Kode/Nama : 421/Teknik Sipil
Bidang Fokus : Material Maju

LAPORAN AKHIR

PENELITIAN TERAPAN UNGGULAN PERGURUAN TINGGI

Pengembangan NanoGrout dan NanoHardener untuk Menciptakan *Entrepreneur* Material Maju

Tahun ke 1 dari rencana 2 tahun

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Sesuai dengan Kontrak Penelitian Tahun Anggaran 2018
Nomor : 008/KM/PNT/2018, Tanggal 06 Maret 2018

UNIVERSITAS PANCASILA

NOVEMBER 2018

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UNIVERSITAS PANCASILA DEKAN

Menyetujui,
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IDENTITAS DAN URAIAN UMUM

1. Judul Penelitian : Pengembangan NanoGrout dan NanoHardener untuk Menciptakan *Entrepreneur* Material Maju
2. Tim Penelitian

No	Nama	Jabatan	Bidang Keahlian	Instansi Asal	Alokasi Waktu (Jam/ Minggu)
1	Dr. Ir. Jonbi, MT., MM., MSi	Ketua	Struktur dan Material	Universitas Pancasila	10
2	Dr. Ir. A.R. Indra Tjahjani, MT.	Anggota	Transportasi dan Statistik	Universitas Pancasila	10
3	DR. Ir. A.M. Pattinaja	Anggota	Lingkungan	Universitas Pancasila	10

3. Objek Penelitian: pada tahun ke-1 menghasilkan material NanoGrout.

   Pada tahun ke- 2. menghasilkan material NanoHardener, mesin produksi. Diharapkan selama dua tahun akan dihasilkan material NanoGrout, NanoHardener, mesin produksi sehingga dapat tercipta Entreprenur bidang Material Maju.
4. Masa pelaksanaan

   Mulai : Bulan Juli tahun 2018

   Berakhir : Bulan November tahun 2019
5. Usulan Biaya DRPM Ditjen Penguatan Risbang
   - Tahun Ke-1 : Rp. 365.000.000, ***Dana disetujui Rp. 100.000.000***
   - Tahun ke-2 : Rp. 380.000.000
6. Lokasi Penelitian: Lab. Balai Besar Bahan dan Barang Teknik (B4T), Bandung, Lab. Pusat Survei Geologi Bandung dan Lab. ITB, Bandung
7. Instansi lain yang terlibat adalah cv. John Hi-Tech Contrindo, dengan kontribusi bantuan dana penelitian sebesar Rp. 15.800.000, data tentang material Grout dan Hardener, pemasaran material yang akan dihasilkan.
8. Temuan yang ditargetkan berupa material NanoGrout, NanoHardener dan mesin produksi
9. Kontribusi mendasar pada suatu bidang ilmu adalah inovasi pada bidang material, dengan mengembangkan material NanoGrout dan NanoHardener. Hal ini penting, karena selama ini material Grout dan hardener yang ada (beredar dipasar) masih dalam skala mikro. Sedangkan NanoGrout dan NanoHardener yang dikembangkan dalam skala nano, yang memiliki sifat mekanik dan durabilitas lebih baik.

10. Jurnal ilmiah yang menjadi sasaran dan tahun rencana publikasi adalah tahun pertama dan tahun ke dua:

- KSCE Journal of Civil Engineering (impact factor: 0.600)
- Structural Concrete (impact factor: 1.023)

11. Rencana luaran berupa luaran wajib dan luaran tambahan seperti pada tabel di bawah ini :

No	**Jenis Luaran**				**Indikator capaian**	
1	**Kategori**	**Sub Kategori**	**Wajib**	**Tambahan**	**TS [1)]**	**TS+1**
	Artikel Ilmiah dimuat dalam Jurnal	Internasional bereputasi		v	accepted/ published	accepted/ published
		Nasional terakreditasi		v	Accepted/ published	Accepted/ published
2	Artikel Ilmiah dimuat di prosiding	Internasional Terindeks		v	draft	Sudah dilaksanakan
		Nasional		v	Sudah dilaksanakan	Sudah dilaksanakan
3	Hak Kekayaan Intelektual (HKI)	Paten sederhana	v		Terdaftar	Sudah dilaksanakan
4	Teknologi Tepat Guna		v		produk	penerapan
5	Tingkat kesiapan Teknologi (TKT)		v		5	6

DAFTAR ISI

Halaman

RINGKASAN

Perkembangan material bangunan khususnya material kimia konstruksi (material maju) mengalamai kemajuan yang sangat pesat. Namun sayangnya bisnis material kimia konstruksi tersebut masih dikuasai oleh pihak asing (PMA), sehingga kontribusi bagi perekonomian Indonesia sangat kecil. Untuk itu perlu dilakukan inovasi melalui penelitian yang dapat menghasilkan material sejenis yang memiliki kualitas lebih baik. Salah satu cara yang dilakukan mengembangkan material tersebut dengan menambahkan material nano silika. Penelitian ini dilakukan dalam dua tahun, pada tahun pertama dihasilkan material NanoGrout. Material yang dihasilkan harus lebih baik kualitasnya dengan material sejenis yang ada di pasaran. Untuk itu material NanoGrout yang dihasilkan diuji: kuat tekan, kuat tekan lentur, kuat tarik, kuat lekat, susut, kelecakan, pengujian SEM dan FT-IR. Penelitian pada tahun kedua dihasilkan material NanoHardener, untuk material NanoHardener dilakukan pengujian tingkat kekerasan, keausan dan SEM. Pada tahun ke dua dihasilkan juga mesin produksi (tepat guna) yang memiliki keunggulan: mudah penggunaannya, praktis dan harga relatif murah. Hasil penelitian selama dua tahun, akan dihasilkan material NanoGrout dan NanoHardener, serta teknologi tepat guna (mesin produksi) sehingga dapat menjadi pemicu terciptanya *entrepreneur* dalam bidang material maju.

Keyword : Material kimia konstruksi, NanoGrout, NanoHardener, entrepreneur

BAB I. PENDAHULUAN

1.1 Latar Belakang

Pembangunan bidang konstruksi di Indonesia mengalami kemajuan yang sangat pesat, hal ini dapat dilihat dari maraknya pekerjaan konstruksi seperti gedung bertingkat, pabrik, pekerjaan infrastruktur jalan dan jembatan. Didalam melaksanakan pekerjaan konstruksi tersebut diperlukan teknologi, metoda kerja dan material. Material Bangunan sebagai salah satu komponen yang sangat penting, agar pekerjaan konstruksi yang dihasilkan berkualitas baik. Sejak sepuluh tahun terakhir untuk pekerjaan konstruksi terkait pekerjaan beton, telah menggunakan material maju yang dikenal dengan kimia konstruksi seperti *admixture*, *waterproofing*, *grout*, *hardener* dan sebagainya. Penggunaan material tersebut terbukti sangat membantu. menghasilkan mutu bangunan, gedung dan infrastruktur menjadi lebih berkualitas.

Namun sayangnya pengadaan material kimia konstruksi tersebut masih dikuasai oleh pihak asing antara lain: PT. Sika Indonesia, PT. Fosroc Indonesia dan PT.BASF sehingga Indonesia hanya dijadikan sebagai pasar (*market*) saja. Indikatornya hingga tahun 2016, masih sangat sedikit perusahaan lokal yang dapat menyediakan material kimia konstruksi. Dengan demikian tingkat ketergantungan terhadap pihak luar menjadi sangat besar dalam pengadaan material dan penetapan harga produk, hal ini tentu berpengaruh terhadap penyelesaian proyek - proyek yang ada.

Indonesia memiliki peluang untuk mengembangkan atau memproduksi material kimia konstruksi tersebut, karena memiliki sumber daya alam berupa pasir silika dan semen yang merupakan bahan utama material kimia konstruksi. Beberapa daerah seperti: Bangka, Lampung, Kalimantan dan Papua memiliki potensi sumber pasir silika yang sangat besar, namun belum dimanfaatkan menjadi material yang bernilai.

Dalam mengembangkan material kimia konstruksi masih banyak kendala antara lain: selalu ditanamkan pemikiran oleh pihak asing kepada para pelaku konstruksi di Indonesia, bahwa untuk membuat material kimia konstruksi harus berteknologi tinggi (*Hi-Tech*), dan biaya tinggi sehingga dikesankan Bangsa Indonesia tidak akan mampu untuk memproduksi material kimia konstruksi tersebut.

Untuk itu perlu dilakukan suatu terobosan dalam mengatasi permasalahan yang ada, hal ini sejalan dengan renstra Universitas Pancasila yakni menumbuh-kembangkan budaya riset yang inovatif dalam menghasilkan produk penelitian yang dibutuhkan pemerintah, masyarakat dan industri. Berdasarkan permasalahan yang ada, perlu suatu inovasi melalui penelitian berkaitan dengan pengembangan material kimia konstruksi seperti material Grout dan Hardener. Pengembangan yang dilakukan adalah material Grout dan Hardener semula dalam skala mikro, ditambahkan dengan nanosilika dalam ukuran kurang dari 100 nanometer, sehingga dihasilkan material NanoGrout dan NanoHardener. Dalam penelitian ini, cv. John Hi-Tech Contrindo sebagai salah produsen lokal sangat mendukung dengan harapan akan muncul *entrepreneur*, sehingga dapat memicu pertumbuhan ekonomi yang pada akhirnya akan menuju kemandirian Bangsa Indonesia.

1.2. Tujuan Khusus

1. Menghasilkan material Nanogrout, NanoHardener dan mesin produksi (teknologi tepat guna) yang dapat menumbuhkan *Enterpreneur* material maju.
2. Meningkatkan peran serta masyarakat dalam mengelola sumber alam lokal menjadi material maju.

1.3. Urgensi (Keutamaan) Penelitian

Hasil penelitian yang diperoleh diharapkan :

1. Tumbuhnya e*ntrepreneur* di Indonesia di bidang material maju, mengingat bahan utama yakni pasir silika dan semen sangat melimpah.
2. Dapat dikembangkan menjadi model Industri kimia konstruksi yang akan mendorong kemandirian bangsa Indonesia khususnya dalam bidang material konstruksi

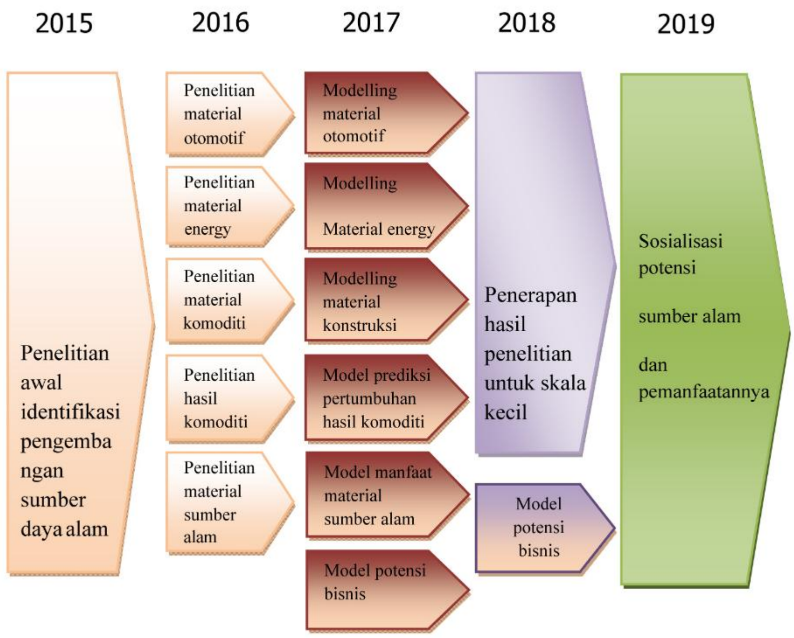
Tabel 1. Rencana Target Capaian Tahunan

No	**Jenis Luaran**				**Indikator capaian**	
	Kategori	**Sub Kategori**	**Wajib**	**Tambahan**	**TS 1)**	**TS+1**
1	Artikel Ilmiah dimuat dalam Jurnal	*Internasional bereputasi*		v	*accepted/ published*	*accepted/ published*
		Nasional terakreditasi		v	Accepted/ published	Accepted/ published
2	Artikel Ilmiah dimuat di prosiding	Internasional Terindeks SUDAH terlaksana		v	draft	Sudah dilaksanakan
		Nasional		v	Sudah dilaksanakan	Sudah dilaksanakan
3	Hak Kekayaan Intelektual (HKI)	*Paten sederhana*	*v*		*Terdaftar*	*Sudah dilaksanakan*
4	Teknologi Tepat Guna		v		produk	penerapan
5	Tingkat kesiapan Teknologi (TKT)		v		5	6

BAB 2. RENSTRA DAN ROAD MAP PENELITIAN PERGURUAN TINGGI

Rencana Induk Penelitian Universitas Pancasila 2015-2019 bertujuan agar Universitas Pancasila mampu berperan aktif dalam mewujudkan visi universitas menjadi perguruan tinggi yang unggul dan terkemuka berdasarkan nilai-nilai Pancasila. Rencana Induk Penelitian diarahkan untuk meningkatkan kualitas dan kuantitas hasil penelitian agar dapat berkontribusi dalam pengembangan ilmu pengetahuan dan teknologi, meningkatkan daya saing bangsa dan kesejahteraan masyarakat. Selain itu Rencana Induk Penelitian ini untuk menumbuh- kembangkan budaya riset yang inovatif dalam menghasilkan produk penelitian yang dibutuhkan pemerintah, masyarakat dan industri.

Rencana Induk Penelitian Universitas Pancasila berisikan rencana penelitian unggulan yang mendukung agenda penelitian nasional, sedangkan rencana penelitian unggulan yang lain berisikan penelitian unggulan Fakultas Teknik (Gambar 1) yang mampu berperan dalam meningkatkan daya saing nasional dan kesejahteraan masyarakat.



Gambar 1. Peta jalan unggulan fakultas teknik universitas pancasila

Pengembangan kemampuan inovasi dan kewirausahaan melalui tahapan penelitian awal, dasar, terapan dan industri sehingga menghasilkan produk peneltian yang dapat dimanfaatkan oleh masyarakat dan industri. Peningkatan pemanfaatan hasil penelitian dan pengabdian masyarakat dalam upaya peningkatan mutu pendidikan peningkatan jumlah artikel ilmiah dosen yang diterbitkan di jurnal internasional

Luaran penelitian tersebut diarahkan untuk mendukung kegiatan pengabdian masyarakat dan meningkatkan mutu bahan ajar sehingga akan berdampak positif terhadap mutu proses pembelajaran. Disamping itu, luaran penelitian diharapkan mampu meningkatkan reputasi Universitas Pancasila dalam dunia akademik melalui artikel ilmiah yang fokus dalam membangun IPTEK yang unggul berwawasan lingkungan dan berkesinambungan.

