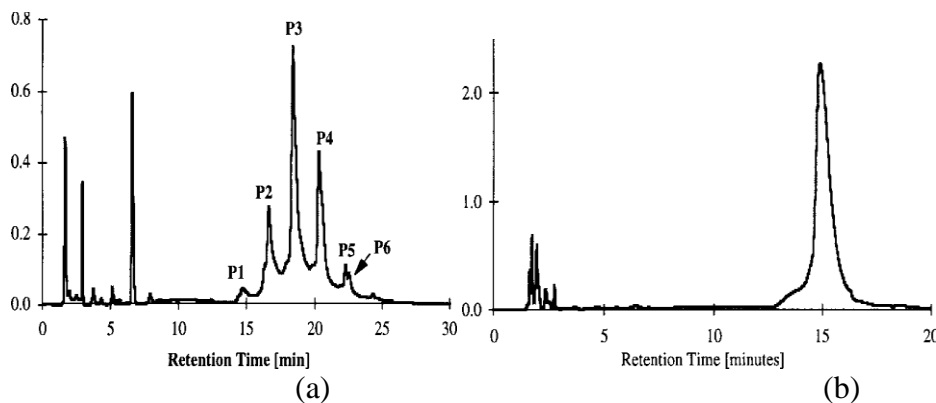

Figure 9: HPLC chromatogram of Superplasticizer solution with (b) or without (a) cement. [7]

In 1998, [7] proposed the method of chromatography (fig. 10a&b) showed that total organic carbon analyzer work on the principle of carbon depletion. According to [7] superplasticizer was first tested in the total organic carbon

analyzer to determine the amount of carbon in the superplasticizer, after mixing with cement the solution is tested to determine the amount of carbon consumed. This principle is the same as UV spectrophotometer and dynamic light scattering except that energy and light respectively were used to determine the carbon content with or without superplasticizer. However as stated by [7] there are carbons absorbed (in the organo mineral) in the solution after cement reacted with superplasticizer. They are shown by chromatogram before the 15 mark (fig 10b) and were truly not adsorbed and they were not in the precipitate (precipate are values in the chromatogram before the 15 mark) but were absorbed by superplasticizer. The saturation point is at the 15 mark. This assertion was supported by [20&21]

3. Conclusion

After a thorough review of literatures available on scopus database and analyzing the literature to identify gaps in the topic of cement and superplasticizer, these below deductions are made;

1. This review has shown that based on results from past literature, total organic carbon analyzer, UV spectrophotometry and light scattering cannot really predict the adsorption of superplasticizer on cement.
2. High Performance Liquid Chromatography or Gel Permeation Chromatography or Gas Chromatography-Mass Spectrometry is better analytical tool to predict adsorption of superplasticizer on cement.

References
[1]Aïtcin, PC High performance concrete, London & New York, *E & FN Spon*. 1998 https://doi.org/10.4324/9780203475034
[2]Neville, AM Properties of concrete (Fifth ed.), England: *Pearson Educational Limited*. 2012
[3]Flatt R Superplasticizers and the rheology of concrete In: Roussel N. (Eds). Understanding the rheology of concrete. *Woodhead Publishing Limited* 2012, 144-201
[4]Aïtcin PC & Eberhardt AB Historical background of the development of concrete admixtures In: Aiicin, PC., & Flatt, RJ., (Eds). *Science & Technology of Concrete Admixture*. Elsevier 2016, 6, 87-94
[5] Flatt, RJ.& Houst, YF A simplified view of chemical effect perturbing the action of superplasticizer. *Cement and Concrete Research*. 2001, 31, 1169-1176. http://dx.doi.org/10.1016/S0008-8846(01)00534-8
[6]Banfill, P.F.G., The Rheology of Fresh Cement and Concrete- *A Review of Proceedings of 11th International Conference on Cement Chemistry,* Durban, South Africa, 2003, 50-62
[7]Flatt RJ, Houst YF , Oesch R , Bowen P , Hofmann H , Widmer J, Sulser U, Maeder U and Bürge TA, Analysis of superplasticizers used in concrete, *Analusis Magazine*, 1998, 26, 2 DOI: http://dx.doi.org/10.1051/analusis:199826020028
[8]Marchon, D. Mantellato, S. Eberhardt, AB. & Flatt, RJ Adsorption of Chemical Admixture. In: Aiitchin, PC. & Flatt, RJ. (Eds). *Science & Technology of Concrete Admixture*. Elsevier 2016, 10, 219-248
[9]Ibrahim S.& Meawad A. Towards green concrete: Study the role of waste glass powder on cement/superplasticizer compatibility, *Journal of Building Engineering*, 2022, 47 DOI:10.1016/j.jobe.2021.103751
[10]Yoon J. Choi B.I. Kim J.H. Adsorption properties of polycarboxylate ether-based superplasticizer on cement particles and their resultant dispersion, *Frontiers of Structural and Civil Engineering,*2022 8, 506-514. DOI: 10.1007/s11709-022-0813-5
[11]Tang X. Zhao C. Yang Y. Dong F. Lu X. Amphoteric polycarboxylate superplasticizers with enhanced clay tolerance: *Preparation, performance and mechanism, Construction and Building Materials*, 2020 252. DOI: 10.1016/j.conbuildmat.2020.119052
[12]Govin A. Bartholin M.-C. Schmidt W. Grosseau P. Combination of superplasticizers with hydroxypropyl guar, effect on cement-paste properties, *Construction and Building Materials*, 2019 215, 595 – 604 DOI: 10.1016/j.conbuildmat.2019.04.137
[13]Song S. Tan Y. Ju B. Zhang S. Dispersion and weak retardation performance of sulfate-based starch maleic acid monoesters in cement, *International Journal of Biological Macromolecules,* 2023, 230. DOI: 10.1016/j.ijbiomac.2023.123442
[14] Wang G. Song Y. Synthesis of polycarboxylate superplasticizer modified by self-made functional monomer for improving clay tolerance, *Advances in Cement Research ,2022. DOI: 10.1680/jadcr.22.00118*
[15]Tan H. Deng X. Gu B. Ma B. Luo S. Zhi Z. Guo Y. Zou F. Effect of borax and sodium tripolyphosphate on fluidity of gypsum paste plasticized by polycarboxylate superplasticizer. *Construction and Building Materials*, 2018 176 394-402. DOI: 10.1016/j.conbuildmat.2018.05.005

