Original Article

Semi-permeable membrane fabricated from organoclay/PS/EVA irradiated by $\gamma$-rays for water purification from dyes

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**ABSTRACT**

This article summarizes the modification of bentonite to organoclay consisting of aniline monomer incorporated into the bentonite matrices. The organoclay (OC) hybrid has been exposed to gamma rays at dose of 50 kGy resulting the aniline polymerization. Organoclay's color is dark red. The blend polymer (PS/PEVA) was mixed with 33 wt% organoclay in Toluene solvent and then irradiated to 50 kGy. Many characterization techniques have been used to identify changes in clay in organoclay (OC) have relatively high surface area, strong dye adsorption and highly variable surface area. XRD analysis shows increased of interplanar distance (d) of bentonite after aniline modification that confirmed by FTIR analysis and also when composite with blend polymer (PS/PEVA). SEM reveals the irregular pores structure of semi-permeable membrane ranged from 35 to 3 $\mu$m. In this article, novel membrane's ability to purify water polluted with three different dyes: Toluidine Blue (TB), Amido Black (AB) and Remazol Red (RR). It is inferred from results that the aniline treatment enhances dye adsorption by bentonite and increases dye adsorption when composite with blend polymer. This future is give effective water purification membrane. It was found that over 99% TB molecules in water solution were adsorbed by OC/PS/PEVA in fifteen second.

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1. Introduction

Clay is used as filler in large commercial applications such as reinforcing of polymers can be thermoplastics and thermosets. A rethinking of how best to utilize them is resulting in easier-to-process second-generation products with improved surface modification. From this point bentonite has high efficiency in water treatment as mentioned by Abdullah et al. [1], e.g. removed of organic compounds as mentioned by Zhu and Zhu [2]; Stockmeyer [3]. Bentonite is known as layered clay minerals and is environmentally friendly and has drawn significant interest from the scientific community due to its promising inherent characteristics such as ion exchange properties, large surface areas, adsorption capability and good swelling behavior. Bentonite is a clay significantly enriched with minerals of smectite, generally montmorillonite (MMT) and beidellite. Smectites are characterized by three layers aluminosilicates consisting of one octahedral sheet sandwiched between two tetrahedral sheets. This is formed by unit layers where one tetrahedral sheet of one unit layer is adjacent to another tetrahedral sheet of another layer. Moreover, in smectites, some Al$^{3+}$ and Si$^{4+}$ ions are isomorphically substituted with different cations in smectites. It is therefore confirmed the adsorption / capture of guest molecules/ions within the clay matrix is induced by chemical interactions between clay and guests molecules.

Recently clay has been modified by organic materials as performed by de Paiva [4]. In several literatures, the introduction of organic compounds into the interlayer space of clay minerals was considered [5–7]. The researchers seek to focus on how to combine organic compounds with clay minerals. The combine of organic molecules with clay is specified by several chemical interactions: Van der Waals forces, charge transfer, acid base reactions, coordination bonds, ion–dipole interaction, and hydrogen bonds. Most clay minerals are hydrophobic by forming covalent bonds between organic species and reactive clay surface groups as described by Ref. [8]. The adsorption of the organic ions into clay minerals, leads to increase in the spacing between layers than those of the same clay minerals as founded by Refs. [9–11]. Consequently, this causes the reduces of the attractive forces and increases in the interlayer spacing between the layers of clay that made the intercalation of the polymer and the clay is conceivable as mentioned by Ref. [12]. The absorption and displacement reactions occur when other polar molecules take over interlayer water in clay particles. The possible reactions that used to prepare organoclays are two reactions eg: solid-state and cation exchange reactions [13]. concluded that the swelling degree controlled by three factors: 1) the nature of the organic liquid 2) the extent of other organic matter on the surface of the clay particles and 3) the capacity saturation degree of the clay mineral by organic cations, Therefore, an evaluation of organoclay dispersion in polymer matrices is important where the properties of composite is depend on the three compounds (organic compounds, clay and polymer kinds) as studied by Ref. [14]. For organoclay come true in the polymer matrix, the three methods should be considered. 1) The monomer mixed with clay and then polymerization process is beginning. 2) The melt polymer is easy to diffuse through the clay layers [15]. 3) In case hydrophobic polymers such as polystyrene, polyvinylchloride, polyethylene is necessary to add of compatibilizer containing polar groups to improve the diffusion of them into the clay layers [16]. In previous study [17] found the gamma ray is could act as compatibilizer because of an attractive combination of benefits, such as low cost, more efficiency, no waste and wide field applications. The gamma irradiation of PS/PEVA blend polymer causes a crosslinking of chains and increased of the compatibility and the crystallinity. Gamma irradiation is an encouraging technique to create a various materials particularly polymeric materials Ghobashy and Khafaga [18]; Ghobashy and Elhady [19]; Ghobashy and Khafaga [20]; Ghobashy [21].