Mengacu pada renstra Universitas Pancasila, maka penelitian pengembangan material maju yakni: material NanoGrout, NanoHardener dan mesin produksi (teknologi tepat guna), sangat sejalan dan relevan. Hasil penelitian ini dapat dikembangkan untuk menumbuhkan *entrepreneur* bidang material maju, sehingga memberi kontribusi bagi perekonomian nasional.

BAB 3. TINJAUAN PUSTAKA

3.1 Perkembangan Riset Nano silika

Efek penggunaan nanosilika terhadap peningkatan sifat mekanik pada beton dan mortar sudah dilakukan oleh beberapa peneliti. Singh et al. (2015) membandingkan efek dua jenis serbuk silika nano dan koloidal terhadap sifat mekanik beton. Hasil penelitian menunjukkan bahwa nanosilika bubuk efektif untuk memperbaiki sifat mekanik semen mortar. Sedangkan Hou et al. (2013) melaporkan penambahan nanosilika koloidal 5% dan Fly ash 40%, secara signifikan meningkatkan proses pengerasan dan meningkatkan kuat tekan pada pasta semen. TorabianIsfahani et al. (2016) melaporkan durabilitas beton dengan rasio pengikat air yang berbeda, cenderung menghasilkan variasi sesuai dengan kandungan nano silika.

Haruchansapong et al. (2014), menyatakan nano silika dapat meningkatkan sifat komposit semen melalui mekanisme yang berbeda, Nano silika dan silika fume, adalah pozzolan yang sangat reaktif dan dapat mengubah mekanisme kalsium hidroksida (CH) menjadi C-S-H.

Biricik & Sarier, (2014), melaporkan dalam penggunaan nano silika perlu diperhatikan efeknya terhadap permeabilitas, absorpsi, kemudahan kerja, durabilitas dan creep pada beton dan mortar

3.2 Material Grout dan Hardener.

Material Grout adalah bahan bubuk *(powder*) siap pakai yang dicampur dengan air. Material grout digunakan untuk perbaikan struktur, *honeycomb*, gompal (*Spalling*) pada kolom, balok atau beton precast. Selain itu juga grout banyak digunakan untuk dudukan mesin-mesin industri, *bearing pads* dan sebagainya. Keunggulan material grout adalah : memiliki kuat tekan (*compressive strength*) yang tinggi, non shrinkage (*tidak menyusut*), mudah digunakan hanya dicampur dengan air, tahan terhadap air laut, tahan terhadap vibrasi, tidak korosif dan tidak beracun. Hasil penelitian Khayat et al. (2008), bahwa pencampuran dengan menggantikan semen dengan silika fume 3%, fly ash 10-30% dan 40 % *slag* dapat menghasilkan bahan grout yang baik.

Penelitian yang dilakukan oleh Hua (2011) memperlihatkan bahan Grout memiliki ketahanan terhadap asam. Sedangkan menurut Kamal et al. (2011), campuran Grout dapat digunakan untuk memperbaiki lubang-lubang pada bangunan bawah tanah. Sedangkan Yang et al. (2014) menggunakan semen, fly ash dan slag sebagai bahan utama dicampur dengan waterglass sebagai material grout untuk dinding beton penahan tanah yang tercemar logam berat.

Anggelis and Shiotani (2009), menyatakan grout dapat digunakan sebagai bahan Injeksi untuk perbaikan pekerjaan pada bangunan yang mengalami kerusakan. Dalam banyak kasus injeksi beton menggunakan grout akan menutup rongga-ronga yang ada.

Material Hardener merupakan material siap pakai, yang digunakan bersamaan dengan pengecoran lantai beton, tujuannya agar permukaan beton yang dihasilkan menjadi lebih kuat (tahan abrasi) dan tidak berdebu. M. Collepardi et al. (2006), mengaplikasikan 60% pasir silika dan 40% semen dengan dosis 1,5-2,0 kg/m^3, pada lantai industri ternyata dapat meningkatkan ketahanan abrasi. Hardener umumnya digunakan untuk : lantai pabrik, gudang, parkir dan garasi. Penelitian yang dilakukan Silfwerbrand and Farhang (2014). menggunakan hardener yang ditambahkan dengan admixture kedalam beton ternyata resiko retak pada lantai beton lebih rendah dibandingkan dengan beton konvensional

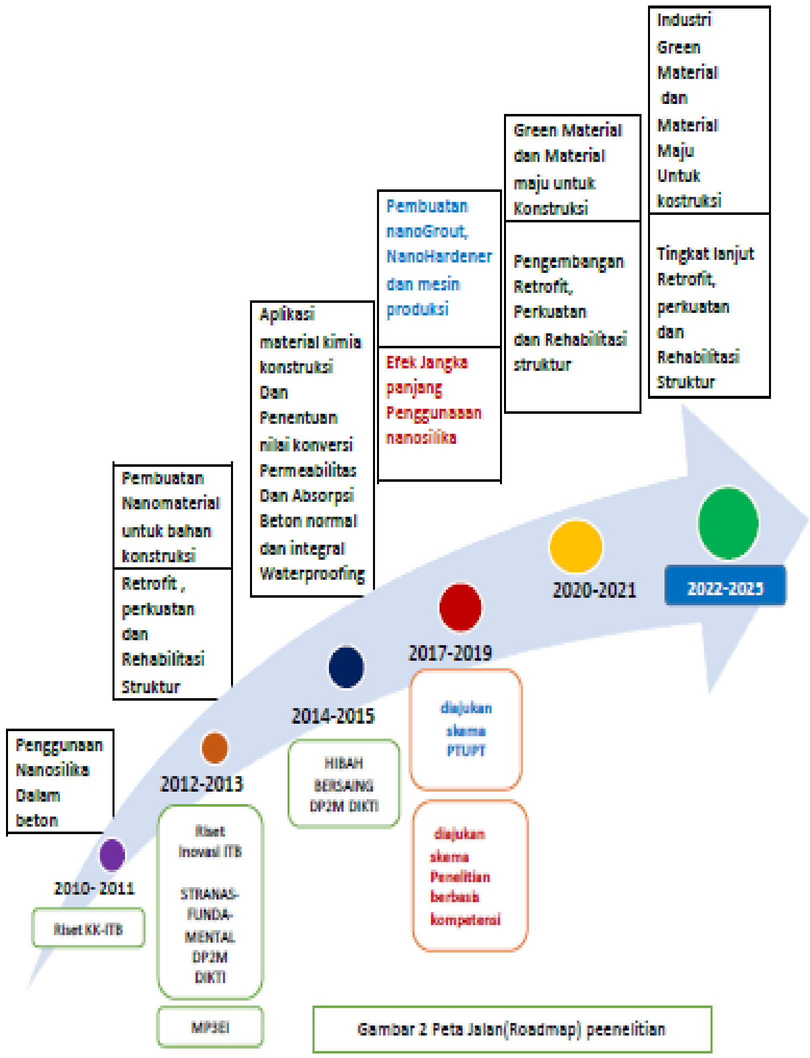
3.3. Peran *Entrepreneur* dalam Perekonomian

Global Entrepreneurship Monitor (GEM) menunjukkan bukti hubungan antara *entrepreneur* dan kemakmuran suatu negara. Peluang –peluaang yang ada akan memotivasi *entrepreneur* untuk berkontribusi bagi kemakmuran suatu negara, tetapi hanya sampai titik tertentu, tidak semua orang harus menjadi *entrepreneur*. Namun demikian kemakmuran suatu negara tidak cukup hanya dengan meningkatkan jumlah *entrepreneur* saja (Naude et al. 2013).

Perkembangan terbaru teori evolusi industri secara langsung memperlihatkan keterkaitan *Entrepreneur* dengan pertumbuhan ekonomi, fakta menunjukkan *Entrepreneur* mendorong pertumbuhan ekonomi suatu negara (Burns, 2011). *Entrepreneur* menjadi penting untuk pertumbuhan ekonomi karena melalui inovasi dapat menciptakan permintaan untuk produk dan jasa yang sebelumnya tidak tersedia (Kressel dan Lento, 2012)

3.4. Peta Jalan Penelitian

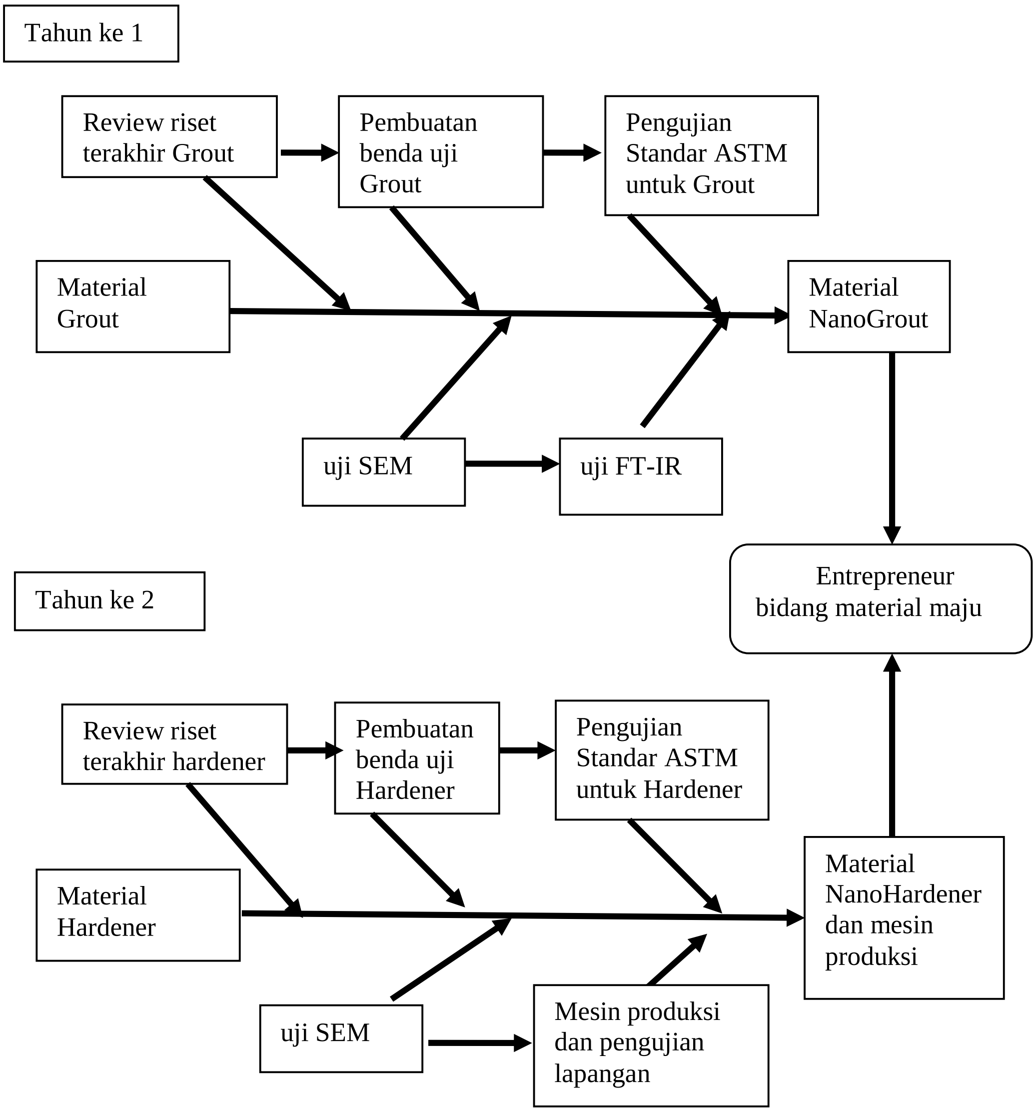
Peta Jalan(*Roadmap*) penelitian dapat dilihat pada Gambar 2. Pada tahun 2010-2011 penelitian tentang penggunaan nano silika untuk beton. Kemudian tahun 2012-2013 pembuatan nanomaterial dengan nanoteknologi untuk konstruksi; tahun 2014-2015 penelitian tentang aplikasi material konstruksi dan menentukan nilai konversi permeabilitas dan absorpsi pada beton normal dan beton integral waterproofing. Penelitian tersebut di atas didana oleh ITB dan DP2M DIKTI. Untuk tahun 2017-2019 ada 2 penelitian yang dilakukan: pertama Pengembangan NanoGrout dan NanoHardener untuk menciptakan *entrepreneur* material maju. Penelitian kedua tentang efek jangka panjang penggunaan nano silika terhadap sifat mekanik dan durabilitas beton. Hasil penelitian yang telah dilakukan sebelumnya berupa produk, metode dan buku ajar. Selain ini hasil penelitian telah dipublikasikan dalam jurnal bereputasi dan artikel ilmiah yang dimuat dalam prosiding yang terindeks.



Gambar 2 Peta Jalan(Roadmap) peenelitian

BAB 4. METODE PENELITIAN

Metode penelitian dilakukan melalui tahapan penelitian seperti terlihat pada Gambar 3, dengan jangka waktu selama dua tahun. Penelitian ini telah diawali dengan penelitian sebelumnya yang telah dijelaskan dan dapat dilihat pada Gambar 2. Dengan demikian penelitian ini merupakan penelitian lanjutan. Tahapan penelitian pada tahun pertama dimulai dengan mereview riset terakhir tentang material grout, pembuatan benda uji grout. Selanjutnya dilakukan pengujian sesuai standar ASTM berupa: kuat tekan, kuat lentur, kuat tarik, lekat, susut dan kelecakan di B4T Bandung. Kemudian dilakukan pengujian SEM di Pusat Geo;ogi Bandung dan uji FT-IR di lab. Farmasi ITB Bandung. Hasil tahapan penelitian pada tahun pertama berupa material NanoGrout, yang merupakan capaian wajib, disamping itu dihasilkan luaran tambahan berupa jurnal internasional bereputasi secara lengkap dapat dilihat di Tabel 1



Gambar 3. Tahapan penelitian selama 2 tahu

Pada tahun kedua dimulai dengan melakukan review riset tentang material hardener, pembuatan benda uji. Kemudian dilakukan pengujian tingkat kekerasan, keausan dan SEM. Pada tahun ke dua juga dihasilkan mesin produksi dan diuji aplikasinya di lapangan. Sehingga pada tahun kedua dihasilkan produk berupa material NanoHardener dan mesin produksi sebagai luaran wajib dan jurnal internasional bereputasi sebagai luaran tambahan. Hasil akhir penelitian tahun ke 1 dan tahun ke 2, berupa material NanoGrout, NanoHardener dan mesin produksi diharapkan dapat menjadi pemicu terciptanya entrepreneur material maju.