[16] Li R. Chen W.-C. Lei L. Plank J. Dispersing Efficacy of Tailored IPEG PCEs in AAS Binders: Elucidating the Impact of PCE Molecular Weight, *Industrial and Engineering Chemistry Research*. 2023, 62, 1776-1787.DOI: 10.1021/acs.iecr.2c03820

[17] Li Z. Zhou T. Liu H.Jin Y. Pang Y. Lou H. Yang D. & Qiu X. Study on the dispersion performance and mechanism of polycarboxylate superplasticizer by the long side-chain dicarboxyl terminated, *Journal of Applied Polymer Scien.* 140. DOI: 10.1002/app.53931

[18] Ma B. Qi H. Tan H. Su Y. Li X. Liu X.; Li C.& Zhang T. Effect of aliphatic-based superplasticizer on rheological performance of cement paste plasticized by polycarboxylate superplasticizer, *Construction and Building Materials*, 233.DOI: 10.1016/j.conbuildmat.2019.117181

[19] Ma B. Li C. Lv Y. Ta n H. Wang H.; Qi H.; Liu X. Yang Q. & Chen P. Preparation for polyacrylic acid modified by ester group in side chain and its application as viscosity enhancing agent in polycarboxylate superplasticizer system, *Construction and Building Materials,* 233 DOI: 10.1016/j.conbuildmat.2019.117272

[20] Liu M. Gao Y. Zhang L. Jiang G. Zeng C.&Wang P. The application of thermal analysis to study the hydration behaviour of tricalcium aluminate-gypsum in the presence of polycarboxylate-based superplasticizers. *Thermochimica Acta*, 696 DOI: 10.1016/j.tca.2020.178821

[21] Pei J. Wang Z. Ren J. & Liu D. Synthesis of polycarboxylate superplasticizers using an acrylic acid-rich wastewater from acrolein production, *Advances in Polymer Technology*, 37, 2561-2567. DOI: 10.1002/adv.21931

[22]Khan N. Qureshi MI. Mustapha I. Irum S. & Arshad RN. A Systematic Literature Review Paper on Online Medical Mobile Applications in Malaysia. *iJOE* 2020 16. https://doi.org/10.3991/ijoe.v16i01.12263

[23] Jayasree, C., Santhanma, M., & Gettu, R. Cement-superplasticiser compatibility - Issues and challenges. Indian Concrete Journal. 2011 85, 7,44-60

[24] Chen, Y., & Zheng, B. What happens after the rare earth crisis: A systematic literature review. Sustainability (Switzerland). 2019. https://doi.org/10.3390/su11051288

[25] Peng J. Qu J. Zhang J. Chen M. & Wan T. Adsorption characteristics of water-reducing agents on gypsum surface and its effect on the rheology of gypsum plaster, *Cement and Concrete Research,* 2005, 35 527-531DOI: 10.1016/j.cemconres.2004.04.016

[26] Bessaies-Bey H. Baumann R. Schmitz M. Radler M. Roussel N. Organic admixtures and cement particles: Competitive adsorption and its macroscopic rheological consequences*, Cement and Concrete Research.* 2016, 80 1-9. DOI: 10.1016/j.cemconres.2015.10.010

[27]Yamada, K., Sugamata, T., & Nakanishi, H., Fluidity Performance Evaluation of Cement and Superplasticizers, *Journal of Advance Concrete Technology*,2006, 4, 241-249 http://dx.doi.org/10.3151/jact.4.241