In this study the Egyptian bentonite treated in the laboratory with aniline monomer and subject to gamma irradiation at a dose of 50 kGy. The blend polymer PS/PEVA was composited with organoclay. Polylyaniline has two advantages: first, the compatibility between polymer and bentonite is increased and second, the adsorption of dye is improved. Organic compounds in wastewater, for example, pigments and dyes are harmful as mentioned by Ref. [22] or have deadly impact on amphibian living and human. The organic pollutant specially dyes is removed from contaminate water by several techniques such as catalytic degradation as explained by Qin et al., 2019$^1$, and Fu et al 2019$^2$, is used gold nanoparticles as a reduction catalyst for highly efficient reduction of nitroaromatics of dyes. The gold nanoparticles also can be used as sensor for organic compounds Qin et al., 2017$^5$. Photocatalytic pollutant degradation is widely studied as by Li et al 2018$^4$. Organic dye pollutants, especially Amido Black (AB), Remazol Red RR (and Toluidine Blue (TB)) are stable to light, heat or oxidizing agents and are extremely difficult to remove by conventional wastewater treatment methods. Some new techniques with high dye adsorption have been established by late researchers; however, a subsequent adsorbent purification method can not be prevented after water treatment, which is often complicated and is not appropriate for practical water treatment. The filtration technique is always quick, fast

and low cost among several traditional adsorbent purification processes that are technically complicated and not suitable for water treatment.

In this study, the approached method increased the efficiency of bentonite as a dye adsorbent with a simple purification process that encourages the use of organoclay/PS/PEVA as advanced adsorbent materials for the functional purification of water.

2. Experimental

2.1. Materials and methods

After strong grinding, bentonite (from Aswan Egypt) is converted from grain dust to fine dry powder. Aniline monomer 99% from Sigma-Aldrich Germany. Polystyrene with average molecular weight is 192,000 (PS, 99.99%, Sigma-Aldrich). Poly Ethylene-Vinyl Acetate, vinyl acetate with ethylene content 25 wt. % (PEVA, melt index19 g/10 min. 190 °C/2.16 kg Sigma-Aldrich). Toluene solution with purity of (99.9%) from (Sigma-Aldrich) were used as received without further purification. Remazol Red (RR) an azo-reactive dye, was obtained from DyStar (Germany). The Toluidine Blue (TB) is a basic thiazine metachromatic dye and Amido Black (AB) is an amino acid diazo dye was obtained from Sigma-Aldrich (Germany). The chemical structures of different dyes are represented in Scheme 1.

2.2. Preparation of the organoclay (OC) samples

The aniline monomer (5 ml) has been mixed perfectly with (5 g) of the raw bentonite powder. The mixture stood up overnight before being subjected to a gamma ray of 50 kGy. The polyaniline/clay powder washed with water/ethanol solvents several times and filtered to eliminate the unreacted aniline monomer. Upon polymerization, polyaniline is incorporated in layers of bentonite forming organoclay. A blending polymer of (1:1) PS: PEVA dissolved in Toluene was irradiated with 50 kGy of gamma rays. The irradiated solution of (PS/PEVA) was mixed with 33 wt% of organoclay. The mixture was poured to Petri dish until the Toluene solvent evolved and the Semi-permeable membrane of (OC/PS/PEVA) was obtained.

2.3. Gamma radiation source

The irradiation process of the samples was carried out with the 60Co Indian irradiation facility gamma rays at a dose rate of 1.66 kGy/h. The irradiation cell was constructed by the National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority of Egypt (AEAE) Cairo.