Prosedur penelitian dilakukan sebagai berikut: pembuatan benda uji menggunakan bahan Grout eks cv. JHC , kemudian pada material grout diberi tambahan nano silika dengan prosentase (1, 3, 5, 7)%. Nomenklatur untuk benda uji dibuat sebagai berikut : Go (tanpa nano silika), G1 ditambahkan nanosilika 1%, G3 (NS 3%), G5 (NS 5%) dan G7 (NS 7%).

Selanjutnya dilakukan pengujian seperti pada Tabel 2.

Tabel 2. Pengujian untuk NanoGrout

Benda uji	Pengujian pada Grout umur 1,3,7 dan 28 Hari							
	Kuat tekan	Kuat lentur	Kuat tarik	Kuat lekat	susut	Kelecakan	SEM	FT-IR
Go	✓	✓	✓	✓	✓	✓	✓	✓
G1	✓	✓	✓	✓	✓	✓	✓	✓
G3	✓	✓	✓	✓	✓	✓	✓	✓
G5	✓	✓	✓	✓	✓	✓	✓	✓
G7	✓	✓	✓	✓	✓	✓	✓	✓

Benda uji untuk NanoHardener: pembuatan benda uji menggunakan material Hardener eks cv. JHC untuk dosis 3 kg/m^2. Pada material hardener tersebut ditambahkan nano silika (1, 3, 5, 7)%, dengan nomenklatur dibuat: Ho (Tanpa nano silika), H1 ditambahkan nano silika 1%, H3 (NS 3%), H5 (NS 5%) dan H7 (NS 7%). Kemudian dilakukan pengujian seperti terlihat pada Tabel 3.

Tabel 3. Pengujian untuk NanoHardener

Benda uji	Pengujian pada Hardener umur 1,3,7 dan 28 Hari		
	Tingkat Kekerasan	Keausan	SEM
Ho	✓	✓	✓
H1	✓	✓	✓
H3	✓	✓	✓
H5	✓	✓	✓
H7	✓	✓	✓

BAB 5. HASIL DAN LUARAN YANG DICAPAI

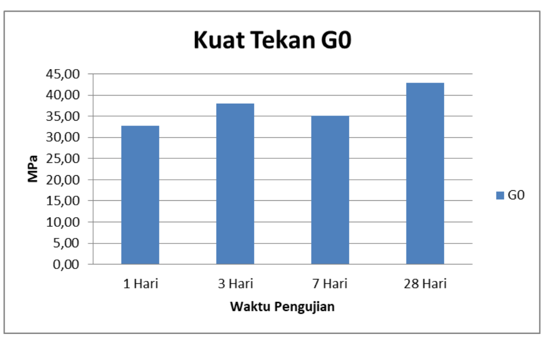
Hasil yang sudah diperoleh sampai bulan **November 2018,** proges penelitian telah selesai 100 %, seperti terlihat pada Tabel. 4.

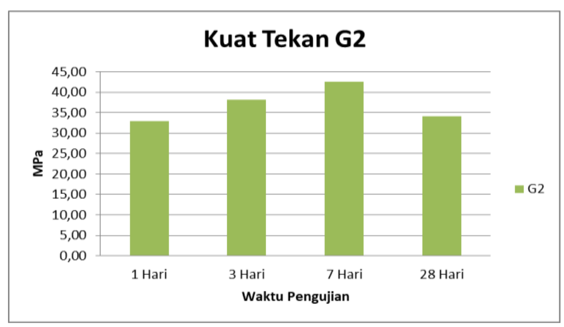
Tabel 4 Penelenitian yang telah dilakukan

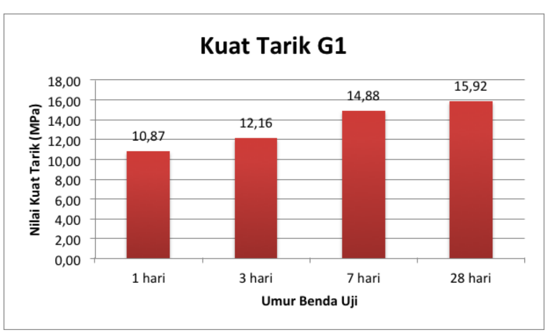
Benda uji	Pengujian pada Grout umur 1,3,7 dan 28 Hari				
	Kuat tekan	Kuat tarik	Kuat lentur	SEM	FT-IR
Go	✓	✓	✓	✓	✓
G1	✓	✓	✓	✓	✓
G2	✓	✓	✓	✓	✓
G3	✓	✓	✓	✓	✓
G5	✓	✓	✓	✓	✓

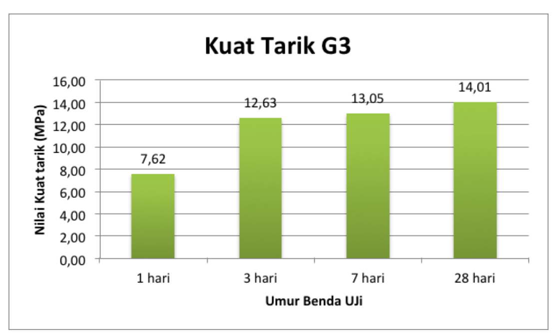
Selesai

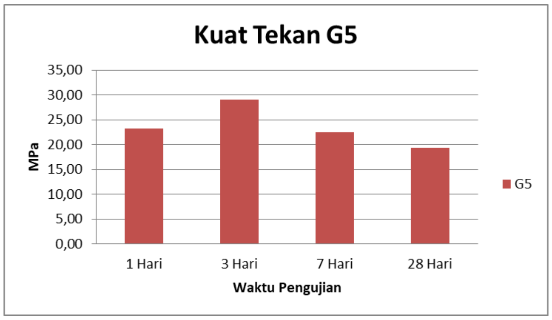
Beberapa hasil yang sudah diperoleh

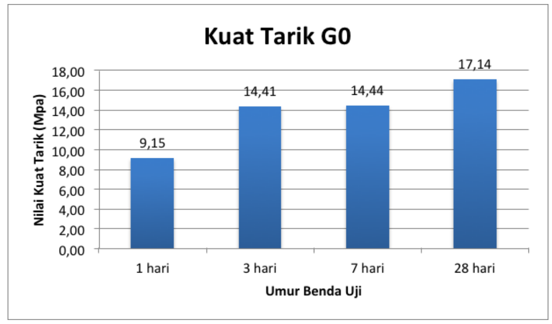


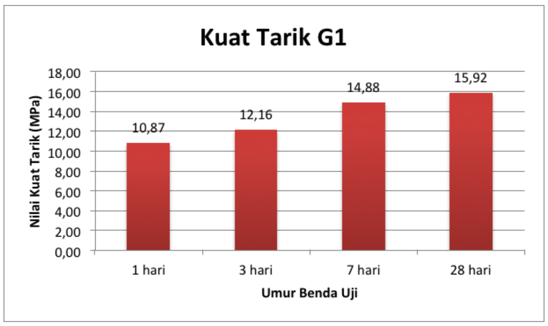


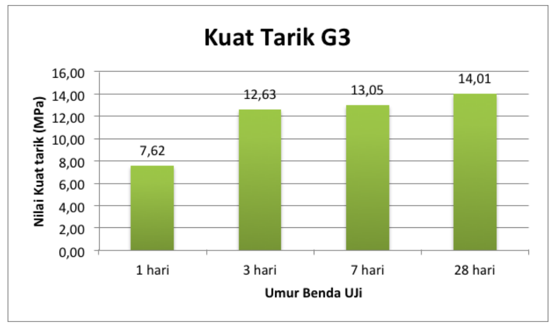


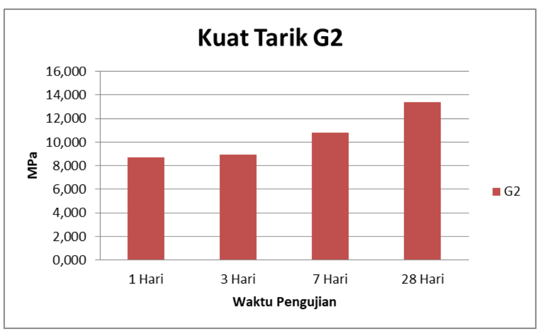


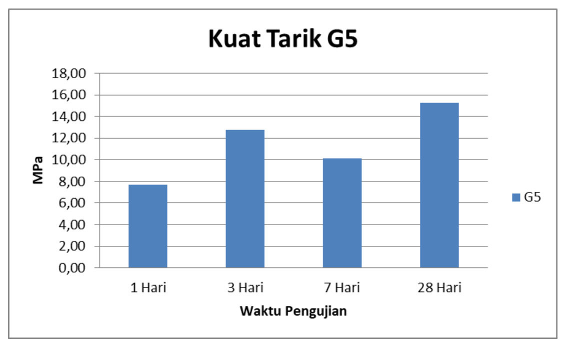

Kuat Tekan G5
MPa
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1 Hari
3 Hari
7 Hari
28 Hari
Waktu Pengujian
G5

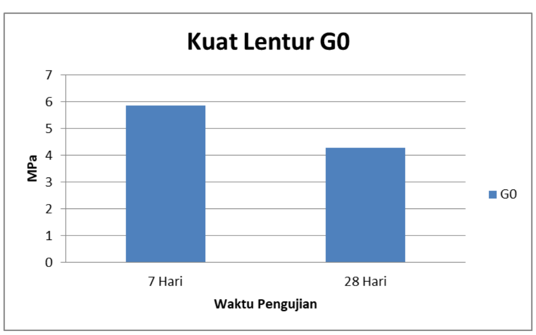

Kuat Tarik G0
Nilai Kuat Tarik (Mpa)
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
9,15
14,41
14,44
17,14
1 hari
3 hari
7 hari
28 hari
Umur Benda Uji

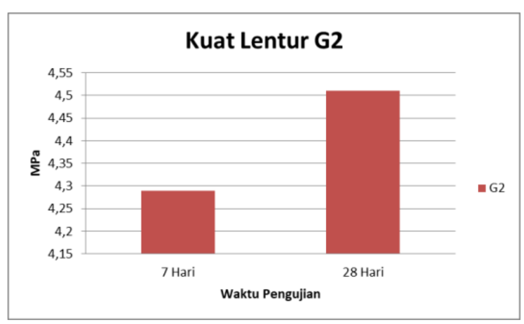

Kuat Tarik G1
Nilai Kuat Tarik (MPa)
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
10,87
12,16
14,88
15,92
1 hari
3 hari
7 hari
28 hari
Umur Benda Uji


Kuat Tarik G3
Nilai Kuat tarik (MPa)
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
7,62
12,63
13,05
14,01
1 hari
3 hari
7 hari
28 hari
Umur Benda UJi

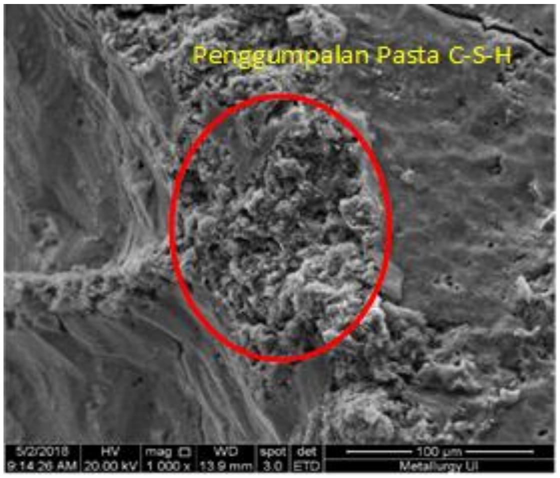

Kuat Tarik G2
MPa
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0,000
1 Hari
3 Hari
7 Hari
28 Hari
Waktu Pengujian
G2

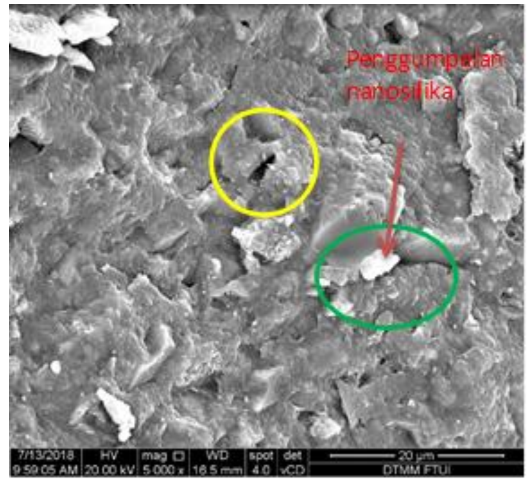

Kuat Tarik G5
MPa
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
1 Hari
3 Hari
7 Hari
28 Hari
Waktu Pengujian
G5

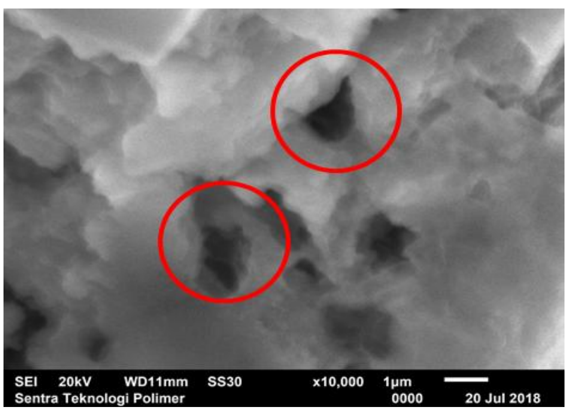

Kuat Lentur G0
MPa
7
6
5
4
3
2
1
0
7 Hari
28 Hari
Waktu Pengujian
G0

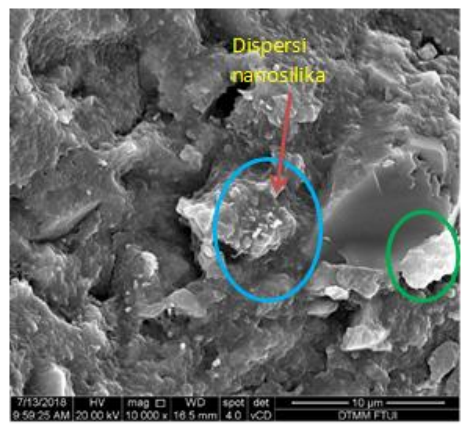

Kuat Lentur G2
MPa
4,55
4,5
4,45
4,4
4,35
4,3
4,25
4,2
4,15
7 Hari
28 Hari
Waktu Pengujian
G2

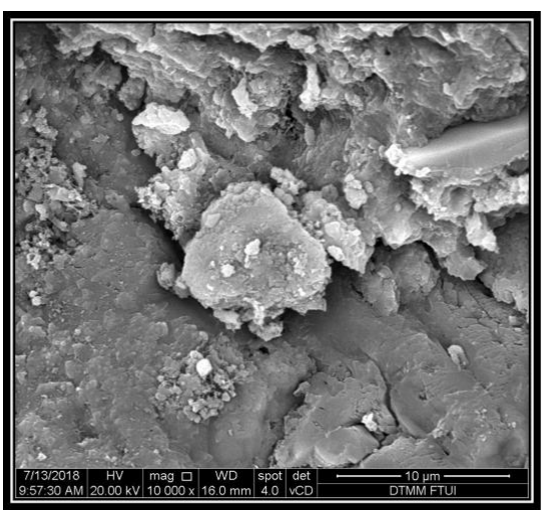
Hasil Uji SEM

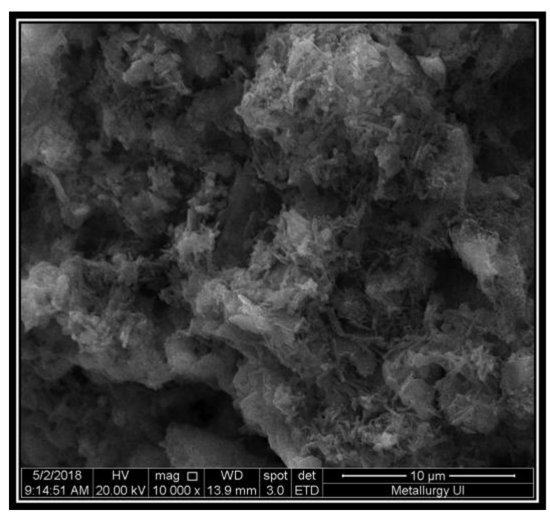












- **Persentase Kemajuan kegiatan penelitian : 100%**

Terkait paper Luaran penelitian yang telah dihasilkan : :

- Application of the kinetic and isotherm models for better understanding of the behavior of silver **nanoparticles** adsorption onto different adsorbents dipublikasi pada **Journal of Environmental Management 218 (2018) 59-70 Q1 terindeks scopus**

- Effect od added the Polycarboxylate ether on slump retention and compressive strength of high-performance concrete di ICRMCE 2018 dipublikasi di **Matec Web conferences** 195 01020 (2018) **terindeks Scopus**

Paper yang akan dipublikasi terindeks SCOPUS

- Mechanical properties of nanogrout as advanced material for construction akan dipresentasikan pada **BATAVIA INTERNATIONAL CONFERENCE (BIC 2018) SUSTAINABLE MARITIME SCIENCE AND ENGINEERING DEVELOPMENT 21-22 NOVEMBER 2018, JAKARTA, INDONESIA.**

BAB 6. RENCANA TAHAPAN BERIKUTNYA

Rencana Tahapan berikutnya :

- Mendaftarkan **paten** produk, telah melakukan kunjungan ke KEMENKUMHAM sedang dalam proses dengan mengisi Web WWW.DGIP.GO.ID

- Publikasi paper yang akan di submit ke **ASIAN JOURNAL OF CIVIL ENGINEERING (Q3)**

BAB 7. KESIMPULAN DAN SARAN

Kesimpulan :

- Riset ini telah memperlihatkan hasil yang siginifikan dengan proposal yang diajukan.
- Secara umum belum ada hambatan dan kesulitan dalam melakukan kegiatan riset.
- Riset telah mencapai 100% (selesai).

Saran

- Prosentase pencairan dana yang disetujui yang terlalu sedikit/kecil dari dana yang diajukan, cukup menyulitkan peneliti

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Review

Application of the kinetic and isotherm models for better understanding of the behaviors of silver nanoparticles adsorption onto different adsorbents

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ABSTRACT

It is the first time to do investigation the reliability and validity of thirty kinetic and isotherm models for describing the behaviors of adsorption of silver nanoparticles (AgNPs) onto different adsorbents. The purpose of this study is therefore to assess the most reliable models for the adsorption of AgNPs onto feasibility of an adsorbent. The fifteen kinetic models and fifteen isotherm models were used to test secondary data of AgNPs adsorption collected from the various data sources. The rankings of arithmetic mean were estimated based on the six statistical analysis methods of using a dedicated software of the MATLAB Optimization Toolbox with a least square curve fitting function. The use of fractal-like mixed 1, 2-order model for describing the adsorption kinetics and that of Fritz-Schlunder and Baudu models for describing the adsorption isotherms can be recommended as the most reliable models for AgNPs adsorption onto the natural and synthetic adsorbent materials. The application of thirty models have been identified for the adsorption of AgNPs to clarify the usefulness of both groups of the kinetic and isotherm equations in the rank order of the levels of accuracy, and this significantly contributes to understandability and usability of the proper models and makes to knowledge beyond the existing literatures.

Contents

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0301-4797/

1. Introduction

Silver nanoparticles (AgNPs) have been widely used in many industrial applications due to they have many advantageous properties of such as antibacterial, antifungal, antiviral, anti-inflammatory, anti-angiogenic and anticancer agents, as well as high electrical conductivity and high sensitivity (Desireddy et al., 2013; Kumar et al., 2008; Le Ouay and Stellacci, 2015; Naik et al., 2002; Park et al., 2012; Zhang et al., 2016). However, the excessive amount of AgNPs released from industrial products of such as detergents, textiles, toys, cosmetics and medical devices can have the potential to cause the risks to human health and the environment because of its antimicrobial effects and subsequent product applications, and the presence of AgNPs in the environment poses undesirable effects on plants of being inhibited seed germination and growth and has substantial adverse to microbial communities in engineered or natural ecosystems (Chen et al., 2017; Quadros and Marr, 2010; Tripathi et al., 2017). The content of AgNPs released from industrial products becomes more important and concerned in many countries because it can cause toxicity to aquatic biota near sources such as sewage discharges.

Adsorption found to be effective and cheap method among the available heavy metals removal methods and has been widely used to remove AgNPs from water. The use of nitrogen rich core-shell magnetic mesoporous silica as adsorbent has been proven to be effective for the removal of AgNPs from water with an adsorption capacity of 909.1 mg g^{-1} (Zhang et al., 2017). The use of glass beads as adsorbent can remove up to 75% of AgNPs (Polowczyk et al., 2015). The use of aged iron oxide magnetic particles synthesized by a simple solvothermal method can remove up to 90% of AgNPs for a contact time of 90 min (Zhou et al., 2017). The elimination of AgNPs from synthetic wastewater by electrocoagulation has been proven to be effective by using four different routes (Matias et al., 2015).

Many theoretical and empirical models have been proposed for describing mechanisms of AgNPs adsorption from aqueous solution. However, the report provides practical guidance for choosing an appropriate method by comparing two, three or four models only. Four kinetic models of Lagergren pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion have been tested for modeling the adsorption kinetics of AgNPs from aqueous solution to justify that two-parameter equations of pseudo-second-order showed more applicability than six-parameter equations of pseudo-first-order, Elovich and intraparticle diffusion (Ruíz-Baltazar et al., 2015). Application of four kinetics models and three isotherm models has been proposed for simulating the experimental data of AgNPs adsorption onto different adsorbents to show that all the data can have a better fit for both the kinetic model of pseudo-second-order and the isotherm model of Langmuir (Zhou et al., 2017). Two kinetic models (i.e., pseudo-first-order and pseudo-second-order) and three isotherm models (i.e., Dubinin-Radushkevich, Freundlich and Langmuir) have been proposed to test the experimental data of AgNPs adsorption and confirmed that using the pseudo-second-order and Langmuir models can get more accurate estimates of the parameter equations (Wu et al., 2017). The use of two kinetic models (i.e., pseudo-first-order and pseudo-second-order) and two isotherm models (i.e., Freundlich and Langmuir) has been used to simulate the experimental data of AgNPs adsorption to show that the most reliable estimates of the parameter equations were found with the pseudo-second-order and Langmuir models (Zhang et al., 2017). The use of Langmuir model has been proven to be better than that of Freundlich model for describing the adsorption of AgNPs on the surface of sodium montmorillonite nanoclays (Zarei and Barghak, 2015). Three models of pseudo-first-order, pseudo-second-order and Langmuir have been used to explain many observations in adsorption of AgNPs on the surface of a natural material of added *Aeromonas punctate* strain to show that the experimental data were fit well with the Langmuir and pseudo-second-order models (Khan et al., 2012). Modeling of experimental data for the adsorption of AgNPs from aqueous solution using the copper-based metal organic framework nanoparticles would fit well with the pseudo-second-order and Langmuir models, and the Langmuir isotherm does describe equilibrium behavior better than the Freundlich isotherm due to the adsorption does not continue beyond a monolayer (Conde-González et al., 2016). However, the experimental data for the adsorption of AgNPs on commercial activated carbon showed that the Freundlich isotherm can describe equilibrium behavior better than the Langmuir isotherm because of the adsorption continues beyond a monolayer (Gicheva and Yordanov, 2013). The conclusions obtained from different studies did show that the usefulness of statistical tests in model validation for the adsorption of AgNPs on the surface of a material is very limited.

The interpretation of adsorption isotherms has been reviewed for the applications of one one-parameter isotherm of Henry's model, thirteen two-parameter isotherms of Hill-Deboer, Fowler-Guggenheim, Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Flory-Huggins, Hill, Hasley, Harkin-Jura, Jovanovic, Elovich and Kiselev models, eight three-parameter isotherms of Redlich-Peterson, Sips, Toth, Koble-Carrigan, Kahn, Radke-Prausnits, Langmuir-Freundlich and Jossens models, four four-parameter isotherms of Fritz-Schlunder, Baudu, Weber-Van Vliet and Marczewski-Jaroniec models, and one five-parameter isotherm model developed by Fritz and Schlunder whereas the error analysis was performed using the nine methods of Sum of Square of Errors (ERRSQ), Hybrid Fractional Error Function (HYBRID), Average Relative Error (ARE), Marquardt's Percent Standard Deviation (MPSD), Sum of Absolute Errors (EABS), Sum of Normalized Errors (SNE), Coefficient of Determination (R^2), Nonlinear Chi-Square Test (X^2), Coefficient of Nondetermination ($1.00 - R^2$). This review concludes that the level of accuracy would be dependent on the successful modeling and interpretation of adsorption isotherms

(Ayawei et al., 2017). Even if the mass transfer factor (MTF) models to describe the adsorption kinetics of AgNPs solely in water (Fulazzaky, 2011, 2012) and the modified MTF models to describe the adsorption kinetics of AgNPs accompanied with multifarious solute in water (Fulazzaky et al., 2013, 2014; 2017) have not been used to possibly distinguish between the film mass transfer and the porous diffusion and to determine the resistance of mass transfer, it could be a challenge of verifying the possibility of using many other mathematical models to understand the behaviors of AgNPs adsorption. The aim of this study was to evaluate the use of fifteen kinetic models and that of fifteen isotherm models for describing the behaviors of AgNPs adsorption onto different adsorbents from aqueous solution. In the present work, the use of dedicated software program of the MATLAB Optimization Toolbox with a least square curve fitting (lsqcurvefit) function can be used as a framework to systematically manipulate and compare the application of six statistical methods of analysis toward a better understanding on the adsorption behaviors of AgNPs.

2. Materials and methods

2.1. Data collection

The data of AgNPs adsorption provided by secondary data sources were used as input to a numerical simulation process. The biological and non-biological adsorbent materials were all considered being testable in this study. The experimental data of AgNPs adsorption onto the synthetic materials of glass beads (GB) collected by Polowczyk et al. (2015), aged iron oxide magnetic particles (AIOMP) collected by Zhou et al. (2017), Fe_3O_4@ polydopamine core-shell microspheres (FPC) collected by Wu et al. (2017) and poly (ethylenimine) functionalized core-shell magnetic mesoporous silica composites (PFC) collected by Zhang et al. (2017) as well as those onto the natural (biological) material of using the strains of *Aeromonas punctata* (AP) collected by Khan et al. (2012) were reviewed to assess the reliability of a model and to compare different models.

2.2. Numerical simulation

2.2.1. Adsorption kinetic models

This study used the fifteen kinetic models to assess the behaviors of AgNPs adsorption onto different materials. To date, some of these models have been used as systemic approaches to simulate the secondary data (Khan et al., 2012; Polowczyk et al., 2015; Wu et al., 2017; Zhang et al., 2017; Zhou et al., 2017) in spite of many other models such as the MTF and modified MTF models (Fulazzaky, 2011, 2012; Fulazzaky et al., 2013, 2014; 2017) are still not considered for the analysis of the data.

In this work, the first-order model as proposed by Gupta et al. (2001) for dynamic modeling of lead and chromium removal from aqueous solution on red mud was used to assess the reasonableness of accounting its two-parameter equations and this can be mathematically written as follows:

$$q_t = q_e - \exp(-k_1 t) \tag{1}$$

where q_t is the adsorption capacity (mg g^{-1}) at time t (min), q_e is the adsorption capacity at equilibrium (mg g^{-1}), and k_1 is the first-order rate constant (min^{-1}).

The Ritchie second-order model has been used to describe the adsorption of cadmium ions from effluents using bone char (Cheung et al., 2001) and can be mathematically formulated (Cheung et al., 2001; Khambhaty et al., 2009) as:

$$q_t = \frac{q_e}{1 + q_e k_2 t} \tag{2}$$

where k_2 is the second-order rate constant (min^{-1}).

The pseudo-first-order model, firstly proposed by Lagergren (1898) to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal and then used by Ho and McKay (1998a) to describe the pseudo-first order sorption kinetics of phosphate onto tamarind nut shell activated carbon, can be mathematically written as the following formula:

$$q_t = q_e[1 - exp(-k_{p1} t)] \tag{3}$$

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), and k_{p1} is the pseudo-first-order rate constant (min^{-1}).

A kinetic model of the pseudo-second-order as proposed by Ho and McKay (1998b) to describe the chemisorption of divalent metal ions onto peat may be used to compare protocols and tests and this can be expressed as follows:

$$q_t = \frac{k_{p2} q_e^2 t}{1 + k_{p2} q_e t} \tag{4}$$

where k_{p2} is the pseudo-second-order rate constant (min^{-1}).

The intraparticle diffusion model (Plazinski and Rudzinski, 2009) to describe the transportation of species from the bulk to solid phase of porous material in solution may take the following form:

$$q_t = k_{ip}\sqrt{t} + c_{ip} \tag{5}$$

where k_{ip} is the measure of diffusion coefficient (mg g^{-1} $min^{-1(1/2)}$) and c_{ip} is the intraparticle diffusion constant (mg g^{-1}).

A power model of describing the adsorption behaviors as proposed by Khambhaty et al. (2009) can be mathematically written as follows:

$$q_t = k_p t^{v_p} \tag{6}$$

where k_p and v_p are the power constants of the model.