2.4. Characterizations

The surface morphology of the blend organoclay/PS/PEVA membrane was carried out using JSM-5400 Scanning electron Microscope (SEM) can be used for understanding of the surface morphology by rotating them. The whole series of operation including vacuum evacuation, image observation, focusing, and photographing have been automated, JEOL Ltd., Tokyo, Japan. X-Ray Diffraction patterns were obtained with The XRD-6000 series, including stress analysis, residual austenite quantitation, crystallite size/lattice strain, crystallinity calculation, materials analysis via overlaid X-ray diffraction patterns Shimadzu apparatus using nickel-filter and Cu-Katarget, Shimadzu Scientific Instruments (SSI), Kyoto, Japan. Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) Vertex 70 FTIR spectrometer equipped with HYPERION™ series microscope (BrukerOptik GmbH, Ettlingen, Germany) over the 4000-500 cm⁻¹ range at a resolution of 4 cm⁻¹, was used. Software OPUS 6.0 (Bruker) was used for data processing, which was baseline-corrected by the rubber peak method with exclusion of CO₂ peaks.

3. Results and discussion

3.1. Procedure for fabrication of an organoclay/PS/PEVA

Fig. 1a illustrates the experimental procedure for the manufacture of organoclay/PS/PEVA composite membrane. The aniline monomer and bentonite clay were taken according to this composition (5 ml and 5 g), respectively. The mixture was stood overnight and then washed with water-ethanol solvents several times. After that the mixture of clay and aniline monomer was exposed to gamma radiation with dose of 50 kGy. The color of bentonite converts from light brown to reddish brown of organoclay powder as demonstrated in Fig. 1a. on the other hand, part of polystyrene (PS) polyethylene vinyl acetate PEVA (1 gm for each) were dissolved in 20 ml toluene solvent and mixed with 33 wt% of organoclay. Then the mixture solution was exposed to 50 KGY gamma rays and casted in Petri dish for forming semi-permeable membrane of OC/PS/EVA. The solution was exposed to 50 KGY to increase the compatibility of the two polymers. The prepared membrane was stored at ambient condition for further study. Fig. 1b shows interlayer space that change as a result of bentonite modification and organoclay formation. This interlayer space changing was used for using as adsorbent. This space in the interlayer was used as an adsorbent space. For the three dyes adsorption, kinetics of adsorption and isotherm adsorption are evaluated.

3.2. FTIR-ATR of the bentonite clay and organoclay/PS/PEVA

The FTIR-ATR spectrum of organoclay (bentonite and bentonite modified with polyaniline) at Fig. 2a and b showed the peaks at 3691 cm⁻¹ and 3694 cm⁻¹, respectively are due to the stretching vibrations of OH groups in the surface of bentonite. The peak at 3619 cm⁻¹ in Fig. 2a and at 3616 cm⁻¹ in Fig. 2b is responsible for free uncomplexed hydroxyls (inner structure) [23]. As well as the peak 1635 cm⁻¹ and 1630 cm⁻¹ responsible for bending H—O—H for water molecules. The two peaks at 456 and 454 cm⁻¹ are due to Si—O—Si bending vibrations for Fig. 2a and b, respectively. The peaks at (789, 742 and 687 cm⁻¹ in Fig. 2a) and at (789, 747 and 689 cm⁻¹ Fig. 2a) show the presence of quartz and free (amorphous) silica admixture for the two samples Hayati-Ashtiani [24,25]. The very strong absorp-
Fig. 1 – (a) Organoclay semi-permeable membrane processing procedures using gamma irradiation techniques (b) Models for the effect of intercalation of aniline in bentonite at two different interlayer space 4.05 nm for blank bentonite and 6.63 nm for organoclay.