The Avrami's model to describe the kinetics of phase transformation under the assumption of spatially random nucleation has been used for assessing the adsorption of either methylene blue or Hg(II) from aqueous solution (Lopes et al., 2003; Royer et al., 2009) and can be expressed by the following equation:

$$q_t = q_e[1 - exp(-k_{av} t)^{n_{av}}] \tag{7}$$

where k_{av} the Avrami rate constant (min^{-1}) and n_{av} is the Avrami component (dimensionless).

The Bangham model has been used to describe the adsorption of anionic and cationic dyes on activated carbon from aqueous solution (Rodríguez et al., 2009) and can be written in the form of:

$$q_t = k_b t^{1/m} \tag{8}$$

where k_b is the adsorption rate constant (mg g^{-1} min^{-1}) and m is the indicator of adsorption intensity (dimensionless).

A kinetic model derived from the pseudo-first-order and pseudo-second-order called the mixed 1, 2-order model as proposed by Marczewski (2010) to assess the kinetics of dye adsorption onto mesoporous carbons from aqueous solution can be proposed in this work to assess the behaviors of AgNPs adsorption. The formula of the mixed 1, 2-order model can be written as follows:

$$q_t = q_e \frac{1 - exp(-kt)}{1 - f_2 exp(-kt)} \quad (9)$$

where f_2 is the mixed 1,2-order coefficient (dimensionless) and k is the adsorption rate constant (mg g^{-1} min^{-1}).

An exponential form of the kinetic equation (Haerifar and Azizian, 2013) can be used to describe the pattern of adsorption rate with time where its mathematical equation can be written in the following form:

$$q_t = q_e ln[2.72 - 1.72 exp(-k_e t)] \quad (10)$$

where k_e is the constant of the exponential model (mg g^{-1} min^{-1}).

A modified exponential model called as the fractal-like exponential model has been proposed by Haerifar and Azizian (2013) for the adsorption on heterogeneous solid surface and can be written in the form of:

$$q_t = q_e ln\left[2.72 - 1.72 exp\left(-k_{fle} t^{\alpha}\right)\right] \quad (11)$$

where k_{fle} is the fractal-like exponential rate coefficient (mg g^{-1} min^{-1}) and α is the constant of the model (dimensionless).

The Boyd's model as proposed by Kumar et al. (2014) to predict the actual slowest step in the adsorption process and by Viegas et al. (2014) for estimating intraparticle diffusion coefficients in adsorption processes can be used to assess the behaviors of AgNPs adsorption and this can be expressed as:

$$q_t = q_e \left[1 - \frac{6}{\pi^2} exp(-Bt)\right] \quad (12)$$

where B is the coefficient that covers the effective diffusion process and radius of the particles (min^{-1}).

A modification of the pseudo-first-order model called as the Fractal-like pseudo-first-order model has been proposed by Haerifar and Azizian (2014) to introduce the fractal concept and can be written as:

$$q_t = q_e \left[1 - exp\left(-k_{flfo} t^{\alpha}\right)\right] \quad (13)$$

where k_{flfo} is the fractal-like pseudo-first-order coefficient (mg g^{-1} min^{-1}) and α is the fractal-like pseudo-first-order model constant.

A modification of the pseudo-second-order model called as the fractal-like pseudo-second-order model proposed by Haerifar and Azizian (2014) to introduce the fractal concept can be mathematically written as:

$$q_t = \frac{k_{flso} q_e^2 t^{\alpha}}{1 + k_{flso} q_e t^{\alpha}} \quad (14)$$

where k_{flso} is the fractal-like pseudo-second-order coefficient (mg g^{-1} min^{-1}) and α is the fractal-like pseudo-second-order model constant.

A modification of the mixed 1, 2-order model called as the fractal-like mixed 1, 2-order model proposed by Haerifar and Azizian (2014) to introduce the fractal concept can be written in the mathematical expression of:

$$q_t = q_e \frac{1 - exp\left(-k_{flfs} t^{\alpha}\right)}{1 - f_2 exp\left(-k_{flfs} t^{\alpha}\right)} \quad (15)$$

where k_{flfs} is the fractal-like mixed 1, 2-order coefficient (mg g^{-1} min^{-1}) and α and f_2 are the fractal-like mixed 1, 2-order model constants.

2.2.2. Adsorption isotherm models

To do a computation of performance of an adsorption system for selecting the most appropriate model, this study used the fifteen isotherm models to assess the behaviors of AgNPs adsorption onto different materials.

The Langmuir model proposed by Langmuir (1918) has been widely used to describe the adsorption occurred on homogenous surface by monolayer sorption with a finite number of identical sites such as for the adsorption of 2,4,6-trichlorophenol on coconut husk-based activated carbon (Hameed et al., 2008) and this can be mathematically expressed as:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (16)$$

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity per unit weight of the adsorbent (mg g^{-1}), C_e is the concentration of adsorbate at equilibrium (mg L^{-1}) and K_L is the Langmuir constant relating the affinity of the binding sites (L mg^{-1}).

The Freundlich model empirically developed by Freundlich (1906) would be suitable to describe sorption of several compounds to heterogeneous surfaces or surfaces supporting sites of varied affinities, assuming that stronger binding sites are occupied first and then binding strength decreases with increasing degree of site occupation (Silva et al., 2013), and can be expressed in the form of:

$$q_e = K_f C_e^{1/n} \quad (17)$$

where K_f is the Freundlich constant relating the sorption capacity (L g^{-1}) and n is the sorption intensity of adsorbent (dimensionless).

The Langmuir-Freundlich models would be suitable for describing both types of Langmuir and Freundlich adsorption isotherm (Jeppu and Clement, 2012) and can be written as:

$$q_e = \frac{q_m (K_a C_e)^n}{1 + (K_a C_e)^n} \quad (18)$$

where K_a is the affinity constant representing the degree of adsorption (L mg^{-1}) and n is the heterogeneity index.

The Redlich-Peterson model offers a compromise between two isotherm models of Langmuir and Freundlich by assuming the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption (Wang et al., 2005) and can be formulated as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^b} \quad (19)$$

where K_{RP} and a_{RP} are the Redlich-Peterson isotherm constants (L g^{-1}) and b is the exponent that lies between 0 and 1.

The Toth model as empirical modification of the Langmuir model aims of reducing the error between experimental data and predicted values of equilibrium data (Ayawei et al., 2017; Sivarajasekar and Baskar, 2014) and can be written as:

$$q_e = \frac{q_m C_e}{\left(K_T + C_e^{n_T}\right)^{n_T}} \quad (20)$$

where K_T is the Toth isotherm constant (mg g^{-1}) and n_T is the Toth model exponent (mg g^{-1}).

The Khan isotherm model has been used to describe the experimental data with the minimum average percentage error for the adsorption of some pollutants from aqueous solutions by comparing several multicomponent adsorption isotherms (Ayawei et al., 2017; Khan et al., 1997) and can be expressed in the generalized mathematical expression of:

$$q_e = \frac{q_m b_K C_e}{(1 + b_K C_e)^{a_K}} \tag{21}$$

where b_K is the Khan isotherm constant (L mg^{-1}) and a_K is the Khan isotherm model exponent.

The Jovanovic model developed based on the assumptions contained in the Langmuir model with the possibility of some mechanical contacts between the adsorbing and desorbing molecules (Ayawei et al., 2017; Shahbeig et al., 2013) and can be formulated as follows:

$$q_e = q_m[1 - exp(-K_J C_e)] \tag{22}$$

where K_J is the Jovanovic constant (L g^{-1}).

The Koble-Corrigan model proposed by Koble and Corrigan (1952) as a three-parameter equation of isotherm model which incorporates both Langmuir and Freundlich isotherms for representing equilibrium data of adsorption on heterogeneous surfaces (Ayawei et al., 2017; Shahbeig et al., 2013) and can be represented by the following formula:

$$q_e = \frac{q_m a C_e^d}{1 + b C_e^d} \tag{23}$$

where a, b, and d are the Koble-Corrigan isotherm constants.

The Rake-Prausnitz model developed based on the concept of thermodynamic ideal solution by Radke and Prausnitz (1972) has several important properties which makes it more preferred in most adsorption systems to low adsorbate concentration (Ayawei et al., 2017; Sivarajasekar and Baskar, 2014) and can be expressed as:

$$q_e = \frac{q_m a_{RP} C_e}{[1 + a_{RP} C_e]^{n_{RP}}} \tag{24}$$

where a_{RP} is the Radke-Prausnitz equilibrium constant (L mg^{-1}) and n_{RP} is the Radke-Prausnitz model exponent.

The Fritz-Schlunder model proposed by Fritz and Schluender (1974) as an empirical equation can fit a wide range of experimental data (Ayawei et al., 2017) and can be expressed as follows:

$$q_e = \frac{a_{FS} C_e^{c_{FS}}}{1 + b_{FS} C_e^{d_{FS}}} \tag{25}$$

where a_{FS} and b_{FS} are the Fritz-Schlunder equilibrium constants (L g^{-1}) and c_{FS} and d_{FS} are the Fritz-Schlunder model exponents.

The Baudu model developed from the estimation of the Langmuir coefficients model by the measurements of tangents at different equilibrium concentrations (Ayawei et al., 2017; McKay et al., 2014; Sivarajasekar and Baskar, 2014) can be expressed as follows:

$$q_e = \frac{q_m b_B C_e^{1+x+y}}{1 + b_B C_e^{1+x}} \tag{26}$$

where b_B is the Baudu equilibrium constant (L mg^{-1}), x and y are the Baudu model parameters.

The Marczewski-Jaroniec model known as the four-parameter general Langmuir equation has bee developed on basis the distribution of the supposition of local Langmuir isotherm and adsorption energies distribution in the active sites on adsorbent (Chen, 2003; Sivarajasekar and Baskar, 2014) and can be expressed by the following formula:

$$q_e = \left[\frac{q_m a_{MJ} C_e^{b_{MJ}}}{1 + a_{MJ} C_e^{b_{MJ}}}\right]^{m_{MJ}/b_{MJ}} \tag{27}$$

where a_{MJ} is the Marczewski-Jaroniec equilibrium constant (L mg^{-1}) and b_{MJ} and m_{MJ} are the Marczewski-Jaroniec model exponents.

The Hill model developed by Hill (1910) based on the assumption that adsorption is a cooperative phenomenon with adsorbates at one site of the adsorbent influencing different binding sites on the same adsorbent (Rania and Yousef, 2015) can describe the binding of different solutes onto homogeneous adsorbent and can be written as:

$$q_e = \frac{q_m C_e^{n_H}}{K_H + C_e^{n_H}} \tag{28}$$

where K_H is the Hill isotherm constant and n_H is the Hill coefficient. Notes that the values of $n_H > 1$, $n_H = 1$ and $n_H < 1$ indicate positive cooperativity, non-cooperative or hyperbolic binding and negative cooperativity in binding, respectively.

The Brouers-Sotolongo model is an adsorption isotherm model given by a deformed exponential function of Weibull distribution (Podder and Majumder, 2016) and this can be written by the following formula:

$$q_e = q_m[1 - exp(-K_{BS} C_e^{n_{BS}})] \tag{29}$$

where K_{BS} is the Brouers–Sotolongo equilibrium constant (L mg^{-1}) and n_{BS} is the Brouers–Sotolongo model exponent.

The Unilin model is one of the empirical correlations to express experimental data for representing the adsorption (Valenzuela and Myers, 1989) and can be mathematically formulated as follows:

$$q_e = \frac{q_m}{2b_U} ln\left(\frac{a_U + C_e exp(b_U)}{a_U + C_e exp(-b_U)}\right) \tag{30}$$

where a_U is the Unilin equilibrium constant and b_U is the Unilin model exponent.

2.3. Error analysis for application of the kinetic and isotherm models

This study used the dedicated software of the MATLAB Optimization Toolbox with its lsqcurvefit function to simulate and analyze the experimental data of AgNPs adsorption on the natural and synthetic adsorbent materials. The algorithms can perform calculation, data processing and automated reasoning tasks based on the nonlinear lsqcurvefit function found in the MATLAB to find the coefficient of determination (R^2), root mean squared error (RMSE), percentage of error in maximum estimated value (E_{max}), percentage of error in minimum estimated value (E_{min}), mean absolute percent error (MAPE) and mean absolute deviation (MAD) for statistical analysis significance tests for all the kinetic and isotherm models. The first condition induces a ranking of the arithmetic mean for every model in terms of accuracy. Because of the arithmetic mean is the most commonly used and readily understood measure of central tendency, the selection of a potential model with comparison of the other models as a function of the number of terms in each model is based on the arithmetic mean information criteria. Finally, the best model order can be determined using the minimum value of average ranking (AR). The mathematical equation of the statistical analysis methods can be described as follows:

(1) For the coefficient of determination,

$$R^2 = 1 - \sqrt{\frac{\sum \left(x_{obs,\ i} - x_{model,\ i}\right)^2}{\sum \left(x_{obs,\ i} - \overline{x}_{obs}\right)^2}} \tag{31}$$

(2) For the root mean squared error,

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} \left(x_{obs,\ i} - x_{model,\ i}\right)^2}{n}} \tag{32}$$

(3) For the percentage of error in maximum estimated value,

$$E_{max} = \left|\frac{x_{model,\ max} - x_{obs,\ max}}{x_{obs,\ max}}\right| \times 100\% \tag{33}$$

(4) For the percentage of error in minimum estimated value,

$$E_{min} = \left|\frac{x_{model,\ min} - x_{obs,\ min}}{x_{obs,\ min}}\right| \times 100\% \tag{34}$$

(5) For the mean absolute percent error,

$$MAPE = \left(\frac{1}{n}\sum \frac{\left|x_{obs,i} - x_{model,i}\right|}{\left|x_{obs,i}\right|}\right) \times 100\% \tag{35}$$

(6) For the mean absolute deviation,

$$MAD = \frac{1}{n}\sum \left|x_{obs,i} - x_{model,i}\right| \tag{36}$$

where $x_{\mathrm{obs,i}}$ is the data obtained from observation at time i, $x_{\mathrm{model,i}}$ is the data modeled for observation at time i, n is the number of data, $x_{\mathrm{model,max}}$ is the maximum value of the modeled data, $x_{\mathrm{obs,max}}$ is the maximum value of the observed data, $x_{\mathrm{model,min}}$ is the minimum value of the modeled data, and $x_{\mathrm{obs,min}}$ is the minimum value of the observed data.

3. Results and discussion

3.1. Results

The requirement to define a proper model for the adsorption of AgNPs onto different adsorbents has been becoming a concern in terms of AgNPs removal (Sheng and Liu, 2017). In this work, the following criteria were used to rank the goodness-of-fit testing of the kinetic and isotherm models to experimental data that the value of $AR < 3.75$, that of $3.75 \leq AR \leq 7.50$, that of $7.50 < AR \leq 11.25$ and that of $11.25 < AR \leq 15$ represent the very good, good, satisfactory and poor adsorption performance, respectively. The results of ranking the values of every statistical analysis method for the adsorption of AgNPs onto different adsorbents were analyzed on the basis of measuring the values of the parameter equations of each model (see Tables 1 and 2 in Supplementary materials) and can be then used to verify if one kinetic or isotherm model could fit the data better than others.

3.1.1. Adsorption of AgNPs on glass beads

The results (Table 3 in Supplementary materials) of ranking the values of arithmetic mean being obtained from every statistical analysis method for the kinetic models of AgNPs adsorption on GB show that the statistical analysis for the fractal-like mixed 1, 2-order, fractal-like pseudo-first-order and fractal-like exponential models gives a very good fit to experimental data as their AR values of 1.2, 2.3 and 3.3, respectively, have been verified with a best fit being obtained for the fractal-like mixed 1, 2-order model due to its lowest AR value of 1.2. A good fit can be obtained for the fractal-like pseudo-second-order, Power, Boyd and Bangham models as their AR values of 3.8, 5.5, 5.7 and 6.2, respectively, were verified. The model-data fit can be considered satisfactory for the intraparticle diffusion, pseudo-second-order, mixed 1, 2-order and exponential models since the AR values were verified as high as 8.3, 9.3, 9.3 and 11.2, respectively. The statistical analysis for the pseudo-first-order, first order, Avrami and second-order models gives a poor fit to the data due to their AR values of 13.0, 13.2, 13.3 and 14.3, respectively, were verified and this reveals a very poor fit being obtained for the second-order model because of its AR value of 14.3 is higher than others.

The analysis of using the values of arithmetic mean for the isotherm models of AgNPs adsorption on GB (see Table 4 in Supplementary materials) shows that the Fritz-Schlunder and Baudu models give a very good fit to experimental data as their AR values of 1.67 and 2.67, respectively, have been verified with a best fit being obtained for the Fritz-Schlunder model verified by its lowest AR value of 1.67. A good fit can be found for the Khan, Toth and Radke-Prausnitz models as it can be verified by observation of their AR values of 3.67, 4.17 and 4.67, respectively. The verification of model-data fit carried out using the Brouers-Sotolongo, Hill, Redlich-Peterson, Jovanovic, Maczewski-Jaroniec, Koble-Corrigan and Langmuir models can be considered satisfactory since this view deals with the AR values as high as 7.67, 8.00, 8.17, 9.33, 10.00, 10.38 and 11.17, respectively. The statistical data analysis gives a poor fit for the Langmuir-Freudlich, Unilin and Freundlich models as it has been verified by the observation of the AR values as high as 12.00, 12. 17 and 13.83, respectively, and this verification reveals a very poor fit for the Freundlich model due to its AR value of 13.83 is higher than others.

3.1.2. Adsorption of AgNPs on aged iron oxide magnetic particles

The results (Table 5 in Supplementary materials) of numerical simulation by the kinetic models of AgNPs adsorption on AIOMP show that the statistical analysis for the fractal-like mixed 1, 2-order, mixed 1, 2-order and fractal-like pseudo-first-order kinetic models gives a very good fit to experimental data as their AR values of 1.33, 1.83 and 2.83, respectively, have been verified with a best fit being obtained for the fractal-like mixed 1, 2-order model due to its lowest AR value of 1.33. A good fit can be obtained for the fractal-like exponential, fractal-like pseudo-second-order, pseudo-first-order and Avrami models since their AR values of 4.00, 5.00, 6.33 and 7.00, respectively, were verified. The model-data fit can be considered satisfactory for the exponential, pseudo-second order and power models because of the AR values were verified as high as 8.17, 9.17 and 10.67, respectively. The statistical analysis for the Bangham, Boyd, intraparticle diffusion, first-order and second-order models gives a poor fit to the data due to their AR values of 11.33, 11.33, 12.00, 14.33 and 14.67, respectively, were verified and this reveals a very poor fit being obtained for the second-order model because of its AR value of 14.67 is higher than others.

The analysis of using the values of arithmetic mean for the isotherm models of AgNPs adsorption on AIOMP (see Table 6 in Supplementary materials) shows that the only Brouers-Sotolongo model gives a very good fit to experimental data due to its AR value of 1.00 has been verified. A good fit can be found for the Langmuir-Freudlich, Fritz-Schlunder, Baudu, Koble-Corrigan, Hill, Maczewski-Jaroniec and Jovanovic models as it can be verified by observation of their AR values of 4.00, 4.50, 4.50, 4.67, 4.83, 5.50 and 7.00, respectively. The verification of model-data fit carried out using the Toth, Khan and Radke-Prausnitz models can be considered satisfactory since this view deals with the AR values as high as 9.67, 9.83 and 10.50, respectively. The statistical data analysis gives a poor fit for the Langmuir, Unilin, Redlich-Peterson and Freundlich models as it has been verified by the observation of the AR values as high as 12.33, 12.67, 14.33 and 14.67, respectively, and this verification reveals a very poor fit for the Freundlich model due to its AR value of 14.67 is higher than others.

3.1.3. Adsorption of AgNPs on Fe_3O_4@ polydopamine core-shell microspheres

The results (Table 7 in Supplementary materials) of ranking the values of arithmetic mean being obtained from every statistical analysis method for the kinetic models of AgNPs adsorption on FPC show that the statistical analysis for the fractal-like mixed 1, 2-order and pseudo-second order models gives a very good fit to experimental data because of their AR values of 1.17 and 2.83, respectively, have been verified with a best fit being obtained for the fractal-like mixed 1, 2-order model due to its lowest AR value of 1.17. A good fit can be obtained for the pseudo-first-order, first order, exponential, Boyd and Avrami models since their AR values of 4.83, 5.17, 5.33, 5.33 and 5.83, respectively, were verified. The model-data fit can be considered satisfactory for the fractal-like exponential, Bangham, power, fractal-like pseudo-first-order and mixed 1, 2-order models since their AR values were verified as high as 9.33, 10.00, 10.17, 10, 50, and 11.17, respectively. The statistical analysis for the fractal-like pseudo-second-order, intraparticle diffusion and second-order models gives a poor fit to the data because of their AR values of 11.50, 12.17 and 14.67, respectively, were verified and this reveals a very poor fit being obtained for the second-order model due to its AR value of 14.67 is higher than others.

The analysis of using the values of arithmetic mean for the isotherm models of AgNPs adsorption on FPC (see Table 8 in Supplementary materials) shows that the only Koble-Corrigan model give a very good fit to experimental data as its AR value of 2.17 has been verified. A good fit can be found for the Toth, Khan, Brouers-Sotolongo, Fritz-Schlunder, Baudu, Langmuir-Freudlich and Maczewski-Jaroniec models as it can be verified by observation of their AR values of 3.67, 4.00, 5.17, 6.33, 6.33, 6,67 and 7.00, respectively. The verification of model-data fit carried out using the Hill, Jovanovic and Langmuir models can be considered satisfactory since this view deals with their AR values as high as 9.33, 9.50 and 9.83, respectively. The statistical data analysis gives a poor fit for the Unilin, Radke-Prausnitz, Freundlich and Redlich-Peterson models as it has been verified by the observation of the AR values as high as 12.17, 12. 33, 12.50 and 13.00, respectively, and this verification reveals a very poor fit for the Redlich-Peterson model due to its AR value of 13.00 is higher than others.

3.1.4. Adsorption of AgNPs on Poly(ethylenimine) functionalized core-shell magnetic

The results (Table 9 in Supplementary materials) of ranking the values of arithmetic mean being obtained from every statistical analysis method for the kinetic models of AgNPs adsorption on PFC show that the statistical analysis for the fractal-like pseudo-first-order, fractal-like mixed 1, 2-order and fractal-like exponential models gives a very good fit to experimental data as their AR values of 2.00, 2.83 and 3.17, respectively, have been verified with a best fit being obtained for the fractal-like pseudo-first-order model because of its lowest AR value of 2.00. A good fit can be obtained for the fractal-like pseudo-second-order, Boyd, pseudo-second-order, power and mixed 1, 2-order models as their AR values of 4.17, 5.83, 6.67, 7.00 and 7.00, respectively, were verified. The model-data fit can be considered satisfactory for the Bangham, intraparticle diffusion and exponential models since the AR values were verified as high as 7.67, 10.33 and 10.33, respectively. The statistical analysis for the pseudo-first-order, Avrami, first-order and second-order models gives a poor fit to the data due to their AR values of 11.67, 12.33, 14.50 and 14.50, respectively, were verified and this reveals a very poor fit being obtained for the first-order and second-order model because of the same their AR value of 14.50 is higher than others.

The analysis of using the values of arithmetic mean for the isotherm models of AgNPs adsorption on PFC (see Table 10 in Supplementary materials) shows that the only Freundlich model give a very good fit to experimental data as its AR value of 3.67 has been verified. A good fit can be found for the Radke-Prausnitz, Toth, Fritz-Schlunder, Khan, Brouers-Sotolongo, Koble-Corrigan and Baudu models as it can be verified by observation of their AR values of 4.33, 4.50, 5.33, 5.50, 6.67, 7.17 and 7.33, respectively. The verification of model-data fit carried out using the Langmuir-Freudlich, Maczewski-Jaroniec and Unilin models can be considered satisfactory since this view deals with the AR values as high as 8.00, 8.67 and 9.33, respectively. The statistical data analysis gives a poor fit for the Jovanovic, Langmuir, Hill and Redlich-Peterson models since it has been verified by the observation of the AR values as high as 11.83, 12.50, 12.50 and 12.67, respectively, and this verification reveals a very poor fit for the Redlich-Peterson model due to its AR value of 12.67 is higher than others.

3.1.5. Adsorption of AgNPs on Aeromonas punctata

The results (Table 11 in Supplementary materials) of ranking the values of arithmetic mean being obtained from every statistical analysis method for the kinetic models of AgNPs adsorption on AP show that the statistical analysis for the fractal-like mixed 1, 2-order, fractal-like pseudo-first-order and fractal-like exponential models gives a very good fit to experimental data because of their AR values of 1.5, 2.3 and 3.5, respectively, have been verified with a best fit being obtained for the fractal-like mixed 1, 2-order model due to its lowest AR value of 1.5. A good fit can be obtained for the mixed 1, 2-order, fractal-like pseudo-second-order, pseudo-first-order and exponential models as their AR values of 5.7, 5.8, 5.7, 7.3 and 7.5, respectively, were verified. The model-data fit can be considered satisfactory for the Avrami, power, Bangham, pseudo-second-order and intraparticle diffusion models since the AR values were verified as high as 8.3, 8.7, 9.7, 10.3 and 10.7, respectively. The statistical analysis for the Boyd, second-order and first-order models gives a poor fit to the data due to their AR values of 11.5, 13.5 and 13.7, respectively, were verified and this reveals a very poor fit being obtained for the first-order model because of its AR value of 13.7 is higher than others.

The analysis of using the values of arithmetic mean for the isotherm models of AgNPs adsorption on GB (see Table 12 in Supplementary materials) shows that the Maczewski-Jaroniec, Brouers-Sotolongo, Fritz-Schlunder and Baudu models give a very good fit to experimental data since their AR values of 1.33, 2.17, 3.00 and 3.50, respectively, have been verified with a best fit being obtained for the Maczewski-Jaroniec model as verified by its lowest AR value of 1.33. A good fit can be found for the Unilin, Langmuir-Freudlich and Koble-Corrigan models as it can be verified by observation of their AR values of 5.33, 6.50 and 6.50, respectively. The verification of model-data fit carried out using the Hill, Toth, Khan, Langmuir, Jovanovic and Radke-Prausnitz models can be considered satisfactory since this view deals with their AR values as high as 7.50, 9.50, 10.00, 11.00, 11.00 and 11.00, respectively. The statistical data analysis gives a poor fit for the Freundlich and Redlich-Peterson models as it has been verified by observation of the AR values as high as 13.50 and 15.00, respectively, and this verification reveals a very poor fit for the Redlich-Peterson model due to its AR value of 15.00 is higher than others.

3.2. Discussion

3.2.1. Application of the adsorption kinetic models

The error analysis has been one of the most applied tools for defining the best fitting adsorption models because it consists of different statistical methods for determining the values of such as R^2, RMSE, E_{max}, E_{min}, MAPE and MAD (Ayawei et al., 2017; Madhavan et al., 2016; Sivarajasekar and Baskar, 2014). This analysis induces a ranking of the arithmetic mean in term of accuracy for every model. The results (Tables 3, 5, 7, 9, 11 in Supplementary materials) show that the adsorption kinetic models for the adsorption of AgNPs do fit to the experimental data depending on type of the adsorbent. It is an inconsistency in the representational content of different models for the adsorption of AgNPs from aqueous solution and spectrum of the stimulating zone depends on AgNPs properties and environmental conditions (Sheng and Liu, 2017). The experimental evidence of the existence of fractal-like mixed 1, 2-order model for modeling the adsorption of AgNPs on GB, AIOMP, FPC, PFC and AP gives a very good fit to the data as judged by all the AR values of below than 3.75 in spite of the analysis of using the values of $E_{\max}$, $E_{\min}$ and MAPE as high as 4.00 for the adsorption of AgNPs on PFC from aqueous solution gives a good fit. A plot (Fig. 1) of q_t versus t for the fractal-like mixed 1, 2-order model shows that the trend curve is different depending on the adsorbent and can be expressed as parametric model with a growth curve followed exponential pattern within a specific range. The kinetics of AgNPs adsorption on GB, AIOMP, FPC, PFC or AP with an energetically heterogeneous surface determine the adsorption capacity and breakthrough time of the adsorbent of being characterized by its different surface chemical properties (Fayaz et al., 2017; Haerifar and Azizian, 2014). The statistical analysis of experimental data for the adsorption of AgNPs on GB, AIOMP, PFC and AP can be performed using the fractal-like pseudo-first-order, fractal-like exponential, fractal-like pseudo-second-order and mixed 1, 2-order models except for: (1) the use of mixed 1, 2-order model for modeling the adsorption of AgNPs on GB and PFC by using the R^2, RMSE and MAPE values and AP by using the $E_{\min}$ and MAPE values and (2) the use of fractal-like pseudo-second-order model for modeling the adsorption of AgNPs on AP. This conclusion would be due to the use of these models to rank the values of arithmetic mean can provide a good fit within the data range as judged by their AR values of $3.75 \leq AR \leq 7.50$. Previous studies have found the kinetics of AgNPs adsorption on GB, AIOMP, FPC and PFC followed a pseudo-second-order model (Polowczyk et al., 2015; Wu et al., 2017; Zhang et al., 2017; Zhou et al., 2017). It has been reported that the kinetics of adsorption of AgNPs on AP fitted best to pseudo-first-order (Khan et al., 2012). In this work, the use of pseudo-second-order, Boyd, power, exponential, pseudo-first-order, Bangham, Avrami and intraparticle diffusion models can be recommended for modeling the experimental data but it needs to be checked the reliability and validity on a case-by-case basis because of the error analysis of using the different statistical methods for determining the values of R^2, RMSE, E_{max}, E_{min}, MAPE and MAD can have many reasons for coming to different conclusions of very good, good, satisfactory and poor fit to the experimental data. Experimental evidence (see Tables 3, 5, 7, 9, 11, 13 in Supplementary materials) shows that based on the verification of arithmetic mean as a statistical measure the use of first-order and second-order models cannot be recommended for modeling the experimental data except the use of first order model for modeling the adsorption of AgNPs on FPC due to its statistical data analysis gives a poor fit to the data as judged by an AR value of higher than 11.25. In summary, comprehensive performance analysis of the fifteen kinetic models can rank that the use of the fractal-like mixed 1, 2-order for describing the behaviors of adsorption of AgNPs is better than fractal-like pseudo-first-order, better than fractal-like exponential, better than fractal-like pseudo-second-order, better than mixed 1, 2-order, better than pseudo-second-order, better than Boyd, better than Power, better than exponential, better than pseudo-first-order, better than Bangham, better than Avrami, better than intraparticle diffusion, better than first order, and better than second-order model as it can be verified by the overall average AR values of 1.61, 3.99, 4.66, 6.05, 7.00, 7.65, 7.94, 8.41, 8.51, 8.63, 8.98, 9.35, 10.70, 12.18, and 14.33, respectively (see Table 13 in Supplementary materials).