Fig. 2 – (a) FTIR-ATR spectrum of bentonite. (b) FTIR-ATR spectrum of organoclay/PS/PEVA.

tion peak at 990 cm\(^{-1}\) is due to Si–O bending vibration and at 1108 for perpendicular Si–O stretching (Fig. 2a) that shifted to 1110 in Fig. 2b. There was a slight shift in the FTIR peaks of organoclay compared with pure bentonite, indicating the penetration of aniline molecules into the silicate layer of bentonite clay. The peak at 915 cm\(^{-1}\) corresponding to Al–OH was founded in Fig. 2a and b. The peak at 1243 cm\(^{-1}\) is attributed to C–N for polyaniline and the peak 3391 cm\(^{-1}\) is responsible for hydrogen bonds via NH (aniline molecules) and OH (bentonite molecules). In Fig. 2c show the mean peaks of PS are located
at 3079, 3055, and 3020 cm$^{-1}$ for (C–H aromatic stretching); the broad peak ranged from 2850 to 2940 cm$^{-1}$ attributed to (C–H aliphatic stretching); peaks at 1596, 1494, and 1455 cm$^{-1}$ attributed to (C=C aromatic stretching). The peaks at 520 and 454 cm$^{-1}$ are attributed to C–H bending out of plane. The characteristic IR peaks of PEVA at 2850 cm$^{-1}$ related to ethylene groups and at 2940 cm$^{-1}$ related to methyl groups. Furthermore, the two peaks at 1737 cm$^{-1}$ and 1243 cm$^{-1}$ attributed to C=O and C–O groups, respectively.

3.3. XRD measurements of the bentonite clay, organoclay and organoclay/PS/PEVA

FTIR is one of kind technique can give information about the mineral structure, such as the minerals family to which the specimen belongs and the degree of regularity within the structure. Other useful technique is XRD instrument should be combined with FTIR to have a complete characterization of clay nature to complete the image. The XRD pattern in Fig. 3a indicates that the clay is composed primarily of bentonite, with the characteristic diffraction peaks at $2\theta = 6.3^\circ$ and interplanar distance $d_{001} = 14.018\,\text{Å}$ and $2\theta = 19.8^\circ$ with interplanar distance $d_{020} = 4.47\,\text{Å}$ reflections of montmorillonite. In addition, Fig. 3a shows the diffraction peaks at $2\theta = 12.25^\circ$ with inter distance planar $d_{001}$ of 7.21 Å and at $2\theta = 24.99^\circ$ with inter distance planar $d_{002} = 3.56\,\text{Å}$ are corresponding to Ref. [26]. The data in Fig. 2a show the characteristic diffraction peaks at $2\theta = 26.59^\circ$ interplanar distance $d_{101} = 3.349\,\text{Å}$ is characteristic for quartz.

As expected the penetration of polyaniline molecules onto the natural bentonite layers led to increase in the interplanar distance of the host materials as show in Fig. 3b. Seen the characteristic diffraction peaks of montmorillonite, quartz and kaolinite show at any site aniline molecules are pene-
trated. For montmorillonite structure is interplanar distance ($d_{001}$) increased from 14.29Å to 15.46Å at $2\theta = 5.70^\circ$ and from 4.47Å to 4.49Å at $2\theta = 19.37^\circ$. The inter distance planar $d_{001} = 7.21Å$ at $2\theta = 12.25^\circ$ and at $2\theta = 24.99^\circ$ with inter distance planar $d_{002} = 3.56Å$ for kaolinite (in Fig. 3a) were increased to $d_{001} = 7.24Å$ at $2\theta = 12.20^\circ$ and at $2\theta = 24.73^\circ$ with inter distance planar $d_{002} = 3.59Å$. For quartz the interplanar distance $d_{101} = 3.349Å$ at $2\theta = 26.59^\circ$ is increased to $d_{101} = 3.366Å$ at $2\theta = 26.45^\circ$. These results indicated that the penetration of aniline molecules is actually in montmorillonite site. For organoclay/PS/PEVA (Fig. 2c) the interplanar distance still increase to 15.91Å at $2\theta = 5.55^\circ$ and 4.53Å at $2\theta = 19.55^\circ$. As seen the increase in the interplanar distance ($d$) between crystal platelets due to intercalation of aniline polymer chains into the platelet’s gallery especially in montmorillonite crystal.
3.4. **SEM-EDX analysis of the bentonite clay and organoclay**

The two Tables inserted in Fig. 4a and b lists the composition of the bentonite and organoclay analyzed by EDX. The pure bentonite sample was comprised of 02.07 (C), 45.99 (O), 02.26 (Na) 25.71 (Si), 09.67 (Al), 01.83 (Mg), 2.85 (K), 01.38 (Ca) 00.99 (Ti) and 07.25 (Fe) in weight percentage, indicating silica, alumina and iron to be the major constituents, the carbon atom could be attributed to atmospheric CO₂ gas. On the other hand, the organoclay sample was comprised of 05.98 (C), 03.52 (N) 42.88 (O), 01.51 (Na) 24.61 (Si), 09.71 (Al), 01.66 (Mg), 01.22 (K), 01.01 (Ca) 00.91 (Ti) and 06.99 (Fe) in weight percentage, in comparing two sample are indicating that silica, alumina and iron still major constituents, but the weight percent of the two elements of Na and K were differentiate this mean that the aniline polymer replaced of Na and K atoms in bentonite structure.

The surface morphology of bentonite and bentonite organoclay are shown in Fig. 5(a and b) respectively. SEM revealed significant changes between bentonite and bentonite organoclay. Images of pure bentonite show irregular phase are appearance as a heterogeneous surface morphology. It can be seen that the bentonite have plates up plates (smectite interlayer spacing). This smectite interlayer spacing when incooperated with aniline polymer is usually random and increased the size of bentonite granules. The packing of aniline polymer within the interlayer of bentonite is formed a larger block structure. This indicated that bentonite clay treated with aniline polymer shows significant increased in the size and roughness of the bentonite. Due to increase of basal spacing in organoclays than pure bentonite this result was in agreement with XRD data.

3.5. **Surface morphology of obtained semi-permeable membrane organoclay/PS/PEVA**

The scanning electron microscope is important for observing the good mixed polymer with organoclay and for defining porous membrane (PS/PEVA) diameter of the pores and organoclay distribution. Fig. 6 demonstrated the performance of organoclay distribution in the mixing polymer matrix of a larger and a smaller grain length. This can be due to a high viscosity of mixing polymer solution that helps to delay organoclay particle sedimentation. Also Fig. 6 shows the semi-permeable of (OC/PS/PEVA) membrane, the pore size and density of semi-permeable membranes is visual observing and the resulting “tunnels” are formed. Fig. 6d showed the cross section of membrane, the tunnels with irregular width can be observing clearly. The micro particle of organoclay was trapped and good adherent in the wall of membrane. Either the pours size is reduced by 10-80% but not blocked, therefore the hybrid membrane easily used in dialysis technique. This function clearly indicates that the purification of water with dyes contamination can be enhanced by semi-permeable membrane (OC/PS/PEVA), which could be useful in various dialysis applications.

Fig. 6 – The irregular membrane pores opened with 35-3 mm as the organogly was a strong adhesive in the tunnel wall, this tunnel is responsible for the purification of the water. SEM image with magnification (a) 35x, 75x (b) and 1500x (c) while (d) cross-section image 1500x.
3.6. Evaluation of the developed organoclay/PS/PEVA semi-permeable membrane for effective dye removal and water purification

The test of the dye adsorbed by the semi-permeable membrane (OC/PS/PEVA) as an adsorbent, is shown in Fig. 7 it was performed by three dyes (TB, AB and RR). The weight used for the three adsorbents are 0.02, 0.02 and 0.06 g for bentonite, organoclay and organoclay/PS/PEVA, respectively and the volume of dyes solution (2 × 10⁻⁵) mol is 15 ml. The dye removal estimation was carried out by four tubes for each dye. The first tube was 15 ml of dye solution alone (1), the second tube was 15 ml of dye solution and 0.02 gm of organoclay (2), the third tube was 15 ml of dye solution and 0.02 gm of bentonite (3) and the forth tube was 15 ml of dye solution and 0.06 gm of membrane (4). The test tubes were shaken two times and stand for dye adsorption at equilibrium conditions. For each dye study necessary to determine the time required to reach adsorbed equilibrium by time inravel. In Fig. 7a found that the adsorption of TB dye was reach maximum after 50 s. see (https://youtu.be/fQRsmlSsLk), the efficiency of dye removal in case organoclay/PS/PEVA is the best rather than organoclay and bentonite clay. For AB in Fig. 7b the maximum dye adsorbed by OC/PS/PEVA was 120 min and for RR dye in Fig. 7c the maximum dye adsorbed by OC/PS/PEVA was 660 min. By compared with the three adsorbents (bentonite, organoclay and OC/PS/PEVA) in water purification processes it was founded that the dye molecules are not easily desorbed by bentonite alone, treatment by aniline and polymer are very useful to enhancing the ability of clay in water purification. From Fig. 7a, b and c seen that the organoclay/PS/PEVA shows high efficiency in dye adsorption rather than organoclay and bentonite and was found to be highly in order TB > AB > RR.