3.2.2. Application of the adsorption isotherm models

The error analysis may classify the ranking of the arithmetic mean in term of accuracy for the application of fifteen adsorption isotherm models. The results (Tables 4, 6, 8, 10, 12 in Supplementary materials) show that the use of the isotherm models for modeling the adsorption of AgNPs do fit to the experimental data depending on the type of adsorbent. Even though the experimental evidence of using (1) the Fritz-Schlunder, Baudu and Khan models for modeling the adsorption of AgNPs on GB, (2) the Brouers-Sotolongo model for the adsorption of AgNPs on AIOMP, (3) the Koble-Corrigan and Toth models for the adsorption of AgNPs on FPC, (4) the Freundlich model for the adsorption of AgNPs on PFC and (5) the Maczewski-Jaroniec, Brouers-Sotolongo, Fritz-Schlunder and Baudu models for the adsorption of AgNPs on AP shows a very good fit to the experimental data as judged by the AR value of below 3.75, the statistical analysis of ranking the arithmetic mean verified that no one model can be considered as the most reliable estimate of adsorption isotherm parameters for the adsorption of AgNPs on all adsorbents of GB, AIOMP, FPC, PFC and AP. It has been reported that the experimental data best fitted the Langmuir model for the adsorption of AgNPs on GB, AIOMP, FPC and AP (Khan et al., 2012; Polowczyk et al., 2015; Wu et al., 2017; Zhou et al., 2017). Both Langmuir and Freundlich models fitted the experimental data well for the adsorption of AgNPs on PFC (Zhang et al., 2017). This study found that the most reliable way of analysing the experimental data for the adsorption of AgNPs on GB, AIOMP, PFC and AP can be suggested using the Fritz-Schlunder and Baudu models because of the use of these two models to rank the values of arithmetic mean can give a good fit to the data as judged by the AR values of $3.75 \leq AR \leq 7.50$. The trend curve is different depending on the adsorbent and this can be verified by plotting a curve of q_t versus t as shown in Fig. 2 for the application of Fritz-Schlunder model to describe the behaviours of AgNPs adsorption. This study of the adsorption of AgNPs on GB, AIOMP, FPC, PFC or AP evaluated by the fifteen isotherm models involves plotting the experimental data and finding the different behavior accumulation curves and this suggests that the physical and chemical properties of the adsorbent determine the adsorption capacity and concentration of AgNPs at equilibrium (Adane et al., 2015; Azeez et al., 2018). The application of Fritz-Schlunder, Brouers-Sotolongo, Baudu, Koble-Corrigan, Toth, Maczewski-Jaroniec, Khan, Langmuir-Freudlich, Hill, Radke-Prausnitz, Jovanovic and Unilin models can be recommended for modeling the experimental data since the AR values of less than 11.25 were verified in many cases; however, the verification of the reliability and validity of each model is important for any experimental data to provide guidance and clarity on the specific case of adsorption isotherm because of the error analysis of determining the values of R^2, RMSE, E_{max}, E_{min}, MAPE and MAD can reach different conclusions of very good, good, satisfactory and poor fit to the experimental data. The experimental evidence of arithmetic mean verification (see Tables 4, 6, 8, 10, 12, 14 in Supplementary materials) shows that the use of Redlich-Peterson model cannot be recommended for modeling the adsorption of AgNPs on AIOMP, FPC, PFC and AP due to the statistical data analysis gives a poor fit to the experimental data as judged by the AR values of higher than

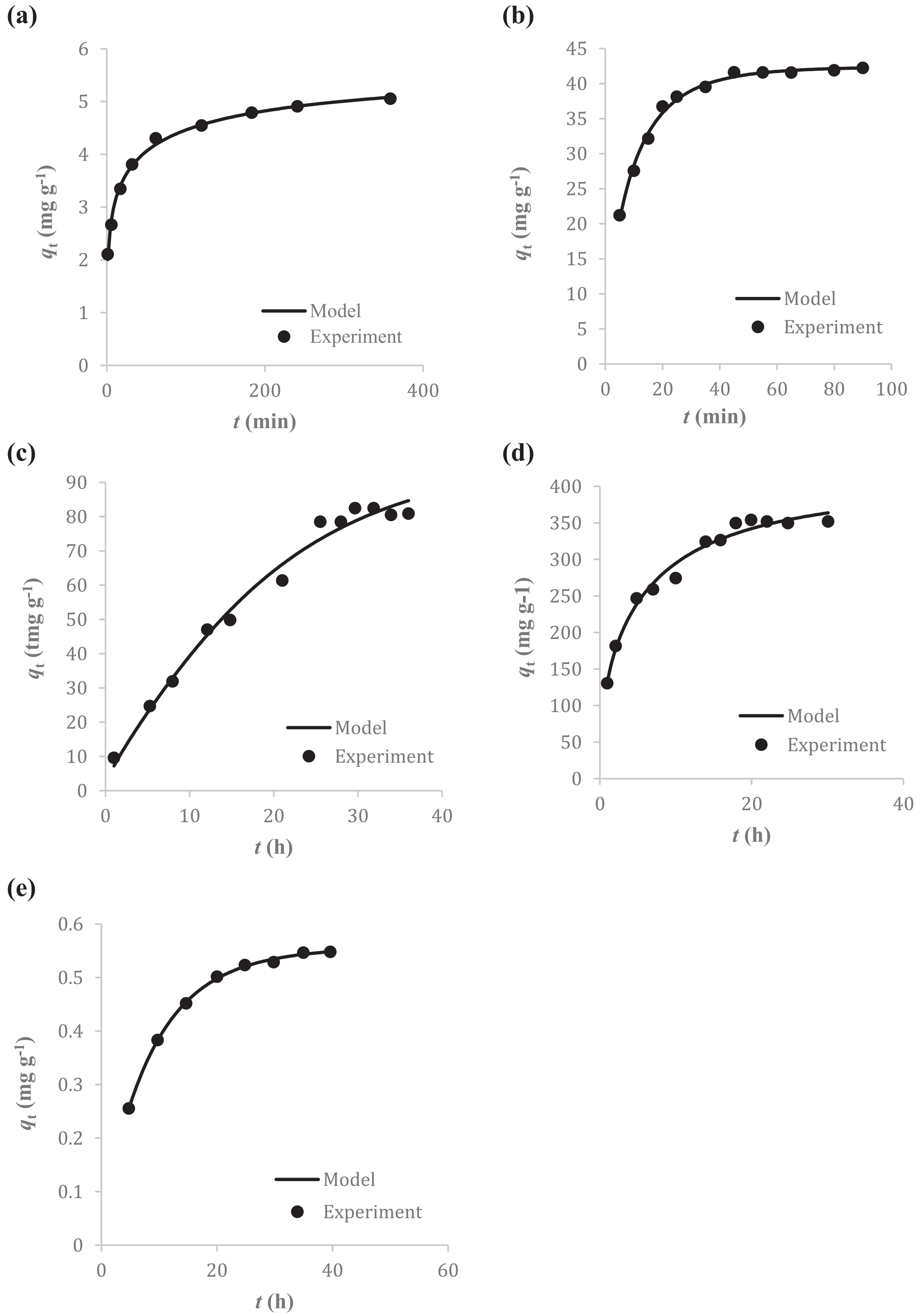

Fig. 1. Curve of plotting q_t versus t for assessing the behaviors of AgNPs adsorption on **(a)** GB, **(b)** AIOMP, **(c)** FPC, **(d)** PFC and **(e)** AP by the fractal-like mixed 1, 2-order kinetic model.

11.25. In general, the statistical analysis of the experimental data to evaluate the performance ranking of the fifteen isotherm models may conclude the Fritz-Schlunder better than Brouers-Sotolongo, better than Baudu, better than Koble-Corrigan, better than Toth, better than Maczewski-Jaroniec, better than Khan, better than Langmuir-Freudlich, better than Hill, better than Radke-Prausnitz, better than Jovanovic, better than Unilin, better than Langmuir, better than Freundlich, and better than Redlich-Peterson as it can be verified by the overall average AR values of 4.17, 4.54, 4.87, 6.27, 6.30, 6.50, 6.60, 7.43, 8.43, 8.57, 9.73, 10.33, 11.37, 11.63, and 12.63, respectively (see Table 14 in Supplementary materials).

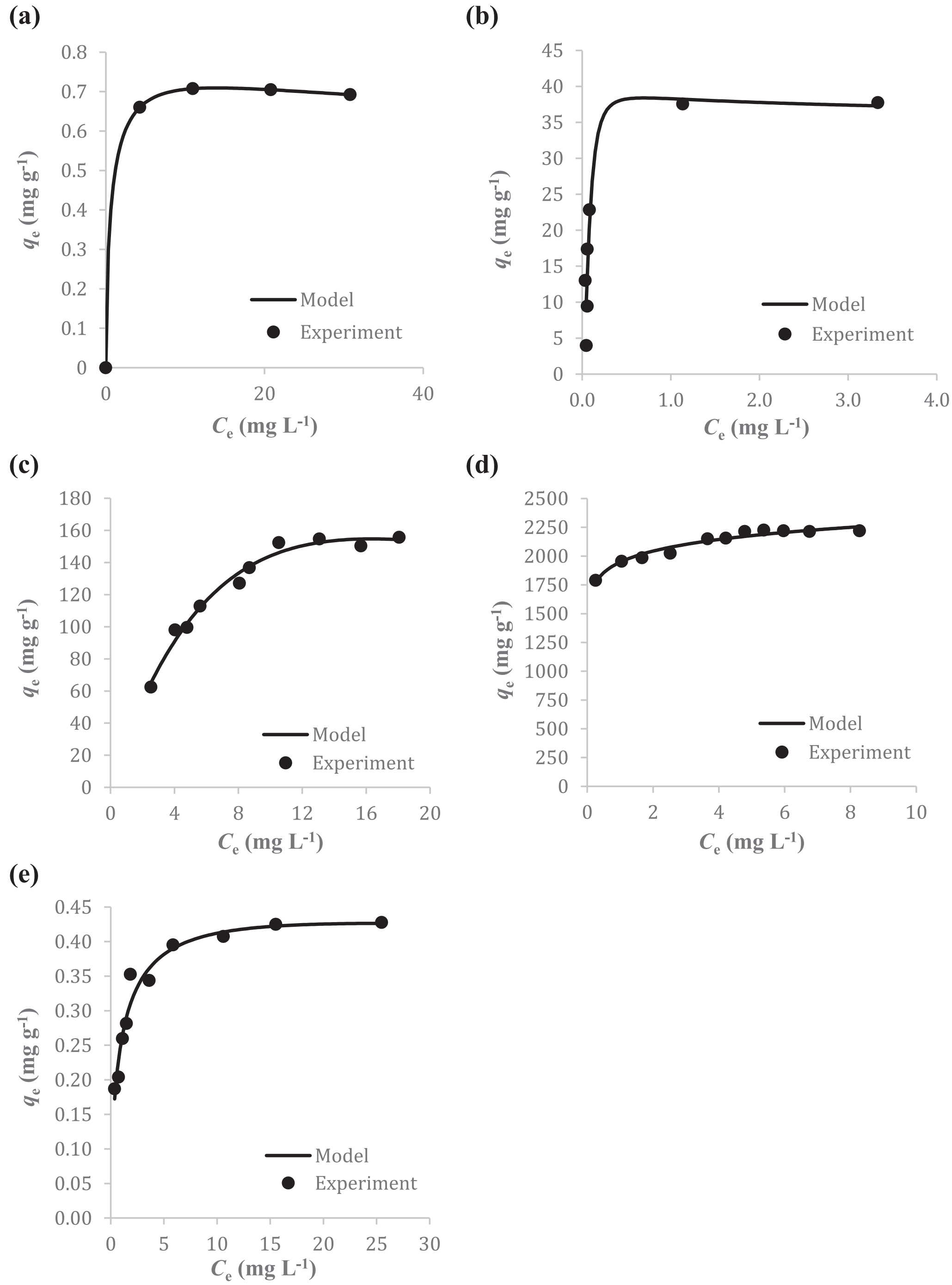

Fig. 2. Curve of plotting q_e versus C_s for assessing the behaviors of AgNPs adsorption on **(a)** GB, **(b)** AIOMP, **(c)** FPC, **(d)** PFC and **(e)** AP by the Fritz-Schlunder isotherm model.

4. Conclusions

This study used fifteen kinetic models and fifteen isotherm models together with six statistical analysis methods to assess the level of accuracy for the adsorption of AgNPs from aqueous solution onto the five types of adsorbent. The results of this study verified that the fractal-like mixed 1, 2-order model is the best one among the fifteen kinetic models to be used for describing the behaviors of adsorption of AgNPs on GB, AIOMP, FPC, PFC and AP and the Fritz-Schlunder and Baudu models are the most reliable isotherm models to be used for describing the behaviors of adsorption of AgNPs on GB, AIOMP, PFC and AP. The verification of the reliability and validity of the match of these thirty models with experimental data would be important to provide guidance and clarity on the kinetic and isotherm studies of AgNPs adsorption on the GB, AIOMP, FPC, PFC and AP adsorbent. The application of other kinetic and isotherm models for studying the adsorption of AgNPs as well as the application of these thirty models for the adsorption of other nanoparticles onto different types of adsorbent would be interested in conducting researches in the future.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jenvman.2018.03.066.