The purification of water contaminated by TB depending on the membrane permeability was checked in the following section. The work described in Fig. 8 for providing more information about the dialysis of dyes onto membrane is given. The permeability of the membrane to dye can be tested by holding square dialysis membrane sample in half of tube as shown in Fig. 8a. The TB dye solution 2 × 10⁻⁵ mol was added carefully as shown in Fig. 8b after certain time the dye was adsorbed and solution becomes clear. This indicate that the dye was diffused through the dialysis membrane in the time of 60 min.

Next step is to confirm the desorption method of dye molecules from the membrane adsorbents to realize the high efficiency of a novel martial (organoclay/PS/PEVA) at future. Fig. 9 demonstrated a spice of membrane was immersed in a test tube containing TB dye solution (2 × 10⁻⁵) mol and kept stand without shaking for 10 min. as shown the concentration of TB dye was varied from bottom than above solution. This well indicates the ability of membrane to binding with dyes. No doubt that the membrane is a good adsorbent potential for the removal of dyes from water solution due to their unique chemical composition.
3.7. Adsorption kinetics

The kinetics of adsorption of RR, AB and TB adsorbed on OC/PS/PEVA membrane were evaluated to determine the mechanism of adsorption using Pseudo-first order and Pseudo-second order kinetics models as shown in Fig. 10(a–c), respectively. These models have been widely used to describe the kinetic of adsorption.

The Pseudo-first order kinetic model rate equation is given by Lagergren\(^6\) equation.

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

The pseudo-second-order rate equation is given as\(^7\)

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]

where \(q_e\) and \(q_t\) are the amounts of adsorbed metal ions (mg/g) at equilibrium and time \(t\) (min). \(k_1\) (min\(^{-1}\)) is the Lagergren rate constant of the pseudo-first order adsorption and \(K_2\) (g.mg\(^{-1}\).min\(^{-1}\)) is the rate constant of pseudo-second order. The linear plots of the curve \(\log (q_e - q_t)\) versus time (min) was used to calculate the values of the rate constant (\(k_1\)), meanwhile, \((t/q_t)\) versus time (min) was used to calculate the values of the rate constant (\(k_2\)).

The correlation coefficient \((R^2)\) of the Pseudo-first-order model (Fig. 10) for RR, TB and AB dyes was 0.99, 0.96 and 0.86,

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The Langmuir model equation is as follows:

\[
\frac{C_e}{q_e} = \frac{1}{K_q q_m} + \frac{C_e}{q_m}
\]

\( q_e \) (mg/g) is the adsorption capacity at equilibrium, \( q_m \) (mg/g) is the maximum adsorption capacity, \( C_e \) is the concentration of metal ions after adsorption (mg/L). Plotting the curve \( C_e /q_e \) versus \( C_e \) to calculate the values of the affinity constant \( K_q \) (L/g) and \( q_m \).

To determine whether the adsorption is favorable or unfavorable, separation factor \((R_i)\) was applied as:

\[
R_i = \frac{1}{1 + K_q C_0}
\]

where \( C_0 \) is the initial concentration of metal ions; \( R_i \) is the Langmuir constant. The value of \( R_i \) between 0-1 indicates a favorable adsorption, \( R_i > 1 \) suggests unfavorable adsorption, \( R_i \) equal 1 suggests the adsorption process is linear adsorption, and \( R_i \) equal 0 represents irreversible adsorption.

The Freundlich equation is given by

\[
\log q_e = \log K_f + \frac{1}{n} \log C_0
\]

where, \( q_e \) (mg/g) is the adsorption capacity at equilibrium, \( C_0 \) is the concentration of metal ions after adsorption (mg/L), \( K_f \) (L/g) and \( n \) (dimensionless) are the Freundlich isotherm constant and the heterogeneity factor, respectively. The Freundlich constants can be obtained by plotting the curve \( \log q_e \) versus \( \log C_0 \).