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Effect of added the polycarboxylate ether on slump retention and compressive strength of the high-performance concrete

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Abstract. It is well known that workability of high performance concrete (HPC) is dependent on slump value of concrete mixture. Moreover, slump retention is the most sensitive compared to a well-known slump value because it represents the durability of concrete mixture for its applications in the field of civil engineering. This research used the polycarboxylate ether (PCE) to increase slump value of concrete mixture and then verified the effect of PCE on the slump retention and compressive strength of different high-performance concretes. 0%, 0.5%, 1%, 2% of PCE were added into concrete mixture to yield a minimum compressive strength of f'c 50 MPa. The slump retention tests were performed at 0, 15, 30, 45, 60 and 75 minutes while the compressive strength tests were carried out at 3, 7, 14 and 28 days for every concrete sample. The result findings showed that the optimal concrete performance can be achieved by adding 2% of PCE to reach at a slump retention value of 45 minutes and a compressive strength of 53.84 MPa. Effect of PCE on the slump retention and compressive strength has been verified to contribute an insight into the application of a proper designed workability of HPC.

1 Introduction

The needs of high performance concrete (HPC) for construction in Indonesia will increase from the year to year due to the government policies have been aligned to focus on infrastructure development as foundation for dynamic economic growth. However, many constraints faced by concrete producers in the manufacturing of HPC should have to look at a dedicated solution. One is how HPC can retain its existing slump retention capability to ensure that the application of HPC in civil engineering industry can achieve the best performance with high workability. Many recent studies highlight established applications

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of nanoparticles such as silver nanoparticles, titania polyvinylalcohol–alginate beads, and polycarboxylate ether (PCE) as superplasticizer to rapidly emerging applications in the civil and environmental engineering and discuss future research directions [1-3]. Therefore, it has been reported that the addition of superplasticizer can improve the workability of HPC by using a very low w/c ratio [4].

Many manufacturers can produce the HPCs of being characterised with a long period of slump retention for maintaining the existing concrete workability. The use of superplasticizer has been proven to be effective in fabricating a long retardation concrete setting and long slump retention. However, uncontrolled use of the PCE as superplasticizer to improve the workability can cause a low compressive strength of the HPC [5].

Further the quantity of superplasticizer added to a concrete mixture is a concern for many producers of HPC in civil engineering industry due to the role of superplasticizers during the hydration of cement is very complex and is still not fully understood [6]. It is suggested that the importance is how to adjust the quantity of PCE added to get a proper mixture of HPC to produce a long slump retention and high compressive strength value [7]. Therefore, the objectives of this study are (1) to obtain a proper quantity of PCE added into concrete's mixture for obtaining optimal composition of HPC and (2) to assess the performance of HPC as it can be verified from the values of long slump retention and high compressive strength. The benefit of this research can help producers in manufacturing HPC with an optimal composition of PCE.

2 Materials and methods

2.1 Materials

This paper evaluates the effects of PCE level in concrete mixture and experimental method on the observed HPC performance of measured using different compositions of PCE with a concrete mix design of added 0% of PCE as the reference. This study used the materials of (1) type-1 Ordinary Portland Cement (OPC), (2) coarse aggregate of quarry Purwakarta, (3) fine aggregate from Galunggung quarry and (4) superplasticizer of PCE (Normet type Tamcem 21 RA).

2.2 Concrete mix design

The local materials were used for concrete mix design and they have been reported previously by Jonbi et al., [8,9]. Table 1 shows the concrete mix design of four different PCE composition.

Table 1. Concrete mix design with *f*'c 50 MPa

Material	Unit	BK0	BK1	BK2	BK3
OPC	kg/m^3	484,12	484,12	484,12	484,12
Fine aggregate	kg/m^3	793,12	793,12	793,12	793,12
Coarse aggregate	kg/m^3	971,04	971,04	971,04	971,04
Water	kg/m^3	193,65	193,65	193,65	193,65
PCE	l/m^3	0	2,42	4,84	9,68

The addition of PCE was classified by a nomenclature that BK0 is the concrete's mix that designed for the addition of 0% PCE, BK1 for the addition of 0.5% PCE, BK2 for the addition of 1% PCE and BK3 for the addition of 2% PCE, as shown in Table 2.

Table 2. Nomenclature and number of compressive strength test

Code	PCE	Age of concrete (d)				Number of Sample
		3	7	14	28	
BK0	0%	3	3	3	3	12
BK1	0.5%	3	3	3	3	12
BK2	1%	3	3	3	3	12
BK3	2%	3	3	3	3	12

2.3 Measurements of slump retention and compressive strength

Figure 1 shows the test of slump retention for the verification of decreasing slump flow according to the standard ASTM C 143-90. The measurements of slump retention were carried out at 0, 15, 30, 45, 60 and 75 minutes.

Fig. 1. Testing of slump retention

This study used a cylindrical tube of having dimensions of 150 mm external diameter and 300 mm high to follow the standard ASTM 39. Figure 2 shows the measurement equipment testing of compressive strength. Compressive strength of the HPC samples was performed at 3, 7, 14 and 28 d of the concrete's age.

Fig. 2. Testing of compressive strength

Correlation between the slump retention and the compressive strength for the HPC sample was verified using the results of testing the slump retention at 0, 15, and 30 minute and testing the compressive strength at 7 and 28 day.

3 Results and discussion

3.1 Slump retention

The results of slump retention for mixture of concrete with the variables of adding PCE by 0%, 0.5%, 1% and 2% and mixing time by 15, 30, 45, 60 and 75 minutes can be analysed to get better understanding of the workability of HPC. Figure 3 shows that the workability of HPC is still able to be used in construction industry since the slump retention behavior of concrete with a composition of 2% PCE can be maintained until 45 mn with a slump value of 10 cm. Meaning that the proper amount of added PCE would be effective in improving the slump retention due to the addition of PCE can induce greater physico-chemical surface interactions through electrostatic interactions [10-12].

Empirical evidence shows that the addition of PCE in a mixture of concrete may improve the workability of HPC. The HPC performance of improved by the addition of PCE by 15% and 20% can reach at 45 mn of slump retention capability. This study verified that the synthesis of designed HPC by adding 2% of PCE superplasticizer can have an optimal slump retention capability of 45 mn, and then after 45 mn the compressive strength slowly continues to decrease [7, 13].

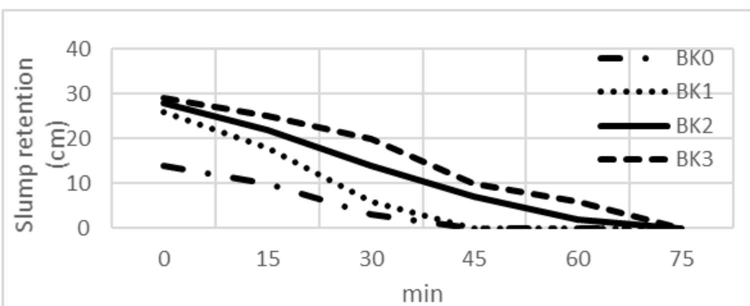

Fig. 3. Results of testing the slump retention

3.2 Compressive strength

Figure 4 shows that the increasing of PCE added into a concrete slurry can increase the compressive strength of HPC to get verified at concrete's age of 3 d. The figure shows the increase in compressive strength from 25.62 to 30.26 to 31.93 to 34.22 MPa because of the addition of PCE into the mix of concrete increases from 0% to 0.5% to 1% and to 2%, respectively. The increase of compressive strength can also be verified at the ages of 7, 14 and 28 d. The compressive strength has never reached at its planned compressive strength of f'c 45 even at age of 28 d due to the addition of PCE by 0%. It can reach at its planned compressive strength of f'c 45 at age of 28 d by the addition of PCE by 0.5%. By adding 1% of PCE into concrete slurry, the compressive strength reaches at 47.87 MPa, which is 2.42 MPa higher than its planned compressive strength of f'c 45, at age of 14 d and 49.81 MPa, which is 4.36 MPa higher than its planned compressive strength of f'c 45, at age of 28 d. Finally, by adding 2% of PCE into a mixture of concrete, the compressive strength can reach at 50.81 MPa, which is 2.94 MPa higher than the compressive strength of HPC of added 1% of PCE, at age of 14 d and 53.84 MPa, which is 4.03 MPa higher than the compressive strength of HPC of added 1% of PCE, at age of 28 d.

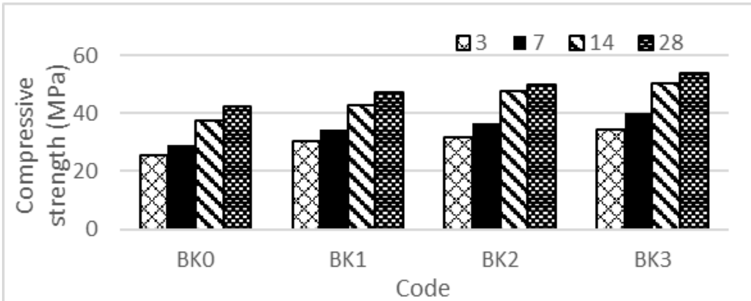

Fig. 4. Results of testing the compressive strength.

The results (Table 3) of testing at age of 28 d with the variable of PCE added by 0%, 0.5%, 1% and 2% have the compressive strengths of 42.47, 47.05, 49.81, and 53.84 MPa, respectively. The maximum value of compressive strength was verified to reach at 53.84 MPa the workability of HPC of added 2% PCE with an increase in compressive strength of 26.77% compared to that of added 0.5% PCE. Empirical evidence verified that the addition of superplasticizer into a mixture of concrete can increase workability of the HPC due to the presence of PCE nanoparticles in concrete slurry fills the cavities of concrete and thus can result in strengthening of bonds among the concrete materials the [14-16].

Table 3. Results of increasing the compressive strength

Addition of PCE (%)	Compressive strength (MPa)	Increase of compressive strength
0	42.47	0%
0.5	47.05	10.80%
1	49.81	17.29%
2	53.84	26.77%

3.3 Relation between slump retention and compressive strength

The results (Fig. 5) of plotting a correlation between the slump retention and the compressive strength reveals that the decreasing of slump retention does not make a significant decrease in compressive strength of the HPC. The compressive strengths of testing at 0, 15 and 30 mn have not clearly affect the value of slump retention at the performance of HPC measured at the ages of 7 and 28 day.

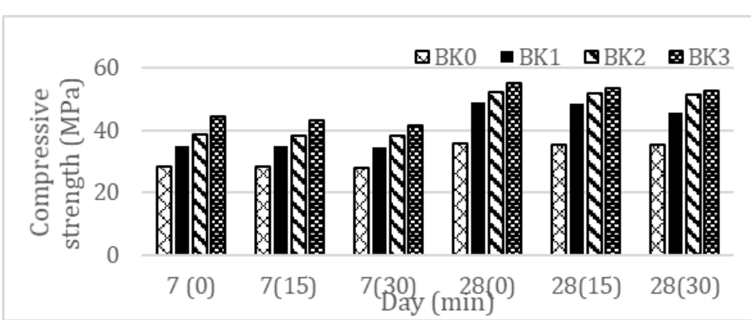

Fig. 5. Correlation between the slump retention and the compressive strength

4 Conclusions

This study used four different concrete mix designs of HPC with the variable of added 0%, 0.5%, 1% and 2% of the PCE to verify the slump retention capabilities and compressive strengths. By analysing the results of slump retention and compressive strength can conclude that:

1. The optimal slump retention of 45 mn with its value of 10 cm can be achieved by adding 2% of PCE.
2. A very high compressive strength of 53.84 MPa for HPC can be achieved by adding 2% of PCE, thre is an increase in the compressive strength of 26.77% compared to the control sample of HPC without addition of PCE.
3. Slump retention does not affect the compressive strength of HPC.

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[Abstract ID: ABS-57]

Mechanical properties of nanogrout as advanced material for construction

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Abstract

Recent development in construction industry has come to the point where it requires a new kind of materials with higher mechanical properties such as compressive strength, tensile strength, and flexural strength. Grout materials are needed for pad bearings and structural repairs. However, grout materials that are readily available on the market only has limited strength, as well as using materials on micro scale. Therefore, it is necessary to develop grout materials using materials at nano scale, like nanosilica, which is able to increase the mechanical properties. The purpose of this study is to determine the optimum content of nanosilica in grout material. Initial mix was given code G0. Then the nanosilica was added with 1% content (code G1), 2% content (G2), 3% (G3), and finally 5% nanosilica content (G5). Compressive strength tests were carried out when the grout were aged 1, 3, 7, and 28 days. Whereas flexural strength test were carried out at 28 days old grout. From the research, it was found that the most optimal nanosilica content was at 3% (G3). The contribution of this research is to introduce nanogrout as an advanced material, to overcome the challenges of increasingly complex construction work in the future **(Approx. 201 words)**

Keywords: mechanical properties, micro scale, nano scale, nanosilica, nanogrout

Topic: Material Science and Engineering

Type: Oral Presentation

Abstract Review Result
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Dear Authors: Jonbi1, A R I.Tjahjani1,W Meutia1, I Yahya1, and J.Shodik1

We are pleased to inform you that your abstract (ABS-57, Oral Presentation), entitled:

"Mechanical properties of nanogrout as advanced material for construction"

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Mechanical properties of nanogrout as advanced material for construction

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Abstract. Recent development in construction industry has come to the point where it requires a new kind of materials with higher mechanical properties such as compressive strength, tensile strength, and flexural strength. Grout materials are needed for pad bearings and structural repairs. However, grout materials that are readily available on the market only has limited strength, as well as using materials on micro scale. Therefore, it is necessary to develop grout materials using materials at nano scale, like nanosilica, which is believed to be able to increase the mechanical properties. The purpose of this study is to determine the optimum content of nanosilica in grout material. Initial mix was given code G0. Then the nanosilica was added with 1% content (code G1), 2% content (G2), 3% (G3), and finally 5% nanosilica content (G5). Compressive strength tests were carried out when the grout were aged 1, 3, 7, and 28 days. Whereas flexural strength test were carried out at 28 days old grout. From the research, it was found that the most optimal nanosilica content was at 3% (G3). The contribution of this research is to introduce nanogrout as an advanced material, to overcome the challenges of increasingly complex construction work in the future