The exponent \((n)\) is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When \( n=1 \), the isotherm is linear, when \( n<1 \), the isotherm is concave and adsorbate is bound with weaker and weaker free energies, and when \( n>1 \), the isotherm is convex and more adsorbate presence on the adsorbent enhances the free energies of further adsorption.

The results obtained from adsorption isotherms for RR, AB and TB dyes by OC/PS/PEVA are shown in Table 1. The adsorption of RR, AB and TB dye by OC/PS/PEVA was well performed by Langmuir isotherm showing high \((R^2)\) of 0.99, and the Freundlich isotherm \((R_f)\) is 0.99 for TB adsorption. The Langmuir constant values \( R_i \) for the tested dyes are in between 0 and 1 which represents favorable adsorption process by OC/PS/PEVA. The results indicate that Langmuir isotherm model is suitable for the adsorption process. In Langmuir model, adsorption occurs as a monolayer process on homogeneous sites.

The enhancement of the adsorption capacity of TB onto OC/PS/PEVA is very cleared high the both RR and AB dyes could be attributed to the presence of the chelation between the electron-donating oxygen- and nitrogen-containing groups in the TB dyes and OC/PS/PEVA semi-membrane.

### 3.8. Adsorption isotherms

Adsorption isotherm model is used to quantify the sorption capacity of OC/PS/PEVA for the RR, AB and RR Langmuir and Freundlich models are two common isotherm models applied to determine the affinity of sorbent and adsorbate and to find the mechanism of adsorption. In Langmuir model, adsorption occurs as a monolayer process on homogeneous sites, while in Freundlich model, adsorption is a multilayer process and adsorbent surface is heterogeneous.

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**Fig. 9** - demonstrates the high efficiency of OC/PS/PEVA membrane for TB dye adsorption.

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The manufactured of semi-permeable membrane from OC/PS/EVA using γ-rays has been succeeded for water purification. Addition polyaniline to bentonite matrix improve the ability of clay to adsorbed dyes. This ability further enhanced by composite organoclay with blend polymer of PS/PEVA. For
answer the question why chains of polyaniline is penetrates through montmorillonite crystal rather than both of kaolinite and quartz phases. This was attributed to the inter-layer distances of montmorillonite; kaolinite and quartz are typically 14.0 Å, 7.2 Å and 3.34 Å, respectively. So the long chains of polyaniline is prefer layers of montmorillonite to insert bentonite clay, which was advantageous to the interlamellar spacing of bentonite increase as the XRD results indicated.

SEM image has tested the permeability of the membrane. The experimental results of water purification showed that organoclay/PS/PEVA eliminated more than 99% of TB molecules in water solution in 50 s. In the meantime, the AB molecules are adsorbed and the solution color changed significantly from blue to colorless. The adsorption of RR molecules show some resistance but organoclay/PS/PEVA still highly adsorbent compared with the two adsorbents (bentonite and organoclay) alone. Pseudo-second order kinetic model was found to be suitable for describing the adsorption kinetics of AB and RR dyes by OC/PS/PEVA aqueous solution. The OC/PS/PEVA showed adsorption capacity 53.30 mg/g for RR while in the case of AB adsorption capacity was determined to be 63.12 mg/g. The adsorption process of TB onto OC/PS/PEVA rather than RR and AB which their adsorption obeys Pseudo-first-order model and showed adsorption capacity 84.81 mg/g. Present study suggests that the OC/PS/PEVA adsorbent can be utilized for the treatment of cationic and anionic dyes from industrial wastewaters.

### Table 1 – Adsorption isotherm parameters for the adsorption of RR, AB and TB onto the OC/PS/PEVA semi-membrane.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$R_l$</td>
</tr>
<tr>
<td>RR</td>
<td>53.30</td>
<td>0.604</td>
</tr>
<tr>
<td>AB</td>
<td>63.12</td>
<td>0.490</td>
</tr>
<tr>
<td>TB</td>
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Conflict of interest

The authors declare no conflicts of interest.

Uncited references

[27,28].

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